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Salt weathering in the coastal environment: The deterioration of wall paintings at Delos, Greece

Petros Prokos

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Institute of Archaeology

University College London

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ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
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Abstract

Salt weathering, apart from being an important geomorphologic agent, comprises a major hazard for both modern and heritage structures. Although its action is witnessed globally, it is particularly aggressive in coastal environments. The coastline attracted in antiquity a considerable part of human activity that has left valuable built traces. Conservation research is frequently called upon to define sustainability in this aggressive context.

Wall paintings comprise an integral part of the built heritage. The particular importance of wall paintings and finishing layers derives from their unique aesthetic function in the building's integrity as well as the plethora of information that they carry. Whereas wall paintings are more susceptible than masonry materials, the tolerance against loss is much smaller due to their descriptive nature and scale. It is not until recently that international heritage organisations recognised the technical particularities of wall paintings suggesting that they must be investigated independently and treated *in situ*.

This project aims to identify the particularities of wall paintings' susceptibility to salt weathering in the coastal environment. The methodology is composed of both *in situ* and *ex situ* experiments. The *in situ* investigation follows a comparative approach, guided by specific variables, in a number of monuments at the archaeological site of Delos island. The goal of the *in situ* investigation is to determine the optimal conditions for preservation, by modeling the salts interactions, in an effort to define sustainability against salt weathering in this aggressive environment. The *ex situ* approach comprises laboratory simulation of the weathering mechanism and aims to describe the particularities of the substrate that lead to the distinct loss of the external finishing layer, which carries the principal information.

The results of the project underline the importance of kinetic deviations deriving from the solution and the substrate properties. Despite the limitations of determining the optimal conditions for preservation, the variables that directed the comparative approach permitted the generation of a periodic model in agreement with the phenomenological observations. The model suggests that the potential of salt damage in real conditions of various contamination pathways and sources cannot be restricted to a single resultant. Although the model follows a certain periodicity in response to the annual climatic cycle, random events and fractionated accumulation lead to the production of mixtures with variable composition. Additionally the results stress the role of solar radiation and air movement as evaporation accelerators. Consequently environmental control against salt weathering should be directed towards multiple components which in the case of coastal environments, mainly due to the presence of marine aerosols, cannot be achieved simply by hygrothermal management. On the other hand we traced specific deviations from the theoretical model of salts interactions, concerning mixtures commonly found in coastal regions that should also be taken into account.

Besides we tested the hypothesis of salts accumulation at the interface of rendering layers, caused by hydraulic discontinuity, with a weathering simulation. The aim of this investigation was to provide evidence descriptive of damage. It has been shown that the external layer of wall paintings is particularly susceptible to marine aerosols and it can be damaged independently and in advance of the bulk mortar. The salts crystallise selectively under the lime wash layer causing gradually its detachment from the mortar. The results of the weathering simulation raise serious implications for remedial and preventive conservation practice and suggest that research must focus as well on the kinetics of particular cases.

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"As when some mighty wave that thunders on the beach
when the west wind has lashed it into fury at sea
it has reared its head afar
and now comes crashing down on the shore;
it bows its arching crest high over the jagged rocks
and spews its salt foam in all directions... "

Homer, Iliad
Scroll 4[422]

To Mini, Takis and Myrto

CHAPTER 1: Introduction

The coastline attracts a large part of human activities. Apart from the operation of trade and war, the marine routes have served since antiquity as cultural channels. The coastal populations, as receivers and crucibles of cultural exchanges, flourished to great civilisations that left abundant traces. The rich built heritage along coasts constitutes material monument of these creative collisions that shaped human history. The preservation of this material heritage has become a major task of the modern social agenda.

On the other hand the coastal zone constitutes a physical boundary between the land and the sea where violent exchanges of matter and energy form an environment subject to weathering. Along with the landforms the human structures are also susceptible to this environment. The science of geomorphology recognised early the distinct role of salt weathering along coasts. Despite the intense research activity around this mechanism it has not been described sufficiently yet. Conservation research focuses on the development of preventive methods aiming to deactivate the action of salts.

The present research aims to evaluate the weathering environment which triggers the action of salts resulting in the deterioration of wall paintings found in the Mediterranean coastal zone. Taking advantage of recent developments concerning the interaction of salts we assess *in situ* the parameters that influence the generation of damage. The *in situ* experiment follows a comparative approach guided by several variables on a small number of monuments. These variables permitted the comparison of the climatic conditions, the origin of salts, the salt content and the pathology of the wall paintings which served in the identification of the optimal conditions for preservation of each case. The assessment concludes by some kinetic considerations of the results. The particularities of the wall paintings have been assessed *ex situ* by a weathering simulation that permitted the evaluation of the conditions causing the loss of the external layer that carries the primary information. The weathering test simulated the presence of marine aerosols.

Chapters 2 to 5 constitute a basic theoretical background for the research. Chapter 2 refers to salt weathering theory divided into distinct topics. Chapter 3 depicts some fundamentals of aerosol properties focusing on the particularities of sea spray generation, transport and deposition. Chapter 5 reviews the literature from various disciplines concerning salt weathering in the coastal zone.

The second section comprises the experimental part of the thesis. Chapter 5 describes the aims of the project, the basic research questions and the general principles of the methodology. Chapters 6-11 describe separately each experimental procedure, the results and a preliminary discussion for each. The climatic monitoring data is initially presented in chapter 6 followed by the investigation of sea spray deposition in chapter 7. In chapter 8 we describe the salt content of the wall paintings concluding with a preliminary approach to the contamination particulars. Chapter 9 includes the thermodynamic investigation of the salt mixtures presented in the previous chapter along with the estimation of the optimal conditions for preservation. The results are reassessed under the prism of some kinetic considerations in chapter 10. Chapter 11 describes the salt weathering simulation of wall paintings. The last chapter, combining the results, includes a general discussion on some topics concerning the sustainability of wall paintings in the coastal zone against salt weathering along with the basic conclusions as well as proposals for further research.

PART I: THEORETICAL

CHAPTER 2. Salt weathering

2.1 Introduction

The action of salts represents, along with atmospheric pollution, a major cause of the loss of architectural heritage. It is widely accepted that the damage is attributed to the phase transitions of the salts that are found in the porous matrix of the building materials. The fluctuations of the ambient relative humidity and temperature induce crystallisation and hydration cycles that generate stresses, resulting in the disintegration of the contaminated material. Still, the phenomenon has not been described in its entirety. *In situ* and *ex situ* research has produced many controversies and a lot of the observed phenomena cannot be explained by the well-accepted salt damage models.

Although it was initially considered that salt weathering particularly affected coastal and arid regions (Wellman and Wilson, 1965) the present awareness sets a global stage for the phenomenon. The implications of salt weathering are frequently reported in case studies within various environments ranging from continental Europe (Arnold and Zehnder, 1991/Switzerland) to the Sub-tropics (Uchida *et al.*, 2000/Cambodia) and from the Poles (Prebble, 1967/Antarctica) to the deserts (Goudie *et al.*, 1997/Namibia).

Scientific inquiry on the weathering effect of the phenomenon on stones was initiated almost a century ago by engineers (Luquer, 1895) and geomorphologists (Jutson, 1918). Interestingly one of the first mentions in world literature can be found in Herodotus *Historia* (around 440 BC) referring to the pyramids of Giza which were considered at the time to be a heritage site and traveler's attraction. The Herodotus reference, apart from the historic value, bares a special interest for researchers: the extent that the phenomenon was recognised and understood in his time. In fact the Herodotus reference does not clearly link the presence of salt to damage. More likely it refers to salt efflorescence (*almin epantheousan* = effloresced salt)[1] although there are disputing translations. A

---

[1] Herodotus, The Histories (ed. A. D. Godley, 1920)
Book 2. ch. 12. par 1
"…and shells are exposed to view on the mountains, and things are coated with salt, so that even the pyramids show it (δελεεσθαι/deleesthai)…'
Some translations refer to the last word as "show" (*δηλω/delo*) while others as "hurt" (*δελεω/deleo*). The difference is obviously very important for salt weathering research.

much later reference in Vitruvius Pollio *De architectura* (around 27-23 BC) leaves no doubt of the awareness of the weathering effect of salts in the ancient world[2]. This small reference holds a great deal of information. Primarily it refers specifically to damage (*diffluunt*) and it specifies that it is attributed to salt - not some abstract parameter like moisture or the sea. It also classifies different stones according to their resistance to salt weathering and other weathering agents, it underlines the intensity of the phenomenon in coastal sites (*maritimam*) due to excess presence of salt (*salsugine exesa*) and it recognises its existence in other environments. Thus salt weathering was recognised in the antiquity at an advanced level. There is no reason to doubt that the ancient builder tried to confront it. Pliny the elder mentions in *Naturalis Historiae* (around 77 AD) that although the encaustic technique cannot be applied in walls it offers protection in paintings executed on vessels against salt water[3]. Unfortunately there has been no attempt to trace such references in ancient literature. On the other hand technological advances in engineering, as documented in heritage buildings, have never been linked to the risk of salt damage. Traditional architecture, still alive in many parts of the world, implies numerous elements that we can speculate as preventive treatments against salt damage. Periodical lime washing for example provides sacrificial layers that protect the masonry. Nevertheless it is not surprising that this important weathering agent is vaguely mentioned in heritage projects, restricted to a small number of expert studies.

Salt weathering research requires a multidisciplinary approach. The many aspects of the weathering mechanism cover a very wide range of physical sciences, making it difficult to follow by non specialists. The vast bibliography on the subject stretches through numerous highly specialised topics like thermodynamics, kinetics, electrochemistry, crystal growth, atmospheric physics, mechanics and surface chemistry, concerning arious disciplines like materials science, geomorphology and engineering among others.

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[2] Vitruvius Pollio, The Ten Books on Architecture (Morgan, 1914)
Book 7, ch. 2, par. 2
"All these soft kinds (of stone) have the advantage that they can be easily worked as soon as they have been taken from the quarries. Under cover they play their part well; but in open and exposed situations the frost and rime make them crumble, and they go to pieces. On the seacoast, too, the salt eats away and dissolves them..."

[3] Pliny the Elder, The Natural History (Bostock and Riley eds., 1855)
Book 35, ch. 41
"Painting of this nature, applied to vessels, will never spoil from the action of the sun, winds, or salt water".

Undoubtedly informatics has boosted inter-scientific collaboration with stunning results during the last decade. The recently developed awareness for the heritage risk is derived from science rather than heritage literature. On the other hand over the last decade quite a few conferences have focused on the deterioration of monuments. The numerous salt weathering references found in the proceedings mostly concern case studies that alone do not hold a particular significance in advancing our knowledge of the phenomenon. Unfortunately conference proceedings do not facilitate comparative surveys (Price, 1996) and thus a very important aspect, that of *in situ* investigations, expends in fruitless regurgitations.

Salt weathering is not an issue of solely academic interest. It constitutes an important hazard with economic, social and ecological implications. The action of salts on soils is a widespread natural phenomenon, responsible for landscape formations throughout the globe. It is even suggested that it is responsible for Martian landscapes (Malin, 1974). Geomorphology is particularly concerned with the phenomenon in coastal and desert regions. Salt weathering plays an important role in coastal management concerning both human activities and ecological resources (Viles and Spencer, 1995). Geotechnical surveys for agricultural and urban development as well as waste and water management are also concerned with the phenomenon (Pariente, 2001). Salt weathering has also a great impact on civil engineering since it causes significant damage to stone and concrete structures like buildings, bridges, damps, and roads. Particularly after the 70's construction boom in Arabia the confrontation of this hazard attracted the interest of concrete research as well as large funds (Haynes, 2002). Although the risk for cultural heritage structures was recognised early, the scientific community has focused on the problem only recently. In past decades the main interest of conservation scientists was focused in atmospheric pollution. Practical conservation has only considered the aesthetic problems of salt efflorescence while structural deformations are still dealt as outcome rather than cause. The recent turn of conservation ethics towards prevention has stirred the interest for this very destructive agent and its confrontation.

2.2 Short review of salt damage mechanism

The mechanism behind salt damage has been challenging scientists for over a century. From a simplistic point of view it seems rather surprising that a growing crystal exerts pressure to a confining pore since its volume is much smaller than that of the solution that filled the pore. Accordingly one wonders why the crystals do not flow through the pore matrix instead of growing against it and why do they continue exerting pressure after the host material has failed. While numerous questions addressing the various individual aspects of the phenomenon remain unanswered, theoretical research is struggling to produce a generalised model that describes the mechanism in its entirety.

According to Steiger (2005) the first published experimental evidence that a growing crystal actually exerts pressure towards its loaded surface, sufficient to lift itself, is provided by Lavalle (1853). Phenomenological evidence of the surprisingly high magnitude of this pressure has been initially given by Becker and Day (1905) who observed that growing crystals can lift additional weights as well.

Although the weathering effect of the phenomenon has been earlier recognised and demonstrated experimentally (Taber, 1916; Cooling, 1930), Correns (1949) proposed the first equation that allows the calculation of the pressure exerted by a growing crystal[4]. Summarising his previous work (Correns, 1926; Correns and Steinborn, 1939) he suggested that a salt crystal continues growing against an opposing pressure if a thin liquid film of supersaturated solution is maintained at the crystal-pore wall interface. The existence of the film is determined by the interfacial tensions between the crystal, the pore wall and the solution and the stress is propagated through it as it might be semi-rigid under these conditions. Correns' equation underlines the importance of supersaturation degree, which is expressed as the ratio between the solute concentrations of the saturated and supersaturated solutions.

Correns' work has been generalised by Weyl (1959). According to this work, precipitation from a supersaturated solution, between the crystal and the pore wall will take place if the ratio of the supersaturation to the stress coefficient of solubility is greater than the average

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[4] $P=R(T/v)\ln(C/C_s)$
where P is the crrystallisation pressure, R the ideal gas constant, T is the temperature, v the molar volume of the solid salt and C/C_s the supersaturation ratio

normal stress between the crystal and the pore wall. The concentration ratio as an expression of supersaturation has been replaced in Neugebauer's work (1973) by solute activities ratio and in Ping and Beaudoin (1992a;b) by ion activity products ratio. Other expressions of Corren's equation have been published from time to time without however any agreement or critical discussion so far (Steiger, 2005). Winkler and Singer (1972) used Corren's equation to calculate that the pressure exerted by some specific salts is high enough to disintegrate common building stones. This work has been widely criticised for the unrealistically high estimations of saturation ratios (Snethlage and Wendler, 1997; Dutlinger and Knofel, 1993).

Price (1991) also challenged the generation of supersaturations that would allow the build up of pressures high enough to exceed the mechanical strength of building materials: "How realistic is to think that one can get significant degrees of supersaturation in a dirty piece of stone, with any number of possible nucleation sites? For example won't the receding front of solution leave behind a supply of unstressed crystals that can act as nuclei?"

An alternative approach has been developed by Wellman and Wilson (1965)[5]. Their thermodynamic model, considering that the free energy of a solid increases with its surface area, predicts that initially crystallisation will occur in the larger pores by solution supplied from the smaller ones. This approach, initially introduced by Everett (1961) for ice crystals radii has been extensively used (La Inglesia *et al*, 1997; Rossi-Manaresi and Tucci, 1991; Zehnder and Arnold, 1989, Fitzner *et al*, 1996) mainly due to its applicability against fictional supersaturation estimations. The findings of the above mentioned applications agree that porous systems of large capillaries connected by micropores are more susceptible to salt weathering, a phenomenon much earlier observed by Schaffer (1932). Putnis and Mauthe (2001) have verified the initial cementation of halite in the larger pores of weathered sandstone thin sections. Rossi-Manaresi and Tucci (1991) moved further, introducing correction factors that consider geometric pore size distributions. Thus sandstone presents flaking due to the higher number of small pores near its surface whereas calcarenite develops alveolar patterns due to higher heterogeneity

---

[5] $\Delta P=2\gamma(1/r-1/R)$
where ΔP is the crystallisation pressure, γ is the surface tension and r, R the pore radii.

in pore size distribution. The latter is very significant for the decay of stratified materials with layers of different porosity, as is the case for wall paintings. We can suppose that in this case the interface between the layers acts as a tension capacitor resulting to the layered weathering pattern most frequently observed in wall paintings.

Rodriguez-Navarro and Doehne (1999) though, argue that the thermodynamic background of this approach is not valid to solid-liquid interactions, according to Evans (1970). Furthermore they point out that as evaporation progresses the solution will more likely retreat to the smaller pores where high supersaturations will be reached by solution supplied by the larger pores. Similarly Kashchiev and Van Rosmalen (1995), Putnis *et al.*, (1995) and Tiller (1991) agree that the smaller pores can maintain higher degrees of supersaturation. Dei *et al.* (1999) alternatively suggested that the shift towards larger pores can be attributed to salt crystallisation between small and coarse pores rather than preferential occlusion to smaller ones. The above mentioned experimental observations of Putnis and Mauthe (2001) are thus in agreement with both expressions. Salts that do not reach high supersaturations as halite might crystallise in the larger pores while under faster evaporation rates they might maintain higher supersaturation degrees. It seems that kinetic factors such as the supersaturation rate depending on environmental, solution and pore properties play the key role in the generation of damage. Still, fracture requires the propagation of the pressure to an area of the host comparable in size to the strength controlling flaws (Scherer, 1999).

Both equations have produced practical controversies failing to generalise the mechanism behind salt damage. Although other authors tried to combine the two leading theories (Benavente *et al*, 1999) Scherer's response set an undisputed advance to the challenge. Scherer (1999) denoted that supersaturation sets an upper bound on the crystallisation pressure and that the stress can be lower than expected by the upper bound if the contact angle is low. This suggests that the two theories are corresponding. Scherer's treatment also explains how the pressure is sustained after the failure of the host pore. The same author, in two more recent studies (Scherer, 2000; 2004), showed how high stresses can occur in large pores when the gap between a crystal and the pore wall serves as a small pore where the water meniscus retreats as long as the interfacial tension between the pore and the crystal is larger than the sum of the interfacial tensions between the pore and the solution and between the solution and the crystal. Another interesting fact that derives from this treatment is that crystallisation does not necessarily produce stress fields large enough for the propagation of critical flaws and thus failure of the material. Scherer's work has been used by Flatt (2002) and Tsui *et al.* (2003) to explain the exceptionally destructive behaviour of sodium sulphate. Based on Scherer's work, Rijniers *et al.* (2003) calculated the pressures generated by sodium carbonate and sodium sulphate by solubility measurements inside the pores using the NMR technique developed by Pel (1995).

However these expressions do not cover two major issues: the anisotropic load of the growing crystal and the interaction between the components of multi salt solutions, addressed recently by Steiger (2005). The loaded surface which is in contact with the stress solution has a higher solubility than the unloaded surfaces. Since the solution is supersaturated against the unloaded surfaces, growth will proceed on these surfaces reducing the degree of supersaturation and consequently the pressure difference. According to Steiger's expression supersaturation cannot be maintained for long periods and hence crystallisation pressure is a dynamic effect taking place during sharp transitions of temperature or relative humidity. This expression also includes the non ideal behaviour of the liquid phase using the ion interaction approach of Pitzer (1973). This much anticipated treatment permits the calculation of crystallisation pressures deriving from multi salt solutions which are closer to real conditions since single salt solutions are rarely found in nature.

As already mentioned the present state of awareness indicates that a number of kinetic parameters such as the nucleation rate, the macroscopic properties of the host and the interaction between the species play the deciding role between preservation and damage. For example Rodriguez-Navarro and Doehne (1999) and Benavente *et al.* (2004) observed microscopically that halite crystallises at the air-solution interface while mirabilite grew inside the solution. As a result halite will more likely produce harmless efflorescence while mirabilite will crystallise inside the pore matrix, potentially causing damage. On the other hand Sunagawa (1981) observed that halite can be particularly harmful when crystallising in the acicular form under conditions that promote a higher nucleation rate. These conditions depend on environmental, substrate and solution properties.

Arnold and Zehnder (1991) discussed extensively the role of the crystallographic character of salts and concluded that whisker like crystals can grow perpendicularly to the masonry surface, due to low supply of moisture, resulting in contour scaling. Scherer (2004) also confirmed experimentally that any salt irrespectively of its standard form will eventually produce whisker like crystals in the drier parts of the host material. Apart from the moisture supply, the crystal habitus is also linked to the crystallisation support (Dei *et al.*, 1999). The crystallographic character might influence the resulting pressure. Mosebach (1951) observed that the 010 face of $K_2Cr_2O_7$ grows at twice the pressure of the 001 plane. Pina *et al.*, (2000) stretch the influence of crystal growth mechanisms, apart from supersaturation ratios, in the composition of multi salt solution end products and they explain the compositional shift from the equilibrium by nucleation rate kinetics.

Nucleation represents the first step of crystallisation. Classic nucleation theory relates the number of nuclei formed per unit of time and volume to supersaturation, interfacial free energy, solubility and other parameters (Nielsen, 1964). Although several authors provided evidence for a relation between solubility and supersaturation (La Iglesia *et al.*, 1997) it is not very clear whether we can classify accordingly the salts as to their ability to cause damage. On the other hand single salts are rarely found in nature. Apart from the other parameters already mentioned, such as the evaporation rate and the crystallisation site, in order to understand nucleation kinetics we must take into account the physicochemical properties of a multi salt system, like phase equilibria, ionic mobility, etc. All salts do not supersaturate at the same rate irrespective of support or environmental conditions. Experimental work on two component solutions has shown that soluble salts do not maintain high supersaturations prior to crystallisation while sparingly soluble salts can reach very high levels of supersaturation (Prieto *et al.*, 1993; Pina *et al.*, 2001; Astilleros *et al.*,2003). He *et al.* (1994; 1995) have also shown that the presence of more soluble salts leads to the increase of the solubility of sparingly soluble salts and hence decrease of the critical supersaturation. Pina and Putnis (2002) suggest that more soluble compositions tend to nucleate even if they are less supersaturated than less soluble compositions and that this effect is more important for compositions with large differences in the solubility products. Putnis *et al.* (1995) also provide experimental evidence for the influence of the solution concentration to the nucleation rate and the critical supersaturation. Obviously the above mentioned treatment of Steiger (2005), which considers the dissociation of salts among others, represents a great advance in the definition of the weathering mechanism.

Other mechanisms, like hydration pressure, osmotic pressure, hydraulic pressure, thermal expansion, and chemical weathering have also been proposed without much attention from the scientific society. More detailed reviews can be found in numerous works. Evans (1970) has provided the first review which also includes many early investigations. Goudie and Viles (1997) presented the most global approach including all the theoretical aspects among many case studies of geomorphology, engineering as well as heritage in the only monograph on the subject. Rodriguez-Navarro and Doehne (1999) and Steiger (2005) incorporate very comprehensive reviews of the theoretical advances in crystallisation pressure equations. Charolla (2000) points out the major questions that remain unanswered and Doehne (2002) classifies brilliantly all the major aspects of the phenomenon including even terminology issues.

Nevertheless, as the mechanisms behind salt damage are becoming clearer, applied research faces a growing challenge to exploit the latest advances of the theoretical toolbox for practical conservation solutions. Regrettably theory and application still produce controversial results. For example Scherer's treatment suggests that surface coatings could be effective against crystallization damage (Tsui *et al*, 2001) while such applications have been already proved rather pessimistic (Price, 1996).

There is no doubt that it is equally important to investigate other aspects of salt damage like the sources of the salts, the pathways of transportation as well as the activation of the damage and the pathology. It is of course prominent to define the mechanism in its entirety, but it might be less significant or even necessary in decision making for conservation purposes, as other parameters. For example the elimination of a source, the blocking of a pathway of salts, or the control of the parameters that can activate salt damage could be rather effective conservation solutions. Unfortunately applied research faces the major obstacle of *in situ* assessment. In the vast majority of case studies the presence of salts alone is considered evidence or risk of damage. The application of theory into practical solutions is still poorly appreciated. Nonetheless *in situ* experimental applications, having the advantage to face directly the confrontation of the hazard, will keep contributing in the solution of this Gordian knot.

2.3 Sources and effective pathways

The salts most frequently referred in heritage literature (table 2.1, p.25) originate from the earth's natural compounds like sea water and crustal material, anthropogenic activities like industry and urban pollution, and the metabolism of organisms. Some salts might also originate from the building materials. Many other minor local sources, natural or not, have been identified, like road de-icing salt. Specifically for monuments, a major and very important source of dissolved salts might be the conservation materials. More correctly one should refer to sources of ions and not salts, since in most cases the resulting salts did not pre-exist but derive as neoformation products of ions with [illegible] origin.

UNESCO has adopted the definition by Szabolcs (1979) of five major cycles of salt production, distribution and accumulation over the globe, involving mixed air, ground and water compound processes:

1. Continental cycles of salts that derive from rock weathering in inland regions and are distributed through the atmospheric pathway or inward flowing drainage.
2. Marine cycles of sea salts distributed through the atmospheric pathway over coastal regions.
3. Delta cycles of both sea and continental salts that mix in estuary regions resulting in complex transport and accumulation processes.
4. Artesian cycles that refer to the evaporation of deep underground waters through tectonic processes.
5. Anthropogenic cycles forced by human actions which refer to a great number of processes including agricultural, watering, industrial, mining, waste management and many other activities that result to the direct production of salts or the disturbance of natural cycles.

Natural waters comprise the main source of solutes. The composition of sea water (see table 3.1, p. 47) is governed by sodium chloride (≈80% pw) but also contains appreciable amounts of sulfates, nitrates, carbon, magnesium and potassium. Crustal materials are mainly composed of calcium, alumina and silica. River waters contain dissolved materials from bedrock and on average their composition is dominated by calcium and bicarbonate. Ground waters are more or less solutions of every salt that can be found in the ground (Millero, 2001). Waters in urban regions are enriched in chlorides because of high sodium chloride consumption. Soils near roads frequently blocked by snow are enriched in chlorides used for de-icing (Klassen and Roberge, 1999).

Building materials contain a large variety of soluble compounds like magnesium, sodium, calcium, potassium and sulphates. Dolomitic stones and mortars frequently release magnesium (Made and Fritz, 1990; Martin *et al.*, 1992) Calcareous stones and mortars may react with acidic atmospheric gases producing calcium sulphates and nitrates. Fired bricks used for masonry, sheltering or mortar additives, contain large amounts of sulphates and potassium while clay might release dissolved alumina and silica (Bowler, 1982). Sand acquired from sea banks to be used as aggregate for mortars contains large amounts of sea salts.

Biological metabolism mainly produces nitrates. The mechanism has been studied thoroughly due to the great importance of the nitrogen cycle in the biosphere equilibrium (Hill, 1996). Animals' excrement contains ammonia which is oxidised to nitrous and then nitric acid by bacteria. Obviously nitrates are abundant in locations of increased human and animal presence. Stables for example have been served as a potassium nitrate source, used for gunpowder. In modern urban areas nitrates are not as abundant as expected due to proper waste management. Nonetheless it has been reported that building stones in urban areas are rich in the bacteria needed for the nitrification of ammonia (Arnold and Zehnder, 1991). Probably their presence is linked to atmospheric ammonium sulphate, a product of pollution and not metabolism. Marine organisms also produce nitrate which constitutes one of the major ions of sea water (Millero, 2001)

The most destructive substances emitted by anthropogenic sources form nitrates, sulphates and ammonia. The gases emitted by industry and vehicles contain sulphur, nitrogen and carbon oxides that may deposit on monuments surfaces. A lot of work has been carried out on the chemical dissolution of calcareous materials by acidic solutions deriving from these gases (Moropoulou *et al.*, 1998; Van Grieken and Torfs, 1996; Zezza 1996a). The conditions under which this weathering mechanism takes place are not yet clear although there is no doubt that it results to the formation of salt crusts and primarily gypsum. On the other hand the role of these crusts in the preservation of the monument has not been thoroughly investigated. In general, conservation practice primarily considers the aesthetic problem of the crusts which contain fly ash, responsible for the "blackening" of surfaces while research is mainly occupied with their occurrence and composition (Price, 1996). Few authors have considered that these crusts actually contain salts that might promote further weathering (Price and Brimblecombe, 1994; Steiger, 2002). Gypsum is considered inactive in salt weathering due to its low solubility. Recently the growing awareness of the interaction between salts has changed our notion of the presence of gypsum. It is characteristic that the rate of material loss of St Paul's Cathedral in the centre of London has not slowed down despite the reduction of air pollution during the last 20 years. Trudgill *et al.* (1991) have attributed this phenomenon to salt weathering by pre-existing gypsum. The other product of calcarenites chemical dissolution, calcium nitrate, is also considered harmless due to its high solubility. Friese and Protz (1998) suggested a synergetic model of further weathering for sulphur and nitrogen gases based on the solubility difference of their products.

The presence of air pollution in the coastal environment might change the composition of marine aerosols. The interaction of sulphur and nitrogen oxides gases with the aerosol leads to a phenomenon called "chloride depletion" and results in the formation of sulphates and nitrates (Zhuang *et al.*, 1999). Considering that this mechanism is the major agent of sulphur removal from the atmosphere we can speculate that it promotes considerably sulphate deposition on the ground or vertical surfaces near the coast.

Wall paintings are cleaned with acidic and alkaline products, consolidated with water glass, Portland cement, alkali silicates, siliconates and other products which contain considerable amounts of soluble compounds. Unfortunately it is already very well known that conservation treatments can be as dangerous as heavy pollution. Nonetheless the ineffectiveness of these treatments has been rarely linked to salt weathering. Usually additives are criticised for aesthetic deformation (discoloration, texture alterations) or structural damage deriving by other mechanisms like thermal expansion. Literature contains numerous examples of case studies on heritage surfaces cleaning (ICOMOS, 2003). These publications focus on the effectiveness of the solvents against soiling, the preservation of historic patinas and the hazards of dissolving authentic pigments. Obviously the vast majority of practitioners are not aware that these solvents will most likely produce salts, especially when acids are neutralised by alkalis.

Portland cement has been extensively used during the last century for structural restoration and consolidation of heritage buildings and despite the warnings of international organisations it is still in use due its applicability and low cost. The release of soluble carbonate and sulphate alkalis from hardened cements has been early recognised (McCoy and Eshenour, 1968; Lea, 1970). Gypsum is regularly added to Portland cement and its presence in restored buildings is expected almost by definition (Fassina, 1996). Ettrengite, thaumasite and calcium mono-chloro-aluminates originate usually from the weathering of concrete by sea water (Regourd, 1982; Duval and Hornair, 1992; Bernabe *et al*, 1996; Collepardi, 1999; Veniale *et al*, 2003).

The identification of a source is not always easy and must be investigated with great prudence, especially when it is very obvious. A great example of the complexity of the origin of salts is given by Arnold (1996). In this work it is graphically stated that "not all chlorides occurring near the sea are from the sea" (p. 134). The latter was remarkably recorded in the case of St. Andrews Church in Norfolk, where the sodium chloride present on the indoors surfaces was more likely to be explained as an additive in conservation lime washes, rather than directly originating from the nearby sea (Watt and Colston, 2000). Similarly Alves and Sequeira Braga (1996), arguing that the distance of the Museo dos Baschaihos (Braga) from the sea could not justify the strong presence of halite, found that a neighbouring building has been used as a salt storehouse in the past. Isotopic identification is a very promising technique but proper methodologies for conservation studies are still under investigation (Klemm and Siedel, 1996).

Calcite	$CaCO_3$	Epsomite	$MgSO_4.7H_2O$
Dolomite	$CaMg(CO_3)_2$	Hexahydrite	$MgSO_4.6H_2O$
Magnesite	$MgCO_3$	Kieserite	$MgSO_4.H_2O$
Neuqeuhonite	$Mg CO_3.3H_2O$	Darapskite	$Na_3(SO_4)(NO_3).H_2O$
Lansfordite	$Mg CO_3.5H_2O$	Mirabilite	$Na_2SO_4.H_2O$
Hydromagnesite	$Mg_5[OH(CO_3)_2]_2.H_2O$	Thenardite	Na_2SO_4
Natron	$Na_2 CO_3.10H_2O$	Arcanite	K_2SO_4
Thermonatrite	$Na_2 CO_3.H_2O$	Bloedite	$Na_2Mg(SO_4)_2.4H_2O$
Nahcolite	$NaHCO_3$	Picromerite	$K_2Mg(SO_4)_2.6H_2O$
Trona	Na_3HCO_3	Boussingaulite	$(NH_4)_2Mg(SO_4)_2.6H_2O$
Kalcinite	$KHCO_3$	Syngenite	$K_2Ca(SO_4)_2.H_2O$
Gypsum	$CaSO_4.2H_2O$	Gorgeyite	$K_2Ca_5(SO_4)_6.H_2O$
Bassanite	$CaSO_4.1/2H_2O$	Aphthitalite	$K_3Na(SO_4)_2$
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$	Thaumasite	$Ca_3Si(OH)_6(CO_3)(SO_4).12H_2O$
Bischofite	$MgCl_2.6H_2O$	Halite	$NaCl$
Antarcticite	$CaCl_2.6H_2O$	Sylvite	KCl
Tachyhydrite	$CaMg_2Cl_6.12H_2O$	Nitrocalcite	$Ca(NO_3)_2.4H_2O$
Nitromagnesite	$Mg(NO_3)_2.6H_2O$	Amm. nitrate	NH_4NO_3
Nitratite	$NaNO_3$	Whewellite	$Ca(C_2O_4).H_2O$
Niter	KNO_3	Weddellite	$Ca(C_2O_4).2H_2O$

Table 2.1 List of salts commonly found on buildings

On the other hand the elimination of a source is not always attainable (considering the case of sea salts) and usually there is not a single source. In the case of Mount Athos Protato Cathedral, the removal of previous conservation mortars near the ground, found to be rich in sulphates, proved to be very successful and such treatments are now routinely carried out by the local authorities. Alternatively it was impossible to remove the concrete ceiling that replaced the wooden one during the 60's (Minos, 1997). In most cases the blocking of the contamination pathway seems more attainable.

Salts can be transported from their source to the surface or the capillaries of a structure through various pathways. Ground water can transport ions, previously existing in the ground or deposited from the atmosphere, by capillary rise through the foundations. This very effective pathway is the most commonly referred in the literature although it cannot explain the presence of salts above the evaporation zone. Lewin (1982) gives a very fluent description of this pathway, in order to calculate the depth of the evaporation front as a function of the rate of evaporation against the rate of capillary supply. Arnold and Zehnder (1991) similarly described the height fractionation of multi salt solutions rising from the ground.

A lot of work has been carried out in past decades towards the confrontation of this problem (Massari and Massari, 1993). The goal was to reduce the surface of the wall in contact with the ground, by creating evaporation spaces between them or by partially isolating them with impermeable materials but the results were not always successful. Massari's claim that the speed of moisture invasion is reduced is true as far as it concerns the time taken for moisture to reach the evaporation surface. Hall and Hoff (2002 / p.154) demonstrated that the rates of water absorption of two identical materials with different source areas ultimately equal and the effects of the reduced area of inflow surface disappear. The flow is determined by the impedance of the entire path and not only by the source. A more successful method is the sorption of ground waters around the monument by electric pumps, activated automatically, but it can only be used as a precaution measure against sudden rises of the water horizon and additionally it is very expensive. More invasive methods like the addition of water repellent materials have not produced spectacular results either (see chapter 4).

The precipitation of meteors like rain and fog also represents a pathway for salts suspended in the atmosphere. The effectiveness of this path though, is not very clear (see Chapter 3.2). Apart from driving rain, poorly maintained water pipes and shelters have also been held responsible for moisture penetration. Suspended matter can also be deposited without the help of meteors. Winds can transport aerosols in very long distances where they can deposit by various dry mechanisms. More details of dry deposition are given in Chapter 3.2. The atmospheric environment can be more easily isolated than the ground. Sheltering has been extensively used and equally criticised in every type of environment. A great number of sheltering solutions is available today but their effectiveness is still in question (Aslan, 1997).

The presence of external sources of liquid moisture is not always necessary for salt transport. Salts are deliquescent materials and can be dissolved in water vapour that they attract from the atmosphere. In this way autochthonous salts and salts released from conservation materials can be transported to other regions of the material by capillary effects while salts deposited dry on the surface can penetrate through the pore matrix. This process is called automigration. Despite the fact that it is considered very slow it might explain the deterioration phenomena above the evaporation zone. The automigration might be a significant mechanism of salt transport in the case of marine aerosols deposition as shown by Chabas and Lefevre (1996).

2.4 The transport of moisture and salts in the pore matrix

General properties

As described previously some mechanisms transport salts directly in the capillaries while others deposit them on the surface of a material. It is clear though that the damage caused by salts is taking place inside the pores and thus the site of accumulation can make the difference between damage and preservation. Salts can be transported inside the pore structure of a material solely in the liquid state. Consequently the transport of moisture in capillaries is of great importance for the understanding of salt damage.

Primarily we must define some basic properties of the porous matrix. Obviously materials without porosity are not susceptible to salt weathering. Porosity can be defined as the proportion of void to solid space of the material while the interconnected matrix through which a fluid can move is called effective porosity. The effective porosity though does not represent a measure of the flow. The interstitial surface area of the pore matrix per unit volume of the material, called specific surface area, affects the maximum amount of fluid that can be hosted by the material and the rate of the flow. Nonetheless since the matrix is highly irregular in size and shape the specific permeability of a material is a function of its pore size distribution. (Robson, 1965; Toracca, 1988). The distinction between macro- and micro-pores is not very clear in literature although in general it is set at the region of 5 microns (Hoffman *et al.*, 1995). Frequently micropores are referred as those of less than 1 micron in diameter, where the Laplace effects take place (Kashchiev and Rosmalen, 1995).

Although salts are transported solely in the liquid state the overall flow of moisture in capillaries depends on the properties of both the liquid and the vapour phase of water.

Vapours inside pores, in the absence of convective air flow, are mainly transported by diffusion. Several mechanisms have been proposed for the liquid transport but the predominant is the viscous flow due to capillarity.

If we immerse a straw in a glass of water we will observe a slight elevation of the water inside the straw. This simple observation describes the phenomenon of capillarity. When two fluids come in contact, an interface is created between them. This interface, called *meniscus*, has got particular physical and chemical properties. The meniscus is curved towards the fluid with the lower pressure. The equilibrium of the convex and the concave pressures, which retains a constant radius of the curvature, can be expressed by the *Laplace equation*[6].

The pressure on the concave site is greater than the pressure on the convex side of the meniscus, and the water in the straw (capillary) is rising upwards until the hydrostatic pressure is equal to the pressure drop against the meniscus. Thomson (Lord Kelvin) applied the Laplace equation to the behaviour of water in a capillary and resulted to an equation known as *Kelvin's equation*[7]. This equation describes as well the condensation of water vapour on surfaces. Nevertheless the movement of moisture in a porous material is more complicated than in a straw. An experimentally derived expression of the flow of a liquid through a porous material is given by *Darcy's law*[8].

Nevertheless these expressions do not take into account that liquid and vapour transport are corresponding. The first attempt to model both phases by Kricher and Vos (Vos, 1969) neglects the temperature gradient. Phillip and de Vries (1957) and Luikov (1966) generalised the expressions of capillarity and diffusivity remarking the generation of [illegible] within the pore matrix. In brief, in the absence of liquid continuity moisture

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[6] $P_1-P_2=2\sigma/r_m$ or $P_1=P_2-2\gamma r$ $(aw=\gamma a\sigma)$
where γ is the surface tension, σ is the surface area and r_m is the mean radius of the curvature.

[7] $P_c=p_w\exp(2\gamma V_m/rRT)$
where P_c is the vapour pressure of water in the capillary, p_w the vapor pressure of a plane surface of water, R the gas constant, T the temperature and V_m the molar volume of water.

[8] $Q = KA\Delta P/\mu l$
where Q is the volume flow rate, K is the permeability of the material, A is the total cross sectional area of the material, ΔP is the pressure difference, μ is the fluid viscosity and l the length travelled in the direction of the flow.

transport continues in the vapour phase. Obviously the properties of the solution play an important role. As already described the presence of liquid islands and their site of accumulation is of great importance for the generation of crystallisation pressures. Moreover Dullien (1979) observes that water flowing through interconnected pores of different radius can bypass the larger pores, where the flow decelerates, leaving behind entrapped bubbles.

Another important factor is that the density and viscosity of a salt solution is higher than pure water and increases with concentration (Kotter and Riekert, 1978). Consequently the capillary flow rate decreases. Salt solutions are transported up to a height where evaporation starts and the concentration increases. Continued evaporation decreases the mobility of the solution and eventually results in the critical saturation for the crystallization of the salt. Furthermore increasing ionic concentration reduces the ability of the solution to wet the pore surface. A more recent study by Pel (2001) shed more light on the implications of the solution properties. Using a Nuclear Magnetic Resonance (NMR) scanner he showed that Na ions tend to accumulate on the surface during absorption of a NaCl solution, while at the beginning of drying all the Na ions were transported to the surface to level out gradually due to diffusion. Thus ionic diffusion does not necessarily follow the moisture's flow.

As already mentioned salts are deliquescent and consequently they attract moisture from the atmosphere and dissolve. Building materials contaminated with salts present thus different hydraulic properties than "clean" materials. Benavente *et al.* (2003) studying the evaporation process from building stones tried to combine the pore properties with the nature of the contaminant salt and the environmental conditions. The resulting equation predicts the equilibrium relative humidity of a saline solution confined in a pore. Sawdy (2001) studied the influence of a number of kinetic parameters in the absorption and desorption behaviour of mortars contaminated with salts. The results revealed that relative humidity and air speed had the most significant effect during adsorption while the support characteristics played the major part during desorption.

Several mathematical models and experimental work on building materials have been carried out. More details about the current understanding of fluid motion in porous materials can be found in Kumaran *et al.* (1994) and specifically for wall paintings in Pender (2001). Wall paintings present the particularities of stratified or layered materials (see next section).

The distribution of salts in the masonry is an issue of increased interest among conservation scientists. There are numerous case studies presenting particular distribution patterns, usually linked to weathering phenomena, as well as investigation techniques. The distribution of salts in height and depth attracts the main interest of research (Steiger, 1996) while some surface as well as 3-dimentional studies have also been published linked primarily to cleaning or desalination treatments (Weber *et al.*, 1996).

Arnold and Zehnder (1991) have produced a sensible model describing the fractionation of salts accumulation in height depending on their solubility. Although this model is frequently observed we must notice that it does not take into account the interaction of the species and it refers solely in ground capillary rise. Moreover linking this model to weathering phenomena is completely unsatisfactory since none of the conditions necessary for damage are met. Rodriguez-Navaro and Doehne (1999) observed in laboratory experiments that halite tends to crystallise on the surface while mirabilite accumulated inside the pores. Again we must notice that the experimental conditions are far from realistic, neglecting the interaction of salts and the contamination complexity. Lewin (1982) has produced a mathematical model to calculate the depth of the evaporation front. I'anson and Hoff (1986) presented also a theoretical model predicting the height of capillary rise as a function of the evaporation rate. Steiger (1996) introduced the issue of salts interaction, using phase diagrams of multi-salt solutions to explain the distribution of salts in a specific sandstone structure.

Nevertheless there is no convincing argument which generalises salt distribution in the masonry or constructs a model that predicts it solely by contamination evidences. The contamination and the redistribution of salts are continuous and irregular processes depending on many parameters. The distribution mapping requires more likely a case to case investigation. On the other hand the geometric distribution changes in time. Any investigation based on a single sampling campaign is obviously biased by the particular conditions during the investigation. Whether the evolution of salt systems in time follows a predictable pattern or not is still a matter of debate. The issue is of great importance since any *in situ* investigation of salt weathering is based on sampling methods.

Interface phenomena

Early studies on interface phenomena focused in the moisture movement in soils (Childs and Bybordi, 1969). Soils however have relatively larger pores than masonry materials and gravitational forces have to be taken into account as well. This led several authors to reevaluate over the last decade the interface phenomena of layered building materials. The interface between two layers with different moisture transport profiles has been generally assumed by the literature as a perfect hydraulic contact and accordingly moisture transport as continuous and undisturbed (Nofal *et al.*, 2001). This assumption has been challenged through theoretical models and laboratory experiments. The hydraulic discontinuity seems to play an important role for salt weathering which under certain conditions might cause crystallisation at the interface.

De Freitas (1991) distinguishes three general contact configurations between layers:
a) Hydraulic continuity, assuming interpenetration of the two layers.
b) Natural contact, assuming physical contact between the layers but not interpenetration.
c) Air space, assuming the existence of an air pocket a few mm thick.
In each case the relationship between the moisture contents of the two layers is established by different functions, based on the principles of liquid and gas moisture transport. Nevertheless experimental evidence suggests the existence of various kinetic deviations deriving primarily from the pore properties of each layer.

Wilson *et al.* (1995a;b) examined the absorption of moisture in various two layered composites of plaster and plaster/sand. In the case of absorption through a higher sorptivity material into a lower sorptivity material they found that the rate of absorption decelerates immediately after the moisture front reaches the interface and it becomes equivalent to the absorption of the second material alone. Thus the material with the lower sorptivity controls the overall flow. Alternatively in the case of moisture transport from a material with lower sorptivity into a material of higher sorptivity they found that the absorption rate increases. In both cases the second material controlled the overall flow. These findings contradicted the assumption that the layer with the lowest sorptivity governs the flow (Fok, 1970).

Pel (1995) challenged the assumption of perfect hydraulic contact in bonded materials. Following the moisture movement by NMR in bonded fired clay brick and mortar he identified a jump in the suction across the interface but he did not give a satisfactory explanation apart from a change in the hygric properties of mortar during the bonding process. Nonetheless this finding means that the properties of separately hardened mortars are not indicative for their behaviour when bonded to other masonry materials. The latter has a great importance for conservation studies considering that in most cases conservation mortars are chosen for their properties against those of the masonry neglecting the interface phenomena (Palomo *et al.*, 1996). Brocken (1998) continuing Pel's work studied the behaviour of the same layered materials during drying and verified the hydraulic discontinuity at the interface as well. Moreover he observed that the layer with the largest pores dries first and the drying behaviour of composite materials is a function of the pore size distributions of both layers.

De Freitas *et al.* (1996) studied the wetting and drying phase of layered materials in *natural contact*. They verified as well the existence of a hydric resistance which limits the flow across the interface. Moreover they observed that during drying the interface causes faster drying of the external layer due to restrictions in the supply of moisture from the internal layer. This observation concerns significantly the salt weathering effects on layered materials. Obviously this disturbance of the drying process might cause salts crystallisation inside the pores which otherwise might have crystallised on the drying surface. Qiu *et al* (2002) found that the hydraulic resistance of bonded or natural contact interfaces decreases after the first layer reaches saturation and that it is also relevant to the experimental time period and the thickness of the samples.

Nonetheless the hydraulic discontinuity at the interface does not by itself provide evidence of disturbed salt distribution in layered materials. Very recently Petrovic *et al.* (2004) combined the works of Pel (1995) and Brocken (1998) in order to follow the salt transport and accumulation in plaster/substrate systems. They observed that when the plaster has smaller pores than the substrate most salt accumulates in the plaster.

Accordingly they assumed that if the plaster had larger pores than the substrate the plaster would dry first triggering salt crystallisation at the interface. Although the latter has not yet been confirmed experimentally there is no doubt that under certain conditions the hydraulic profile of layered materials might disturb the behaviour of salt solutions and potentially cause damage. Still the distinct layered weathering pattern of wall paintings has not been reproduced experimentally and although there is evidence for salt accumulation between the layers we cannot link it to damage.

2.5 Pathology - Damage phenomena

Salt weathering refers solely to mechanical damage, hence failure of the material's mechanical resistance under an opposing force. As described previously this force originates from the pressure exerted during crystallisation. Mechanical failure corresponds to numerous patterns of damage usually connected with the type of stress. The intensity of damage depends on many parameters and primarily the mechanical characteristics of the material and the characteristics of the stress.

Failure is in general considered as any state of the material other than predefined as default. The default definition is obviously relative to the requirements since there is not such a thing as an ideal state for materials. Usually the default state for stones corresponds to freshly cut specimens from the quarry. In engineering any deformation of structure or position of the building materials is considered failure. Building materials such as stone, bricks and mortars are classified as *ceramics* in terms of their mechanical behavior. As such they fail by *brittle fracture*, hence cleavage due to negligible ductility. This behavior is attributed to the presence of both covalent and coordinate bonds that characterize ceramic materials.

Particularly for heritage materials we must underline the presence of previous damage. While in engineering damage comprises the undesirable exception in monuments damage is the rule. According to Griffith's criterion the elastic energy that can be stored in a fissured material is smaller than the energy that could be stored in the same material free of fissures and the energy needed for the propagation of damage corresponds to the decrease of the energy storage capacity (Barenblatt, 1962). Thus geometric deformations that pre-exist in heritage structures comprise tension capacitors weakening the material against mechanical pressures.

Crystallisation pressure is frequently considered a static uniaxial load. In this case the failure criterion is simply described by the maximum elastic deformation allowed. Recent advances though suggest that salt weathering is a dynamic phenomenon and failure cannot be predicted simply by the material's mechanical resistance (Steiger, 2005). Nonetheless for anisotropic materials as porous stones and mortars it would be difficult to predict the site and the pattern of damage even under an external isotropic load. Besides damage by salt weathering is initiated in the micro-scale of the pores and the visual results comprise the outcome of the sum of microscopic fractures. Moreover damage due to salt weathering might trigger other tensions like gravity that will lead to the observed weathering pattern. Salt weathering tests have revealed a decrease in the modulus of elasticity of stones before the propagation of visual damage (Goudie, 1999).

Various weathering patterns have been associated with salt weathering. The most common patterns are all the cumulative result of micro-cracks in the pore matrix and differ primarily in the size of the detached material. Hence, granular disintegration (or sanding, sand disintegration, powdering) refers to the release of pulverised debris at the size of coarse sand while scaling (or flaking for thin fragments) refers to the detachment of larger compact pieces (of larger surface than height and parallel to the exposed surface). Honeycomb weathering is a particular pattern referring to superficial fissures that can extend to massive rock formations called *tafoni* (Kelletat, 1980). Frequently various patterns coexist in the same damaged area suggesting the evolution of the pattern in time. For example compact superficial fragments usually detach only to reveal an inner layer of powdered material. Warke and Smith (2000) identified two distinct layers in weathered sandstone from Belfast, corresponding to superficial scaling followed by increased porosity. Interestingly they attributed the evolution of weathering to progressive contamination (concentration increase) and fragmentation of the salts (halite and gypsum).

Literature on salt weathering presents an uncomfortable variety in terminology damage patterns. There have been several attempts to classify damage patterns of which the most distinctive is that of Fitzner and coworkers (Fitzner *et al.*, 2000). The only on-line photographic database of stone damage is still extremely limited (http://www.stone.rwth-aachen.de/atlas1.htm). Recently several modern diagnostic techniques like IR phottogrametry and digital image processing have contributed in the classification of damage (Zezza, 1996b). General guidelines for stone weathering diagnosis, adopted by international organisations and standards fail to specify clearly the patterns attributed to salt damage (Delgado Rodriguez, 1991). Phenomenological diagnosis on the other hand cannot by itself identify salt weathering activity even in the presence of efflorescence or distinctive patterns. Although in some cases the phenomenological investigation of weathering indicates strongly the action of salts in most cases the produced patterns might originate from various other causes. For example earthquake damage produces large cracks that cannot be mistaken for salt weathering but in time the contact between the new interfaces might result in powdering. Furthermore the existence of previous damage does not indicate present weathering activity. So far there isn't any convincing methodology of *in situ* investigation that can provide solid evidences of ongoing salt weathering. The reason is quite simple: the conditions met for salt weathering are still undefined.

Wall paintings are composed of mortars that suffer all the common weathering effects as other porous brittle materials. A particular pattern frequently observed in wall paintings is the detachment from the masonry and between the layers that compose the rendering. Although it has been attributed to the preferential crystallisation of salts between the layers there is no experimental evidence to support it. Renderings suffer in general tangential crosscutting tensions usually amplified by other loads, like seismic shocks or gravitational deformations of the masonry. Nevertheless we must underline the importance of damage at the external layer that carries the painting. Flaking of the paint layer is a very common damage of every painted material attributed to various causes. Most of these causes like differential thermal expansion do not have a significant effect on wall paintings since the medium is similar to the substrate[9]. The only difference is the negligible porosity of the paint layer that might disturb the hydraulic continuity and cause crystallisation at the interface. Van Hees and Lubelli (2002) attribute sca

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[9] An exception that justifies the rule is the case of Leonardo Da Vinci's "Last Supper" mural which was executed by wax medium and suffered distinctive damage of the paint layer attributed to the incompatibility of the materials (Camuffo and Bernardi, 1991).

existence of a thin surface layer, with properties even slightly different from the rest of the material, while once this layer is gone damage usually continues as powdering. ICOMOS has only recently recognised the need to specify diagnosis, investigation and treatment on the particularities of wall paintings (ICOMOS, 2003).

In many cases specific patterns are attributed to the presence of specific salts (Silva *et al.*, 1996). Considering that the load type exerted by crystallisation is similar for every salt it is difficult to accept the link between specific salts and weathering patterns. More likely the pattern is connected to the crystallisation location. This in turn depends on material properties, environmental conditions and the supply rate of the solution (Lewin, 1982). On the other hand it has been shown that the crystallisation location of halite and mirabilite is responsible for the different weathering ability they present in tests (Rodriguez-Navvaro and Doehne, 1999). In this respect we can except that under specific conditions weathering patterns can be associated to specific salts found in the area but no generalisations can be made. Alternatively it is quite clear that a specific salt might cause different damage patterns (Amadori *et al*, 1989). Therefore the association of damage to the species found during in situ investigations must be considered with great prudence. Lubelli *et al.* (2004) identified two different weathering mechanisms, resulting in different weathering patterns, on the same wall, both triggered by sea salt transported in the masonry by different paths (spray deposition and rising damp). Nonetheless they neglected the fact that sea water is a multi salt solution which due to fractionation might result in various combinations and concentrations of salts with properties much different than pure halite.

The intensity of damage is a largely relative measure. Moderate occurrences of the phenomenon on a geological scale might correspond to complete loss of architectural members while intense weathering of heritage wall paintings is considered tolerable for modern renderings. Nevertheless there have been considerable attempts to model the rate of loss due to salt weathering. Geomorphology studies focus on both field and laboratory observations. The rate of tafoni recession is an area that attracts the interest of many scientists (Matsukura and Matsuoka, 1991; Sunamura, 1996; Turkington and Phillips, 2004). *In situ* investigations have produced great variability in the results. This variability has been primarily attributed to different environmental conditions (Sancho *et al.*, 2003;

Inkpen and Jackson, 2000). Spatial variability has also been observed, at the scale of a few centimetres (Williams and Robinson, 2000). Smith *et al.* (2000) suggest that the complexity and polymorphy of weathering features needs to be addressed in the microscale of the stone/air interface. Recently geomorphologists have used dated historic structures in order to calculate long term weathering rates (Mottershead, 1997). Increasing weathering rates have been attributed to the progressive mechanical weakening of the material as well as to the increased weathered surface area (Cooke *et al.*, 1995). Norwick and Dexter (2002) pointed out that the rate of loss is not linear, starting out slowly, accelerating with increasing salts concentration and then decelerating again. Thus field investigations are always biased by the moment of the observations. This might explain some absurd predictions for the preservation of heritage structures (Beloyannis and Daskalakis, 1988).

Laboratory simulations have also been used for measuring the effects of salt weathering. Although durability tests have long been standardised they still receive criticism and modifications. The variety of tests in the literature is truly immense. Goudie (2000) produced an excellent overview of the variability in tests concerning the sample's properties, size, form and texture, the environmental cycles and the salts used. As expected the results are correspondingly variable and their comparability problematic. On the other hand the standardisation of tests bears a great generalisation risk. For example the use of sodium sulphate in durability tests (Price, 1978) has been widely criticised for unrealistic results referring to an exceptional case (Rodriguez-Navarro *et al*, 2000a). Damage intensity is commonly measured as mass loss in standardised tests, a conception that has triggered long debates. Nicholson (2002) proposed a more holistic approach for the quantification of damage, based on several complementary indicators. As far as it concerns scaling in real time and size there are also significant problems (Viles, 2001).

On the other hand salt weathering simulations provide a good tool for reproducing weathering patterns and study the conditions that caused them. Rodriguez-Navarro *et al.* (1999) studied the origins of honeycomb weathering. Cardell *et al.* (2003) identified the generation of cracks perpendicular to the exposed surface that resulted in flaking. Goudie and Viles (1997) presented a small sample of the variability of environmental cycles simulating real conditions. Also several authors experimented with different salts and mixtures like halite against sea salt (Rivas *et al.*, 2003) or halite-gypsum mixtures (Robinson and Williams, 2000) while others experimented on the results of similar conditions to different stones (McGreevy, 1995) and mortars (Palomo *et al.*, 1996). Although there can be no generalisations, weathering tests serve a great deal in the investigation of individual pathology issues.

2.6 Activation of damage

As discussed earlier the driving forces behind the generation of crystallisation pressures are supersaturation and pore sizes. Although crystallisation does not necessarily cause damage it provokes it. Crystallisation is triggered by environmental fluctuations. Reasonably the frequency of transitions should correspond, conditions met, to the degree of damage. Accordingly the deactivation of phase transitions should prevent the occurrence of damage. The need to set a measurable framework around the phenomenon sensibly leads to the description of the ambient environmental conditions. Environmental control remains the most optimistic area of study towards the confrontation of the hazard.

The transition through solid and liquid phases is governed by the vapour pressure of the solution which in turn is reversely related to concentration. Saline solutions present lower vapour pressure than pure water and correspondingly the relative humidity in equilibrium with solution is also reduced. The reduction in water vapour is attributed to electrostatic forces generated between the ions of the solute and water molecules.

Phase transitions occur at a specific relative humidity for each salt, at a given temperature and pressure, called ***equilibrium relative humidity*** (RH$_{eq}$). This happens because there is a limit of saturation for each salt and thus a limit in the reduction of vapour pressure. The temperature dependence is also salt-specific. Hence niter's RH$_{eq}$ is 94% while halite's RH$_{eq}$ is 75% at 20C^{o}. It could then be easy to predict the rate of salt phase transitions just by correlating the mineralogical identity of the salts present to the monitored hydrothermal conditions of a monument as shown by Aires-Barros (1996) and thereby prevent damage by keeping the relative humidity in ranges below or above this value.

Single salts however are rarely found in nature. In practice buildings are contaminated by salt mixtures, which present a totally different behaviour. The behaviour of salt mixtures has been particularly investigated by atmospheric physics (Ge *et al.*, 1996), geology (Fletcher, 1993) and industrial crystallisation (Mullin, 1993). The rule of thumb is that if two salts share a common ion solubility of both will decrease whereas if they do not have any ions in common solubility of both will increase. In both cases the solubility of the less soluble salt will be more affected. Nevertheless this rule is oversimplified. The behaviour of salt mixtures is far more complicated. As a matter of fact salt mixtures do not present individual RH_{eq} but rather a range of relative humidity within which progressive and multiple crystals growth will occur. This range does not necessarily correspond to the RH_{eq} of the individual components. Thus a mixture of halite and sylvite presents a broader range of relative humidity where phase transitions occur, higher than the RH_{eq} of the less soluble sylvite and lower than the RH_{eq} of the more soluble halite (Steiger and Dannecker, 1995). Furthermore apart from the influence of the components identity, the behaviour of mixtures also depends on the concentration of each. The increasing concentration of halite increases the solubility of gypsum by a factor of four (Price and Brimblecombe, 1994). More details on predictive models can be found in Price (2000).

In the context of salt weathering, the interaction of salts has been studied by Price and Brimblecombe (1994) and Steiger and Zeunert (1996), using the approach of Pitzer (1973). The result of their effort was a computer based model (ECOS), that predicts crystal volumes in a given system under given environmental conditions (Price, 2000). Despite the great advantages that such an evaluation has got to offer in relevant studies, it holds several limitations relating primarily to kinetic deviations (see chapter 9).

As discussed earlier the rate of nucleation is not constant for all salts. Consequently the rate at which the salt system achieves equilibrium with the environment is strongly affected by the kinetic particularities of each component and as a result the behaviour of the system cannot be predicted precisely by thermodynamic calculations. On the other hand we must notice that thermodynamic modelling does not take into account that each time a phase crystallises the composition of the solution changes. Considering that the solid phase is still in contact with the remaining solution, potentially interacting, we cannot predict the behaviour of the new solution individually. Although the evaporation of saline lakes follows a well reported constant precipitation sequence (Krauskopf, 1979), corresponding to the solubilities of the components, laboratory experiments have revealed deviations from the predicted phase diagrams (Steiger *et al.*, 2000). We must also mention that thermodynamic predictions refer to closed systems while in reality the composition of the salt systems of building materials is not constant due to continuous supply from various sources and corresponding withdrawal. On the other hand other parameters apart from relative humidity and temperature, like solar radiation and wind flow which induce evaporation, have been identified to influence salt weathering variously (Mottershead, 1997). Finally, as already described, the pore properties of the host material have a strong effect on phase transitions as well (see chapter 2.2).

As we have discussed in previous chapters the ionic interaction plays an important role in many aspects of salt weathering apart from the activation of damage, like the generation of crystallisation pressures and the transport of salts through the pore matrix. The suspending challenge is the application of prediction models and the confrontation of the limitations. The investigation of kinetic phenomena is an area of increasing interest. Despite the difficulties of *in situ* investigation, Sawdy (2001) has already produced an optimistic example of the judicious use of thermodynamic models in analysing the behaviour of salt mixtures found in heritage materials and predicting the optimal conditions for their preservation.

2.7 Conservation theory and practice against salt damage

The need for preservation against weathering is not a modern concept. A concern for durability has challenged humans since the early tool-users who travelled long distances to obtain the proper durable first materials, while it became a necessity after the transition to dwelling (Childe, 1965). On the other hand the material culture has always been a close companion of ideas and beliefs. Modern conservation of heritage materials, although led by contemporary necessities and ethics, continues a long struggle against the forces of nature.

Salt weathering comprises a natural process. As such it should initially be noted that it operates regardless of human activities. Thus although some human activities influence several parameters of the phenomenon, preservation can not be achieved solely by simple heritage management interventions. The present awareness of the phenomenon indicates that it does not comprise an exception led by specific conditions but the rule, present in every environment to a lesser or greater degree. The absence of weathering evidence or soluble salts does not reduce the risk of future salt damage which must always comprise part of maintenance strategies or restoration practices. Salt weathering might work silently without visible indications and salts might be present in or near every structure waiting to be triggered.

Early conservation practice has not confronted the phenomenon specifically. In most cases the application of general treatments like consolidation was considered adequate against damage (Moncrieff, 1976). The false argument was that by encapsulating the salts with an impermeable substance we could deactivate any interaction with water. However impenetrability of liquid water does not restrict the movement water vapour. As a consequence phase transitions can still be triggered. Furthermore inhomogeneous treatments might cause the preferential accumulation of salts behind the treatment front which otherwise might have crystallised harmlessly on the surface. Berry and Price (1994) have shown that common consolidants used in stone can not prevent the absorption of water vapour by encapsulated salts. Moreover the consolidant films developed cracks from which the salts could escape.

Desalination was the first direct attempt to confront the problem. Bath techniques have been proved successful for salts extraction but obviously they can be applied only to small objects. Poulticing is an alternative method for building materials based on the same principal of diffusion. The concentration difference between the poultice and the contaminated material generates ion movement towards the poultice where the salts finally crystallise. The migration of ions can be enhanced and directed towards the poultice with the help of electrodes. Convective methods based on the application of hydrostatic pressures or suction have also been proposed. New techniques like biological denitrification and microwave desalination are still investigated. In general the concept of desalination seems reasonable but in practice there have been reported several drawbacks. The major problems of poulticing are the depth of desalination and the fragmentation of salts. In many cases desalination by poulticing extracts salts from the superficial few centimetres only for to become soon contaminated again. On the other hand desalination extracts salts sequentially according to their solubility. Apart from the risk of incomplete desalination there is also a chance of triggering salt interactions that might result in further or greater damage. Verges-Belmin (2002) has reviewed extensively the major desalination techniques and their limitations concluding that the present awareness does not permit many expectations as a conservation measure and more importantly it does not provide sufficient controls. We can add that poulticing is rather costly and time consuming for large structures while it is worthless if applied without contamination prevention.

More recently several new techniques have been proposed without whatsoever any spectacular acceptance. The field of crystallisation inhibitors is mainly applied for industrial purposes (Black *et al.*, 1991). It has not been tested thoroughly in heritage conservation probably due to the great risk of further damage by increasing the critical supersaturation. Rodriguez-Navarro *et al.* (2000b) have recently proposed the use of surfactants based on the interaction of salts. They showed in laboratory experiments that in the presence of surfactants halite crystallised harmlessly on the surface of stone blocks but the application to large structures might present difficulties.

Modern conservation theory is turning towards preventive concepts. Maintenance is considered today preferable to restoration. Although since the "Charter of Rome" restoration is considered "exceptional", conservation practitioners still prefer direct remediate interventions than prevention. In the absence though of clearly defined alternatives they cannot be blamed.

Preventive conservation against salt weathering is limited to environmental control and more precisely to the deactivation of salts phase transitions. As already discussed the prevention of contamination is in most cases unrealistic. It is worthy to start by mentioning that environmental control handbooks for museums and sites do not mention salt weathering. The creation of a sustainable environment refers in the vast majority of publications to numerous parameters, from noise levels to visitor management, affecting every possible weathering mechanism apart from salt weathering (Thomson, 1986). This omission is not entirely incomprehensible. We can attribute it to the low awareness of the phenomenon - which in most cases is referred to as moisture rather than salt weathering-, the difficulty in understanding the phenomenon by non specialists, the little advances in theory, the distance between theoreticians and conservation labour, the controversial results of applications and the inability to provide practical solutions. On the other hand relative humidity control aims in most case studies in drying the masonry or maintaining an ill-defined range of optimum conditions (Bernardi *et al.*, 2000). The consequences of such unsophisticated approaches, driven by a misconception against "moisture" as a general term, might be devastating. On the other hand serious damage has been reported in artifacts kept in conditions of very low relative humidity where theoretically the present salts should have been deactivated (Nunberg and Charola, 2001).

Removal of heritage material to indoor display areas or storehouses is an easy solution practised frequently. Reburial is also used in sites that present practical difficulties in maintenance or small interest in exhibition. The most frequent preventive measure is sheltering as a means of creation of a new microenvironment around the structure. Nevertheless none of these techniques ensures preservation if the conditions for the deactivation of salt damage are not met by the new environment. These techniques are based on the abstract concept that indoors is preferable than outdoors. Obviously this is the case for toxic gases and rain, solar radiation, biodeterioration and birds excrements but not for salt weathering. The definition of the optimal conditions for preservation against salt weathering is not limited to "indoor conditions". Quite the contrary, significant damage has been reported in sheltered monuments as well (see chapter 6).

There is no doubt that further understanding of the phenomenon will lead to its confrontation in the future. On the other hand there is a desperate need for temporary maintenance where environmental control suggests an optimistic area of study. The recent proposal for predictive models of multi-salt solutions behaviour as means of definition of the optimal conditions for preservation has been given gross attention but little results. Apart from the theoretical limitations of the method, discussed previously, there are also practical limitations referring primarily to the sampling strategy. These practical limitations are probably the strongest reasons for the timidity by which this field has been accepted by researchers.

CHAPTER 3. Aerosols properties

3.1 General properties and generation

The atmosphere contains particles arising from natural or anthropogenic sources. Whereas technically an aerosol is defined as a suspension of solid or liquid particles in a gas, common usage refers to the particulate component only. *Primary* aerosols are directly emitted from their source and *secondary* aerosols are formed by a gas-to-particle conversion process. After their emission into the atmosphere, particles can change their size and composition by chemical reactions, coagulation, evaporation or condensation.

The size of the atmospheric particles affects their lifetime and their physical and chemical properties. Even though spherical particles are likely to be rare, physicist consider their size in terms of one single dimension of a sphere usually quoted as radius or diameter. There is no general definition of how large must a cluster of molecules become to represent a particle but clusters of 10^{-7} cm are detectable by common sampling techniques. Particles of 10^{-6} - 10^{-5} cm radius represent a much more stable size and have the longest survival because they are the less affected by gravitational settling. Combustion generated particles, such as those produced by automobiles, power generation or wood burning are found in this range.

Sea salts and wind blown dust are generally larger than 1μm (10^{-4}cm) and represent the small end of the so-called "giant" atmospheric particles. Larger particles of 10μm represent the typical size of cloud droplets and from 100μm to 1mm particles occur as wet hydrometeors (drizzle and rain drops). The solid hydrometeors like snow or hail can attain the size of >1cm and even reach the extremely rare size of 10cm, which represents the upper limit of atmospheric particles. Usually literature refers to particles with size <2,5μm as "fine" (which are divided to "nuclei"(<0,1μm) and "accumulation"(0,1-2,5μm) modes), and to those with size >2,5μm as "coarse" (Twomey, 1977).

The soluble giant particles (>1μm) are predominantly composed of sea salt and carbonaceous oily or tarry residuals derived from fires and industry. The non-soluble giant particles can be described as wind-blown crustal material (sand, debris). Particles smaller than 1μm have atmospheric concentrations in the range from ten to several thousands particles per cm^3, whereas larger particles concentrations do not exceed 1 per cm^3.

Neither the geographical distribution of particle sources nor their lifetime is uniform, so concentration and composition of particles vary widely in the atmosphere. Nonetheless in their extensive study of sea salt particles, Blanchard and Woodcock (1957) have found that over the oceans there is a clearly defined and universal relationship between size and number of marine aerosols. The vertical mass and number concentrations of aerosols can be expressed as a function of exponential decrease with height. In areas near local sources (mainly anthropogenic) we can observe of course significant differences to these averages.

Particles can be formed by coagulation of two or more already existing particles. Existing particles can also be detached by surfaces because of wind or other natural and artificial stresses and be resuspended in the atmosphere. New particles can appear in the atmosphere by several mechanisms. Fragments can be detached from solid or liquid phases because of abrasion, cracking, weathering, breaking waves or bursting bubbles. Supersaturated vapours as well are capable of producing elements in liquid or solid form by direct nucleation.

Atmospheric aerosols contain sulphates, nitrates, ammonium, organic material, crustal species, sea salt, hydrogen and water. Apart from the dominant species more than 40 trace elements can be found in the composition of tropospheric aerosol. Among the most frequently appearing in sampling we can trace Fe, Pb, Zn, Cd, As, V, Cu, Mn, Hg, Ni, Sb, Cr, Co, Se. Lead, iron and copper have the highest concentrations while cobalt, mercury, and antimony the lowest.

The so-called “urban” aerosol is composed of primary particulate emissions from industries, power generation, transportation and natural sources and secondary particulate matter formed by gas conversion. Contrary to marine aerosols, the size distribution of urban aerosols might differ a lot from place to place and there is no globally defined relationship.

Extreme concentrations of anthropogenic fine particles can be found near their source, but they rapidly decrease with distance. Fine urban aerosol is produced from combustion sources (accumulation mode) or gas-to-particle conversion (nuclei mode) consisting primarily of sulphate, nitrate and ammonium. The coarse size urban aerosols are generated by mechanical processes and composed of fly ash, soil dust, sea salt, tyre wear particles and so on. Nuclei particles are easily grown to accumulation size by coagulation and condensation of vapours. Accumulation particles are very unlikely to grow to coarse mode by coagulation. Nonetheless both accumulation and coarse particles concentrations can be processed by clouds and fog droplets or in relative humidity approaching 100%. These reactions can lead to the production of sulphate, which is directly related to the decay of monuments in urban areas.

Rural aerosols mainly originate from natural sources though the presence of anthropogenic particles is not negligible (Hobbs *et al.*, 1985). The main components of remote continental aerosols are primary particles like dust, pollens, plant waxes and secondary oxidation products (Deepac and Gali, 1991). Fine particles that represent 40-80% of the mass distribution are mainly composed of sulphate, ammonium and organics. The aerosols of the Arctic and Antarctica have relatively low concentrations. They mainly consist of carboneous materials from mid altitude pollution sources, sea salt and mineral dust.

The size distribution of desert aerosols is similar to that of remote continental aerosol described above, although it is largely influenced by wind speed. An average composition of soil and crustal rock is shown in *table 3.2.* Particles around 100μm in diameter are found near the source, while particles with diameter of around 10μm can be transported by wind as far as 5000 km from the source. Sahara desert aerosols reach frequently the northern Mediterranean coasts, deposited by rain known as red or mud rain, while it has been suggested that they can reach the north American coasts as well (Prospero *et al.*, 1987).

Species	% weight
Cl	55.04
Na	30.61
SO_4	7.68
Mg	3.69
Ca	1.16
K	1.1
Br	0.19
C	$3.5\text{x}10^{-3}$-$8.7\text{x}10^{-3}$
Al	$4.6\text{x}10^{-4}$-$5.5\text{x}10^{-3}$
Ba	$1.4\text{x}10^{-4}$
I	$1.4\text{x}10^{-4}$
Si	$1.4\text{x}10^{-4}$-$9.4\text{x}10^{-3}$
NO_3	$3\text{x}10^{-6}$-$2\text{x}10^{-3}$
Fe	$5\text{x}10^{-5}$-$5\text{x}10^{-4}$
Zn	$1.4\text{x}10^{-5}$-$4\text{x}10^{-5}$
Pb	$1.2\text{x}10^{-5}$-$1.4\text{x}10^{-5}$
NH_4	$1.4\text{x}10^{-6}$-$1.4\text{x}10^{-5}$
Mn	$2.5\text{x}10^{-6}$-$2.5\text{x}10^{-5}$
V	$9\text{x}10^{-7}$

Table 3.1 Sea salt composition (%weight) (Seinfeld and Pandis, 1998)

Element	Soil	Crustal rock
Si	330,000	311,000
Al	71,300	77,400
Fe	38,000	34,300
Ca	13,700	25,700
Mg	6,300	33,000
Na	6,300	31,900
K	13,600	29,500
Ti	4,600	4,400
Mn	850	670
Cr	200	48
V	100	98
Co	8	12

Table 3.2 Average abundances of major elements in soil and crustal rock (ppm) (Seinfeld and Pandis, 1998)

Particles over the remote oceans are almost exclusively of marine origin, because of the absence of transport of continental species (Savoie and Prospero, 1989). The coarse particle mode comprises 95% of the total mass but only 5-10% of the particle number and results from the evaporation of bursting bubbles or wave breaking.

Among the particulate, which enters the atmosphere every year, the marine aerosol has the greatest contribution with estimates of annual formation ranging between 10^9 and 10^{10} tons. Typically the concentrations of sea salt in the marine boundary layer ranges between 5-30 $\mu g\ m^{-3}$. Right after their production, their composition is identical to sea water (table 3.1), but they can rapidly react with other atmospheric species.

The most common chemical reactions between sea salt aerosol and other atmospheric particles are those of sodium chloride with nitric acid (anthropogenic), producing coarse nitrate, and sodium chloride with sulphuric acid, producing sodium sulphate and hydrochloric acid. The last reaction is responsible for the "chloride deficit" in marine aerosol. The marine aerosol that is formed on the surface of the sea can be carried as fine spray by the wind, up to 200 miles inland and at high altitudes. The sharp rise in concentration of chlorides, however, is detected in a zone of 200 m from the coast (Gustafsson and Franzen, 2000).

3.2 Dynamics of single particles and deposition

Dry deposition

The deposition of dry particles involves all the sizes, from the molecular size gases to coarse sand grains. Size plays an important role in single particle dynamics since the aerosols can be described as continuous or discontinuous media. Particles carried in a medium receive a constant bombardment from the molecules of the medium. The average distance travelled by a molecule before collision with another molecule of the fluid is called *mean free path.* For small particles suspended in a fluid, with size smaller than the fluids mean free path, the aerosol acts as a discontinuous medium, since the molecules collide with the particle and move discreetly around. For larger particles with diameter larger than the mean free path, the aerosol behaves as a continuous hydrostatic or hydrodynamic medium.

As we described above fine aerosols have greater concentrations than coarse. If all the particles of an aerosol have the same probability of deposition on a surface then greater concentration would consequently mean that a greater number of particles is likely to deposit. Nevertheless the large concentrations of fine particles are largely attributed to their longer residence time in comparison with the coarse particulate which tends to deposit more rapidly.

The deposition of particles is a very complex process, in fact a result of various causes with a different efficiency depending upon the particle size. Therefore ambient concentrations, which are usually used to determine the decay process or risk of cultural heritage, cannot describe efficiently the aerosol's deposition rate and thus their implications for related decay mechanisms.

The number of particles, of a specific diameter, that will deposit on a unit surface in a unit of time is considered proportional to their concentration and a function called deposition velocity, although the latter is far more important. The deposition velocity is a very complex function of the particle diameter, the air temperature, the gradients of temperature and moisture, the relative humidity, the electric field, the air turbulence, various physical and chemical surface characteristics and many other factors. For example, in a room where the air is forced to pass through an air purifier filter, the turbulence might cause the deposition of a larger number of particles than those deposited in still but "dirtier" air conditions (Nazaroff, 1993). Alternatively Grossi and Murray (1999) suggest a number of stone characteristics that influence strongly the dry deposition of gases overcoming the other parameters.

Brownian motion is the irregular motion of particles due to the thermal bombardment with air molecules, corresponding to their thermal level. The presence of a temperature gradient in the atmosphere can push a particle towards the lower temperature, because of the asymmetry of molecular impacts. Already since the 19th century scientists had observed that no particles were found near very hot bodies. *Thermophoresis* is a very effective deposition mechanism responsible for the blackening on walls usually observed over thermal conductors. In the continuum regime, the mechanism, based on hydrodynamics, depends upon the temperature jump at the gas-particle boundary, which is determined by the thermal conductivity of the gas and the particle (Epstein, 1924). If the surface is colder than the air, the thermophoretic velocity of fine or coarse particles is proportional to the intensity of the temperature gradient in front of the surface where deposition occurs. If however the surface is warmer than the air the inverted thermophoretic force is protecting the surface against deposition.

Water vapor plays an important role in the deposition of particles. Any particle that is suspended in a region where dry air and water molecules are mutually diffusing is subject to two opposite phoretic forces and it is drawn in the direction of the flow which exerts the preponderant action. Because the mass of air molecules is greater than that of vapour the preponderant action is exerted by the dry air flow. More practically, when evaporation occurs from a wall, considering the effect of pure *diffusiophoresis*, all the particles tend to approach the wall and deposit. Consequently the opposite occurs in the event of absorption.

On the contrary *Stefan flow*, constituted by a series of complicated microphysical processes, leads all the particles near the surface during condensation and opposes all the other deposition during evaporation. Around an evaporating droplet, Stefan flow pushes away all the suspended particles, creating a dust free space with diameter 360μm (Vittori, 1973). Although condensation is an exceptional event, considering Kelvin's law for condensation in micropores, Stefan flow can be a very efficient mechanism for deposition. Particles near a condensing surface are under the influence of both diffusiophoresis and Stefan flow, but the latter is much stronger. Besides although diffusiophoresis and thermophoresis do not affect larger particles, Stefan flow has the same efficiency for all particle sizes. So, Stefan flow is simultaneously a protective and a deposition mechanism.

Sedimentation due to gravitational forces is more sufficient for giant particle (>2,5 μm) and then again in calm air. Convective motions and wind turbulence tend to keep the particles in suspension. *Electrophoresis* is the deposition mechanism of particles dragged by an electrostatic force field. A charged particle can generate an equal opposite charge (image charge) and also electrical charges can be generated even if neither of the two bodies was initially charged (contact charging). *Photophoresis* is the phenomenon that describes the motion of a particle caused by an incident light beam. (Cadle, 1965). Photophoresis does not appear to play a role in natural atmospheric aerosols. This phenomenon is measured only in black particles containing elemental carbon, like candle smoke, soot or fly ash generated by combustion.

When an air stream is intercepted by an obstacle, its course undergoes a sudden change. If the inertia force of a particle is greater than the viscous force of its fluid media, the particle will depart from the fluid's trajectory and it will impact on the obstacle. This type of aerodynamic deposition is called *inertial impaction* and is mostly efficient on particles about 4-5 μm and high wind velocities. The larger and heavier the particles are, the greater the conservation of momentum and the departures. Smaller and lighter particles on the other hand will more likely follow the fluid's trajectories around an obstacle.

However, those close to the obstacle's surface might come in touch with it and eventually be deposited. This mechanism is called *inertial interception* and it depends strongly on the collecting surface roughness. It is however less efficient than the inertial impaction (Mark, 1998).

Nevertheless for particles larger than 1μm the efficiency of this mechanism increases again as a function of atmospheric turbulence. Unfortunately there is no clear relation between wind speed and turbulence, so the first can not be mathematically correlated to deposition velocity. In fact, the average wind speed in front of a surface cannot even indicate the deposition rate of particles. High wind velocities might even detach and resuspend particles from a surface but this is a function of adhesion forces between the particle and the surface and will be discussed below.

The deposition rate is more correctly associated to particle mass and the degree of turbulence. Empirically it can be stated that that inertial contribution is greater when the particles are large and the surface rough. Heavy turbulence though might provide the particles with sufficient kinetic energy to overcome the attractive forces of the surface and bounce. Additionally, although a rough surface might be efficient for capturing the particles, when it comes to adhesion and resuspension forces, things become more complicated, as shown in the next chapter.

None of the available dry deposition models can be verified over the wide range of conditions likely to be encountered (Zuffal and Davidson, 1998). Field and lab experiments have the advantage of providing data for specific conditions that can serve the purposes of other applied sciences, but there are questions relating to the extent to which their results can be generalised.

In many case studies and laboratory experiments however it is apparent that deposition increases with increasing wind speed. In the marine environment though, increasing wind speed is linearly related to aerosols ambient concentrations, so the above observations might simply be a function of increasing availability of particles to be deposited. Nevertheless the wind speed does play a part in the development of turbulence and therefore the deposition velocity.

Wet deposition

Wet deposition is a term used to describe the scavenging of suspended particles by two mechanisms known as ***rainout*** and ***washout***. In the first case, suspended atmospheric particles reaching a certain height, can serve as cloud condensation nuclei (CCN), which grow to form droplets and eventually precipitate as rain. This is a very complex mechanism, which will not be described in this work. An important point is that the marine aerosol contributes significantly in the formation of CCN, but generally only 1% of atmospheric particles serve as CCN. The second case refers to the removal of suspended particles after collision with atmospheric meteors such as rain, fog, snow or hail. This mechanism involves processes like collision, coagulation, inertial impaction, diffusion as well as electrophoresis, between the particles and the meteors. The collection efficiency E of falling droplets is given by Slinn (1984) and it is relative to the size (diameter) of the particles d and the droplets D, the velocity of the aerosol and the droplet (u,U), the viscosity of water and air, aerosol diffusivity and the air density. Despite the complexity of this measure it is worth mentioning that experimental data have shown that all particles that hit a hydrometeor stick on it (Pruppacher and Klett, 1980). The composition of rain generally describes the chemical composition of the aerosols in this area. Rain analysis in remote marine environment shows it to be identical to the composition of sea water.

As will be described in the next chapter, the adhesion of a particle on a surface is remarkably enhanced by the presence of a liquid film. Insoluble particles will adhere successfully on a surface even if they are covered by a 1% of their volume water film. Whether rain water will penetrate or flow on a vertical surface though, is a matter of climatic factors and the properties of the collecting surface (Dullien, 1979).

Camuffo (1996) suggests that a layer of water molecules covering the surface of a wall is necessary for rain water to penetrate into the pores. As already mentioned, when the walls of a pore are covered by condensed water, the rain can advance with a concave meniscus without the need of any external work due to surface tension. The concave meniscus forms a lower vapour pressure, which favours the penetration. On the contrary, if the surface is completely dry, the water front will form a convex meniscus and the greater work required against the surface tension and the higher vapour pressure will not permit any further penetration. In this case rain water will just run off. Run off water will probably wash away other deposits. In the same work it is also suggested that pumping mechanisms like the circulation of air around a building, which create pressure gradients, generally favour the penetration of rain water.

The deposition of ions from rain is, however, much more complicated than previously described. Behlen *et al.* (1997) found significant differences in deposition patterns of several ions by comparing the concentrations of rain water and run off water from stones and inert surfaces. In the same paper they conclude that generalisations are not possible due to the complexity of the involved parameters like rainfall characteristics, ambient pollution and most importantly the material properties. Specifically for the case of marine environment the same authors (Steiger *et al*, 1997) showed that the contribution of sea salts from wet deposition is relatively low.

Another interesting observation is that the concentration of dissolved material in rain drops decreases in time (Fritz and Jeannette, 1981). This possibly means that the washout of atmospheric particles happens at the beginning of a rain event, and since the first drops are more likely to be absorbed this might have serious implications for salt input measurements.

In addition the average precipitation, frequently used to describe salt input, is an irrelevant measure since it refers to precipitation in horizontal collectors while the percentage of rain that hits a vertical surface is significantly lower. Here we have to mention as well that the orientation of the surface is a significant parameter, since driving rain often wets only one or two sides of a building. Similarly, weathering differences between rain sheltered and exposed parts of a building are frequently mentioned in the literature.

Adhesion of particles on surfaces

After a particle impacts on a surface it can either bounce or stick on it. Particles stick on surfaces under the influence of an adhesive force. There are three kinds of forces that can develop between a particle and a surface: Van der Waals, electrostatic and the surface tension of a liquid film. These forces are generally affected by the shape the material characteristics and the size of the particle and the surface, relative humidity, temperature and other environmental parameters, initial contact velocity and duration of contact (Zimon, 1982).

The random movement of electrons in any material creates momentary charge concentrations called dipoles. These dipoles induce complimentary dipoles in neighbouring material, which give rise to attractive forces called Van der Waals. These forces decrease rapidly with distance. Actually their influence extends for only several molecular diameters between two surfaces.

At the submicrometer level two surfaces contact only in a few asperities. The separation distance x between them depends on their roughness. Van der Waals forces between a spherical particle and a flat surface can be expressed by the ratio of the particle's diameter to the separation distance's square. Some particles also carry a small net charge q, which creates an attractive force in the presence of an opposite charge. This electrostatic force can be expressed as the ratio of the square of the charge to the square of the distance x of opposite charges. This distance can be different from the separation distance between the surfaces. For particles larger than 1μm the charge q is approximately proportional to square root of the diameter.

Van der Waals and electrostatic forces deform the surfaces in contact to reduce the separation distance and increase the contact area. Consequently the hardness of the material, or its resistance to deformation, also affects the strength of the adhesion forces. Attractive forces also develop between a particle and a wet surface, because of the surface tension of the liquid drawn in to the capillary space.

Particles bounce and resuspension

Several approaches have been proposed for the determination of the forces required to detach a particle from a surface. The resuspension of particles by an air current though can not be calculated easily, because it depends on the flow geometry and assumptions on the boundary layer velocity profile.

In general, removal forces for air currents are proportional to d^2 while the deposition velocity is proportional to d, as was described previously. This suggests that the larger the particles the easier they can be removed from a surface. For particles smaller than 10μm though, their adhesive forces are much greater than the removal forces that they usually experience, such as gravity and winds up to 10m/s.

Every moving particle obtains naturally a certain kinetic energy. When it impacts on a surface its kinetic energy is partly deforming the particle and/or the surface and partly it is converted elastically to kinetic energy of rebound. If the rebound kinetic energy exceeds the adhesive forces, the particle bounces on the surface. In general, the harder the materials, the larger the particle and the greater the velocity, the more likely bounce is to occur (Dahneke, 1971; Cheng and Yeh, 1979). This suggests that it is rather unlikely for a liquid droplet of micron size to bounce on a wall surface. Additionally surfaces coated with elastic materials such as protective resins will capture more easily solid particles.

3.3 Marine Aerosols

Production of marine aerosols

The principal operation for the production of spray is generally well understood and can be summarised as follows: a liquid is drawn into a thread, under the action of an air stream or a pressure differential, where it collapses into small fragments. This process can be seen in waterfalls or wind blown water surfaces. The spray produced according to this principal from breaking waves is composed of significantly large drops, which fall back in to the sea in a limited time and not far from where they were produced. These large drops represent a very small fraction of the marine aerosol. Mainly the marine aerosols are produced by bursting bubbles on the surface of the sea, by a process thoroughly investigated and described by Woodcock (1953) Blanchard and Woodcock (1957), and more recently summarised by Andreas *et al* (1995).

According to this mechanism, the breaking waves produce a number of bubbles under the surface of the sea. When these bubbles reach the surface they collapse into smaller fragments known as film drops. Once the film breaks an excessive hydrostatic pressure is left, which causes a jet to form and be ejected from the base of the depression, which comprised the lower half of the original bubble. Film drops are more numerous (~ 100 per bubble) and smaller (~ 0.1μm) than the jet drops (~ 1μm, 4 to 6 per bubble). The size of these drops indicates that they have a sufficient lifetime and can be carried away for several kilometres. Their composition and concentration right after production is identical to sea water. Globally the seas produce 10^9-10^{10} tons of aerosols per year.

The concentration in the remote sea is lower than on the coast. In the ocean there is a clear correlation between concentration and wind speed. This correlation was usually used to describe the decay of monuments near the sea. However more recent studies proved that these correlations were entirely coincidental. The emission in the coastal zone is independent of the wind velocity and depends mainly on dissipation of wave energy (Chomka and Petelski, 2001). This suggests an intense aerosol emission in the breaker zone. The inland progressive reduction in concentration because of higher turbulence has been clearly described by Gustafsson and Franzen (1996).

A small fraction of the marine aerosol is also represented by the splash drops, which are produced directly by the splash of breaking waves, and the spume drops, which are directly detached from the sea surface by wind. These drops have usually drawn less attention because they were considered too large and heavy to suspend for appreciable times. Recent studies though, have shown that this might have been just due to lack of sufficient measuring equipment (Anguelova *et al.*, 1999). The production and lifetime of these drops is strongly dependent on wind speed and wave period and height. In storm conditions these drops can remain suspended for a considerable time. One way or another a fraction of these large drops, produced on the coastal breaking zone can successfully reach and deposit on surfaces near the coast. The implication for porous surfaces might be that the spume drops, regarding the limited time since their production, reach a surface before evaporating and thus they can penetrate more easily than the supersaturated jet and film drops.

Salt aerosols are transported through two paths. One that is short range (up to ~5 Km) and close to the ground and one that is long range (up to ~150 Km) and travels above the Planetary Boundary Layer (over 700 m). Within the PBL the marine aerosols are more likely to follow the wind streams quite closely (Klassen and Roberge, 1999). Colbeck and

Eleftheriades (1996) studied the particulate matter in the centre of Athens/Greece and found that while anthropogenic pollution (sulphates and nitrates) diffuses around the samplers, marine aerosols present a strong orientation towards the gulf. Moreover coarse nitrate and HCl associated with marine aerosol chloride depletion also presented marine orientation.

Thermodynamics and kinetics of marine aerosols

As described in chapter 2.6, the thermodynamics of salt solutions are governed by the reduction in vapour pressure. The lower the vapour pressure the lower the equilibrium relative humidity which triggers the phase transition of a solution. The nucleation of solid crystals from a solution on a surface is favoured by the contact angle between the crystal and the surface. The lower the angle, as in the case of concavities, the greater the contact and therefore the easier the nucleation.

But for droplets of salt solutions suspended in the air things are a bit different. Numerous laboratory studies have shown that pure atmospheric particles - not containing a pre-existing solid phase – such as sea water in the form of aerosols, do not crystallise until ambient relative humidity reaches a value well below the deliquescence point. This happens because nucleation can not be achieved in homogeneous aqueous solutions until substantial supersaturations are achieved (Seinfeld and Pandis, 1998). The same stands for the formation of ice. In the absence of a nucleation site, pure water does not crystallise into ice until the temperatures reach values of about –38C^{o}. The reason for this great departure is the very high interfacial energy between the crystal and the liquid (see chapter 2.2).

In the atmosphere several aerosols contain pre-existing solid phases, such as crustal material and soot, or they coagulate with them, which provide heterogeneous nucleation sites for the formation of new phases. The supersaturations required in this case are much lower, since the nucleating agent provides a surface with a relatively low interfacial energy with the crystal. The marine aerosols, deriving immediately from the sea, do not normally contain solid phases. So, despite the fact that the deliquescence point of NaCl is around 75%RH, crystallization for marine aerosols will occur at around 42%RH. Such low relative humidities are very rare in marine or coastal areas, so the marine aerosols are not very likely to undergo deliquescence behaviour and they would likely be present as supersaturated salt solutions, known as *brine drops*, even in relatively dry conditions. This meta-stable state is maintained even in the presence of insoluble components. Even *et al.* (2000) calculated that the crystallisation RH of mixed NaCl-soot aerosol is very close to that of pure NaCl.

The latter remark is very important for the deposition rate of marine aerosols. As described previously, droplets will deposit and adhere on wall surfaces more successfully than solid particles. After the deposition, sea water droplets, provided with a nucleation site, will more likely crystallise, assuming that the ambient relative humidity is lower than the deliquescence point. Undoubtedly, the question here is whether the droplets will be absorbed in the pores of the wall and crystallise eventually as subflorescence or whether they will remain and crystallise on the surface, available for resuspension. The decrease in size of the crystallization products favours their adhesion, from one perspective. But alternatively the absence of a water film favours resuspension. It is very difficult to calculate the time scales of this process in order to give sufficient answers. Although these processes have not been investigated, it is certain that no generalisations can be expected.

A number of questions, particularly significant for conservation arise. Does the sea spray penetrate into the pores? Does it penetrate immediately after deposition or after it becomes deliquescent again? What fraction crystallises harmlessly on the surface and what into the pores? And eventually is sea spray a significant pathway of salt input? However the marine aerosol does not contain a single salt and furthermore it interacts with other suspended species, making things even more complicated.

Multicomponent salt solutions present a more complicated thermodynamic behaviour, which does not correspond to the behaviour of their single components. Sea water, apart from Na^+ and Cl^-, contains K, Mg, SO_4, and other ions in significant concentrations. Consequently, despite the dominance of NaCl, sea salt crystals are not homogenous. The heterogeneous nature of marine aerosols has been sufficiently reported by Andreae *et al.* (1986). Furthermore, studies by Cheng *et al.* (1988) revealed the existence of a shell structure of $MgCl_2$ and KCl on the surface of marine aerosols. Recent laboratory studies on the crystallisation of multicomponent salt solutions showed that the surface composition of KCl/NaCl and KCl/KI particles is identical to the eutonic composition and is independent of the original solution mole fraction (Ge *et al.*, 1996). The enrichment of the surface in the minor components might influence the thermodynamic behaviour of marine aerosols, but these processes have not been investigated yet. Nevertheless, the deposition rate will not be affected by such processes and the marine aerosol is more likely to follow the hysterisis behaviour of single NaCl suspended droplets. Still a multicomponent solution, after depositing on a porous surface, will definitely present a fractionation of the crystallisation process as it advances into the capillaries. The significance of such behaviour for ground capillary rise has been described by Arnold and Zehnder (1991) but it is still not known for the deposition of marine aerosols on vertical porous surfaces. It has been reported by both laboratory spraying simulations and coastal field investigations that when sulphates and chlorides are present, sulphates tend to accumulate on the surface while chlorides are found further at depth (see chapter 4). This contradicts other observations for samples immersed in the solution (Rodriguez-Navarro and Doehne, 1999). Whereas this pattern might be coincidental, the results signal that salt weathering tests that imply immersion can not describe sufficiently spray weathering.

Anhydrite	$CaSO_4$
Bischofite	$MgCl_2\ 6H_2O$
Bloedite	$Na_2Mg(SO_4)_2\ 4H_2O$
Carnallite	$KMgCl_3\ 6H_2O$
Epsomite	$MgSO_4\ 7H_2O$
Glaserite	$K_3Na(SO_4)_2$
Gypsum	$CaSO_4\ 2H_2O$
Halite	NaCl
Hexahydrite	$MgSO_4\ 6H_2O$
Kieserite	$MgSO_4\ H_2O$
Kainite	$KMgClSO_4$ 11/4 H_2O
Leonite	$KMg(SO_4)\ 4H_2O$
Polyhalite	$Ca_2K_2Mg(SO_4)_4\ 2H_2O$
Sylvite	KCl
Thernadite	Na_2SO4

Table 3.3 Common marine evaporite minerals (Livingston, 1994)

Fractional crystallisation leads to the deposition of a characteristic sequence of minerals, which can be predicted by thermodynamics. Some of the common evaporite minerals, which can be expected by the crystallisation of sea water, are given in table 3.3. It has been stated that even small amounts of calcite, aragonite and gypsum can precipitate from pure sea water (Livingston, 1994). Ideally the evaporation of sea water would result initially in a brine followed by numerous microcrystals of sulphates, then a crust of relatively large cubic NaCl crystals and finally a film of chlorides. The diameter of the particle after crystallisation shrinks to about one quarter of the parent drop. Despite the globally homogenous composition and concentration of sea drops, the shape of the crystals produced varies a lot. Both *in situ* observations and laboratory tests result in cubic, roundish with cubic facets as well as hollow amorphous particles. Still, recent PIXE studies showed how the contamination of marine particles by other volatile species disturbs their initially cubic shape (Schiavuta, 1996). Soften edges are likely to predict the presence of excess sulphur. The solubility equilibria of oceanic multicomponent salt systems still attracts the interest of research. The model of Pitzer (1973) has been widely used in theoretical studies (Voigt, 2001).

Another process, which is very significant, is the interaction of marine aerosols with other suspended species. These reactions result in the formation of several solids such as ammonium chloride, sodium sulphate and sodium bisulphate, sodium nitrate, and gaseous HCl. The release of HCl is known as “chloride depletion” which can alter significantly the composition of the marine aerosols, and even lead to a total chloride deficiency (Zhuang *et al.*, 1999). These processes are usually not considered in cultural heritage conservation relevant studies. The implications of this omission will be described in Chapter 4.

The most common reactions of marine aerosols in polluted environment are the following:

$NaCl + HNO_3(aq) = NaNO_3 + HCl(g)$

$NaCl + H_2SO_4(aq) = NaHSO_4 + HCl(g)$

$2NaCl + H_2SO_4(aq)= Na_2SO_4 + 2HCl(g)$

Apart from the production of Na_2SO_4, other sulphates as K_2SO_4 have also been reported as composites of marine aerosols (Ganor *et al.*, 1998). The chloride depletion has great implications for the thermodynamic behaviour of sea salt aerosols. Chan *et al.* (2000) showed that the Na_2SO_4-$MgSO_4$ system has a very low evaporation rate due to internal mass transfer limitation, while the system NaCl-$Mg(NO_3)_2$ does not crystallise at all, even below 30% RH. The history of the particle is also important. Ten Brink (1998) showed that nitric acid does not react with NaCl dry particles. The chloride depletion is more likely to occur near the coasts since the concentrations of non-sea-salt sulphate are greater, because of the influence of anthropogenic agents. However the formation of non-sea-salt sulphate is also attributed to natural agents as the oxidation of marine biogenic dimethylsulfide (Ganor *et al.*, 2000). The time scales to achieve equilibrium are generally less than a few hours (Meng and Seinfeld, 1996).

The wind direction is a very important variable here since it controls the transport of pollutants from their source to the site of interest. At this point we have to mention a characteristic of the coastal environment, which is irrelevant to the thermodynamics of the marine aerosols but plays an important role in the mixing processes. The aggressiveness of the coastal environment is attributable to the different heat capacity of the sea and the land (Colacino, 1989). During the cold season the sea acts as heat source and heat and water vapour are transferred to the colder air masses inland. During the summer the sea warms up less than the land and this difference in surface temperature drives the thermally induced breeze towards the sea. The sea and land breezes have a diurnal variation as well. When pollution is present the typical sea breeze regime carries the pollutants cyclically depositing several layers over the coastal area (Zezza, 1996a). These breezes are local phenomena, typical in the coast, and they are independent of the barometrically induced winds.

Sea water stoichiometric constancy

The constancy of the relative ionic composition of seawater has been speculated as long ago as early 19th century. Marcet published in 1819 the first paper suggesting that "specimens of sea water contain the same ingredients all over the world….they differ only as to the total amount of their saline content" which constituted the *Principal of constant proportions*. Almost half a century later (1884) came the first official confirmation from Dittmar who collected and analysed samples of sea water during the circumnavigation cruise of H.M.S. *Challenger* (1873-1877). Dittmar however found some variations, which suggested the existence of some exceptional cases.

The stoichiometry of seawater has been extensively investigated since and today the constancy of the major elements (usually referred as *conservatives* for that reason) is widely accepted (Millero, 2001). Variations in the ratio between some specific species resolve from atypical conditions that have also been investigated and represent a few well-known exceptional cases (Riley and Chester, 1971):

i) In Estuaries and land-locked seas chlorinity as well as the ratio of Na to the major cations are slightly decreased. River water ionic composition is governed by the nature of the bedrocks and usually contains high Ca and HCO_3 dissolved from limestone or Mg from dolomites. However the variations of the major elements in estuarine waters are usually not detectable since the salinity of river water is much lower than that seawater. On the contrary seawater species normally penetrate the estuarine waters at a considerable distance inland. Appreciable variations can be found in land-locked seas, such as the Baltic and Black Seas, where run-off water ionic species from the land accumulate in time.

ii) In the deep waters of certain basins, such as the Cariaco trench and the Norwegian fjords, the oxidative decomposition of organic matter exhausts the available oxygen causing ideal conditions for certain bacteria which convert sulphate to sulphide thus leading to an appreciable decrease in the SO_4/Cl ratio.

iii) In the Arctic and Antarctic Oceans the fractionation due to the freezing of the seawater leads to the depletion of some species. The most important variation, which presents a major interest in the research of marine geochemistry and paleoclimate, is the decrease in the SO_4/Cl ratio.

iv) In warm and shallow waters such as the Bahama Banks calcium carbonate precipitates rapidly causing a significant depletion in the Ca concentration.

v) Submarine volcanism does not have an effect in the concentration of dissolved species apart from the increase of dissolved silica.

vi) The Red Sea represents a special case where all the major elements vary considerably from their typical concentrations. It is believed that highly saline water from geological brines enters the sea through fissures in the ocean floor.

vii) the evaporation of seawater in isolated basins is a very slow process which in the past, under suitable conditions created the geological formation of saline lakes, such as the Chilean Salinas and the Strassfurt deposits. The fractionation during the crystallisation of sea salt mixture must have produced major variations in the composition of the water in these areas during the process but doesn't have an effect in contemporary composition of the seawater.
viii) Chemical processes occurring at the interface between the bulk ocean water and the surfaces of the bedrock, the bottom sediments and the atmosphere lead to ion exchanges that effect the composition of these interfacial layers. At the bedrock and sediments interface Mg has been reported to be depleted, possibly due to formation of dolomite and K enriched possibly because of the hydrolysis of feldspars. Calcium also varies against the bulk concentration. The interaction between the sea and atmospheric species leads to the formation of a thin superficial layer of complicated composition, highly enriched in organic matter.

Contrary to the major elements that tend to be conservative, considerable fluctuations can be detected in the composition of the trace elements. These variations are attributed to the geological and biological reactivity of some of these species, to all the above reasons regarding that their low concentrations will be more severely affected by local volcanic activity and run off waters.

Considering the above we can conclude that apart from (viii) all the exceptional cases of sea water stoichiometric composition do not effect the bulk marine aerosol composition since they either refer to ocean bottom or local trends. Nevertheless modern analytical techniques revealed that the marine aerosol is not absolutely identical to the average composition of the oceans dissolved material, (Culkin, 1965).

The marine aerosol as described previously is produced in a thin layer on the sea surface. This superficial layer contains very high concentrations of organic species. Interactions between these species and sea salt might cause a certain fractionation in the exchange of particles between the sea and the atmosphere resulting in a small enrichment of the major species against Cl and Na in the atmosphere. The high fluctuations of Br and I in different parts of the world still trouble the atmospheric scientists.

While these minor disturbances play a major part in atmospheric processes and carry a distinct importance in the ecological balance they do not have a considerable effect in the equilibrium thermodynamic properties of marine aerosols, which are governed mainly by the presence of Na and Cl. Thus the investigations carried out in this research present an undeniable generalisation potential at least as far as it concerns the constancy of the composition of sea water as a salt enrichment factor of buildings in coastal areas. On the other hand the total concentration of salts that fluctuates in different parts of the oceans is irrelevant to the investigations of this research since the concentration of salts in the aerosol is effected by evaporation and water uptake, processes which are controlled by the atmospheric conditions irrespectively of the aerosols initial concentration.

CHAPTER 4. The susceptibility of coastal cultural heritage. A critical review

Salt weathering is a global phenomenon observed under various environmental conditions and contamination particulars. The exceptional significance of this natural process in the coastal environment has been early stressed by geomorphology research (Bartrum, 1936; Wellman and Wilson, 1965).

However conservation scientists have somehow neglected the investigation of natural causes of decay. Over the last decades most of the efforts focused towards the decay of monuments in the urban environment caused primarily by anthropogenic factors. Only recently there has been some interest in the natural weathering of building materials and especially for the action of sea salts. Zezza (1989) started his introductory lecture in the opening of the "1st International symposium on the Conservation of monuments in the Mediterranean basin" in Bari with the remark that the weathering phenomena of stone along the coasts are very widespread and its dynamics have so far been given little systematic close attention. Since then, there is a growing interest in the dynamics of the coastal environment. Numerous symposiums provide the opportunity for comparison and discussion of case studies all over the world, which introduce a lot of similarities along with striking controversies that restrict, for the moment, any generalisations.

Despite the growing interest, the relatively short time of research does not permit any confident conclusions concerning the confrontation of the risks. At this point it looks as though most of the authors regurgitate the initial enthusiasm. The publications on the susceptibility of heritage structures in the coastal environment fall into three categories concerning *in situ* identifications of salts, either as deposits or as suspended particulate matter, weathering simulations and treatments, primarily desalination. Rarely do these categories intersect. The focus of research is more likely attracted towards the realisation of the phenomenon rather than the confrontation. It is striking that almost all the works on this subject omit very important details. These omissions as well as their implications will be summarised at the end of this chapter.

A common hazard is globally accepted in the coastal environment: the presence of marine originated salts. One way or another the sea salts will reach and penetrate the building materials of monuments found within a certain distance from the sea. The depth of the sea spray influence zone varies of course, depending on the local landscape morphology and climate (Zezza and Macri, 1995). It is generally accepted that weathering decreases with distance and height above the sea level (Mustoe, 1982; Mottershead, 1994; Takahashi *et al.*, 1994) but exceptions have also been reported. At a smaller scale Holmer (1998) has identified distinct zones of weathering in coastal bedrocks, parallel to the distance from the sea. The composition of sea salts is common globally apart from some distinct exceptions (see chapter 3.3). The differences in concentration, or the salinity of the sea, do not seem to have any effect since sea spray, after its production, follows its own hygroscopic properties, which are irrelevant to its previous concentration as sea water. The primary contamination pathway is the aerodynamic deposition of marine aerosols that has been described earlier (see chapter 3.2). Nonetheless the final deposition mechanism and rate might vary depending on many parameters and most importantly the local wind and precipitation regime.

A very interesting similarity in most case studies is that gypsum is present along with the sea salts. The origin of the sulphates varies a lot. They may originate from anthropogenic pollution of the atmosphere or the waters, the building materials, the natural compounds of the sea or biological processes. The importance of this pair of salts is frequently stressed. NaCl affects the behaviour of gypsum, which due to its low solubility is otherwise considered harmless. Because of its hygroscopic nature NaCl causes condensation more frequently and consequently gypsum deliquescence and hydration cycles and presumably mobility. Beside the frequency of the cycles it also increases their intensity. The presence of NaCl in a gypsum solution increases its ionic strength, thereby reducing the activity coefficients of Ca and SO_4. The lower activities in return increase the solubility of gypsum and hence the volume of the material that is dissolved and then reprecipitated (Livingston, 1994). The behaviour of the system $CaSO_4$-NaCl has been studied by Price and Briblecombe (1994), which showed that as the concentration of NaCl increases the solubility of $CaSO_4$ rises by a factor of four. Additionally they showed that whereas $CaSO_4$ alone, with 99.96% ERH, would cause damage only after direct wetting, in the presence of NaCl it crystallises over a range of RH between 75-100%. Arnold (1996) has also shown that the presence of NaCl changes the hard compact layer of gypsum to a fibrous and fluffy efflorescence, which can be easily spalled off exposing unweathered material to the environment. Zehnder (1996) depicted that gypsum can be transported higher vertically by ground moisture capillary rise in the presence of halite. Robinson and Williams (2000) showed that gypsum and halite together are more destructive than each salt alone in weathering tests.

In situ investigations of salt weathering in coastal sites follow the basic principals of sampling approaches. The sampling strategies vary a lot and depend on the particularities of each case. Usually combinations of two or more sample types are extracted. The most common sampling method in most of the case studies is core drilling followed by aqueous analysis. The time, location, depth, period of the drills varies a lot but the aqueous analysis is commonly established since it provides quantitative results. Qualitative analysis, frequently by means of XRD, is sometimes used, either as primary of supplementary analysis. XRF and EDAX have also been used, although they do not offer neither quantitative results nor crystallographic data (Zezza, 1996a). Titrimetric methods are still in use despite the disadvantages against the modern techniques (Moropoulou *et al.*, 1995). Salt extraction by poultices or other techniques supplies fragmentary results due to the different solubility of the salts and is usually used as control of desalination rather than a sampling investigation (Fassina *et al.*, 1996).

Sampling investigations have produced variable results. The distribution in respect to height follows generally a similar pattern (the more soluble salts in higher parts and the less soluble at the bottom) but the depth distribution varies a lot (Silva *et al.*, 1996; Fassina 1996; Fassina *et al.*, 1996; Warke and Smith, 2000). We must notice that single sampling investigations do not offer for comparison since they are biased by the particular environmental conditions during sampling. On the other hand the kinetic data, provided by periodical sampling investigations, has never been correlated to the thermodynamic potential of the present mixtures. There is undoubtedly a large gap as to the behaviour of sea salts in the presence of other species under variable environmental conditions. Sodium and chloride are never exclusively present although frequently dominant. Nevertheless we must stress the limitations of sampling from heritage structures. Modern heritage ethics do not permit statistically acceptable methods and hence the results are frequently fragmented as well as biased by various parameters. Especially in the case of coastal sites the contamination by sea water, a salt mixture containing several ions, might lead to fractionation of the species inside the pore matrix and consequently limited sampling will result in ambiguous results. For example Livingston (1994) found in alveoli fissures fractionated accumulation of sea salts corresponding to evaporite saline lakes. Alternatively McGreeevy (1995) found only gypsum in correspondingly weathered stones in a marine location of NW Ireland which could not explain the presence of honeycomb weathering. Gypsum is frequently found near the surface. Apart from sulphur gases deposition this might also be attributed to fractionated accumulation since gypsum is the less soluble compound of sea spray.

Another method frequently used to evaluate the decay environment is to measure the composition and the concentration of atmospheric aerosols by special collectors. In most cases the collectors are basically composed of a pump and one or multiple polyethylene, polycarbonate, or polyester filters. The air can pass freely through these filters while the aerosols are captured in their fibres. This approach is however very insufficient for the description of the deposition of particles on a vertical surface. Ambient concentrations can only give us an indication of the availability of pollutants and do not describe at all the actual deposition or any of the parameters that influence it. Comparing atmospheric concentrations between coastal and inland locations does not contribute to the understanding of sea spray dynamics. On the other hand, these measurements can serve for indoors and outdoors comparison of atmospheric quality (Fassina, 1996), which might give us a good idea of the buffering provided by shelters or the building itself, or the efficiency of air filtration equipment.

Steiger *et al.* (1997) and Behlen *et al.* (1997), in a much more realistic approach, used stone specimens as aerosol samplers along with adhesive polyester filters and found significant differences in the deposition patterns. Even if we assume that the differences in the total salt deposition do not have serious implications, we cannot neglect the differences in the concentration of each ion, which describe an entirely different decay potential. It is also important to mention the differences of the deposition patterns in each stone specimen, which means that in similar studies great attention must be given in the choice of the materials used as samplers.

Chabas and Lefevre (1996) used nuclepore membranes, which they later analysed with XRF spectroscopy, to measure atmospheric quality on the island of Delos (Aegean Sea). They found a small excess of sulphur concentrations, which correlated with the presence of gypsum in marbles. This information is very important since Delos' atmosphere was considered clear of any anthropogenic pollution, but if we consider that the marbles were consolidated with cement, their conclusions for the contribution of anthropogenic pollutants in the decay of the marbles is rather questionable. In addition these measurements do not give any indication of the form in which sulphur deposited on the marbles and therefore consider the parameters of the decay mechanism.

Rain samples have also been collected with special gauges, in order to describe the wet deposition on the walls. These measurements give very good values of the composition and the concentrations of the solutes in the rain water, but the net salt input cannot be described by precipitation height averages. We must of course consider that vertical surfaces receive a considerably smaller amount of rain (less than 20%) and also the conditions that have to be met for rainwater to penetrate into the pores. In more recent studies a more appropriate method is used where, apart from rain samples, run off water samples are used as well (Roekkens and Van Grieken, 1989, Behlen *et al*, 1997). In all cases the composition of sea salts is reflected in the rain samples. Bacci *et al.* (1989) applied an interesting approach, correlating chemical composition with more detailed meteorological data of precipitation.

Nevertheless the deposition of sea spray does not necessarily comprise a measure of damage. Usually the seaward side of structures present more intense weathering as described by Viles and Goudie (1992) for limestone columns in Weymouth, England and geomorphological features caused by salt weathering like alveoli are strongly oriented towards the sea as depicted by Mottershead (1997). The misconception that the seaward side of structures is more susceptible to salt weathering is based on the fact that the surfaces directly exposed to sea spray receive higher volume of salt input. Although we cannot deny the facts we must underline the importance of the environmental conditions that trigger the mechanism irrespectively of the salt input. The assumption that salt input is the major control of damage has led to questionable conclusions. Moropolou *et al.* (1995) in a comparative investigation in the historic centre of Rhodes, Greece predict weathering rates by relating chemical analysis results to abstract factors of aspect and distance from the sea. Similarly Van Grieken and Torfs (1996) applied the same principal in an even larger context relating the deposition particulars to weathering in a number of Mediterranean coastal sites.

Alternatively exceptions to this rule that have been reported frequently suggest that the degree of sea exposure is not a determining factor for weathering. Dragovich (1997) reports that tombstones at the Australian coast present more intense weathering at the lee of sea spray deposition. Robinson and Moses (2002) also reported asymmetric weathering unrelated to the sea direction on a limestone obelisk in Brighton, England. Considering that marine aerosols deposit by inertial impaction on vertical surfaces it is reasonable to assume that the wind direction also plays an important role. Mitchell and Halsey (2000) provide an excellent example of detailed microclimatic data from vertical surfaces of a cathedral tower facing the four cardinal points. Nonetheless Williams and Robinson (2000) have reported many cases where sandstone tombstones present anomalous aspect behaviour. Also other factors like solar radiation, rain and biofilms might be more important than sea exposure (Mottershead *et al.*, 2003). There can be no doubt that the deposition alone is not sufficient to describe the weathering environment.

Several decay agents have been accused for synergetic effects along with sea spray. Zezza (1996a) depicted the dynamics of polluted marine environment in a number of monuments around the Mediterranean basin, in the EU project "Marine spray and polluted atmosphere as factors of damage to monuments in the Mediterranean coastal environment". Whether the two factors act together or individually is not very clear. It is a fact though that whether their action is simultaneous or sequential their effects are cumulative. A heavily polluted environment, like the one in Elefsis, does not permit the clear evaluation of each parameter. The conclusions for the case of Elefsis, that was part of this project, as given by Moropoulou *et al.* (1998), refer solely to the well-known effects of anthropogenic pollution, despite the initial intentions as described by the title of the project. Apart from the effect of sea breezes on the circulation of pollutants and the increased solubility of gypsum in the presence of NaCl, no other correlation between anthropogenic pollution and coastal environment has been achieved so far. Lubelli *et al.* (2004) proposed an alternative synergetic mechanism according to which the presence of

NaCl leads to the formation of HCl that permits the sulphation to proceed. Zappia *et al.* (1998) suggested that gypsum crusts collected from building materials in continental and marine urban locations in Italy do not present any differences apart from the superficial accumulation of marine aerosols in the latter. The cumulative, if not synergetic, effects of sea spray and air pollution are frequently reported from coastal urban areas found in various climatic zones (Moropoulou *et al.*, 1995/RHodes; Cereceda *et al.*, 1989/Alicante; Warke and Smith, 2000/Belfast). The implications must be more widespread than what suspected.

A clear omission in most of the works on marine decay is the deficient evaluation of climatic parameters. In most cases the climatic data are taken by a nearby meteorological station or airport and represent averages. On the other hand, a lot of work involves solely climatic observations (Cavallini *et al.*, 1997; Camuffo *et al.*, 1997). It is striking to realise that salts analysis, atmospheric quality tests and climatic monitoring have been carried out in the same areas without any attempt for correlation. Alternatively Pagliari (1989) attempted to correlate climatic differences in two Mediterranean locations arguing on the substantial role of rain and due without whatsoever defining it.

Specifically in the coastal environment, some climatic parameters, which are routinely neglected, like the wind direction, have an important effect on the deposition of sea spray and its kinetics. We must mention here that along coasts the wind direction is directly related to the fluctuations of relative humidity. Compared to the continental, the marine originated wind is enriched in water vapours. Another neglected parameter is the direct solar radiation, which favours evaporation, although its influence in coastal salt weathering has been early suggested (Dunn, 1915) and frequently stressed by geomorphologists (Holmer, 1998). Controversial results have been reported for the influence of solar radiation. Cereceda *et al*, (1989) consider the long sun exposure of monuments in Alicante, Spain responsible for the intense salt weathering environment in a location which should normally present higher relative humidity due to its proximity to the sea. On the contrary Mottershead (1997) considers sun exposure a limiting factor for the decay of coastal structures in Devon,UK.

Alternatively, the correlation between environmental and salt data is sometimes problematic. Aires-Baros (1996) depicted the transition frequencies of the salts present in a number of monuments, simply by drawing a line, which represented the ERH of each salt, on the relative humidity chart measurements. NaCl is frequently assumed as the only sea spray deposit and any changes of the relative humidity above or under its ERH indicate the number of phase transitions, consequently the decay rate. This serious misconception could drive to conclusions, which might be entirely false. On the other hand Larsen and Nielsen (1990) reported increasing debris release from bricks in a costal location of Denmark during RH fluctuations around the RH_{eq} of NaCl. Watt and Colston (2000) have also reported similar phenomena in Norfolk. Whether this is an exception or the rule is a matter of further research. We must though state that NaCl is not the only deposit of sea spray, it interacts with other salts and most importantly multi salt solutions present a different thermodynamic behaviour than their constituents, not to mention the implications of porosity. Considering the complexity of real conditions it is very difficult to accept that there is a single potential of weathering in coastal sites.

Apart from the *in situ* investigations, there have also been some laboratory studies during the last decade, related to sea spray stone weathering. Tests that implied immersion in natural or artificial sea water have been used in the past but they more likely described ground capillary than spraying. Dynamic simulations of sea spray, that have been used for industrial purposes like concrete expansion and strength reduction, found over the last years an application in cultural heritage susceptibility as well. Auger's (1989) pioneering accelerated weathering tests with sprayed sea water showed different patterns than those of immersion tests. Most importantly, the accumulation of sulphates on the surface and chlorides in the body of the samples, a pattern frequently reported in coastal case studies, contradicts the well established accumulation of more soluble salts in the surface and less soluble in the internal pores which more likely describes ground water capillary rise.

The same author (Auger, 1996) used later a more dynamic simulator to show clearly that seawater alone is an effective weathering agent in marble samples. Rivas *et al.* (2000) demonstrated that seawater is more destructive than pure halite. Birginie (2000) also investigated the kinetics of sea spray damage, which included a first phase of surface accumulation, an accelerated phase of deep penetration and a final phase of progressive disintegration. Cardell *et al.* (2003) identified calcareous cement dissolution apart from salt weathering in limestone blocks. An interesting fact is that all these tests have resulted in inexplicable sulphate excess. Saline spray weathering tests in treated stone also show interesting results (Alonso and Esbert, 1994). While surface treatments with water repellents seem to cause extensive damage in immersed samples due to the accumulation of salts behind the film, they have the opposite effect in spray tests. The explanation is probably that surface treatments eliminate the spray pathway (inertial impaction) while they permit ground capillary rise. Nevertheless in reality the monuments are already "contaminated" by salts and surface treatments are more likely to have disastrous effects if not preceded by proper desalination. On the other hand the sole contamination by sea spray is rather unrealistic.

Geomorphologic studies on the coasts can contribute a lot to the understanding of sea spray weathering (Viles and Goudie 2002; Pope, 2002). Landscape formation on rocky coasts is widely attributed to the action of sea spray (Mottershead, 1989). The basic principles of weathering mechanisms stand both for buildings and the natural environment. The absence of collaboration between conservators and earth scientists, as well as the implications of the local landscape formation in conservation studies is stressed by Smith *et al.* (1997). Especially considering that the transport of building materials was impractical in the ancient world and the builder usually preferred the local quarries, the geomorphologic formations of the landscape offers an excellent indication of the weathering mechanism acting on buildings. Similarly the building materials extracted fresh from their natural compounds represent a long time exposure experiment, which supplies valuable information on the weathering rate to the geologist. Mottershead (1997) has calculated weathering rates using dated weathered structures as indicators.

Geomorphology also offers a broader context of salt weathering investigations in the coastal environment. Heritage case studies, restrained in sites of significant human activity in the past, present a much localised geographical distribution. The majority of salt weathering case studies comes from the European coastline as well as countries with relevant research activity. Thus the literature of coastal weathering is so far very limited. Regions with immense built heritage like the Indian subcontinent, the SW pacific islands, SE Asia, Africa and South America are misrepresented. Alternatively geomorphology studies refer to a wide variety of climates encountered along coasts globally. Guilcher and Bodéré (1975) investigating a wide range of climatic variability around the Atlantic coastline suggest that the efficacy of coastal salt weathering is reduced as latitude increases. Similar information could be very important for heritage studies.

Numerous practical conservation case studies on monuments found near coasts have also been published. They all imply traditional treatments such as consolidation and desalination (Fassina, 1996). The location of the monument in most of the published work seems to be purely coincidental. Sheltering techniques on the other hand frequently neglect the particularities of the coastal environment and focus on the protection against meteors and direct solar radiation. The implications for salt weathering that can be triggered by the creation of a new microenvironment are not seriously considered. Moreover shelters with open sides permit the transport and deposition of sea spray. The vast costs of the newly founded, so called bioactive, shelter at the coastal site of Akrotiri/Greece were justified for the creation of a stable environment (http://www.santorini.net/94.html). Surprisingly the conditions of stability were not justified as well.

Still, a number of very important aspects for sea spray weathering have been totally neglected so far. The most important aspect is the "chloride depletion" described previously. The implications on conservation are two-fold. The reactive uptake of sulphur by sea aerosols is the most important mechanism of sulphate formation globally, as well as the most successful process for the removal of sulphur from the atmosphere. Therefore the deposition of sulphur as Na_2SO_4 is far easier than the deposition of SO_2 gases. The process of gypsum production, which results in the disintegration of $CaCO_3$, is obvious only in heavily polluted environments, where the atmospheric concentration of SO_2 is rather high. The enhanced removal and consequential deposition of sulphur in the marine environment could have serious implications for the rate of the above gypsum production mechanism. Additionally the increased hygroscopicity of gypsum in the presence of NaCl triggers more intense and frequent phase transitions cycles, which could have explosive results, even more severe than those of the urban environment. The other implication of the "chloride depletion" is the lower concentration of chlorides which of course changes the thermodynamic properties of the mixture of salts present in the monument. The dominant presence of chlorides is considered so definite that frequently the salt input thermodynamic potential is described by the properties of NaCl. Nevertheless, case studies have shown that the chloride depletion can even be complete (Zhuang *et al*, 1999).

Another serious omission involves the hygroscopicity of sea salts. Again, the dominance of NaCl preoccupies the deliquescence of sea salts at 75% RH. Sea salts though are far more hygroscopic due to the presence of an external $MgCl_2$ crust, which lowers the deliquescence point to 34% RH (Cheng *et al.*, 1988). This omission might have serious implications for the understanding of sea salts behaviour after their deposition on walls. Since such low RH is rarely encountered we could assume the constant presence of a liquid film on the walls surfaces, contaminated with sea salts.

Wind velocity is correlated with marine aerosols concentrations. This correlation is always linear but its values vary a lot. Thus we cannot predict concentrations by wind speed measurements. Other parameters such as ***wave energy*** or ***white cup coverage*** are more safely related to marine aerosols production. These parameters are routinely measured globally by satellites and can be provided easily through the Internet. Less complicated measures like wave height and direction could also describe a case study more thoroughly than wind speed alone. Moreover as noted previously another serious misunderstanding is the correlation between wind speed and deposition.

The last important omission is the hysteresis in the phase transition of marine aerosols. Sea spray droplets do not crystallise at their ERH but at a much lower RH (~40%), in the absence of a nucleation site. Consequently, the marine aerosol will more likely exist as a supersaturated solution, a brine drop, than a crystal. The latter have serious implications in the deposition rate and the penetration of marine aerosols in a porous material, as described in a previous chapter.

PART II. EXPERIMENTAL

CHAPTER 5. The present research

5.1 Aims and objectives

The aim of this study is to investigate the dynamics of salt weathering in coastal sites. Towards this direction it is necessary to assess the sources of salts, the properties of contamination and the activation of damage, under the influence of the marine environment. The objective of this investigation is a more thorough understanding of this aggressive context, in which we are frequently called to define sustainability. The awareness of monument susceptibility in coastal sites and the realisation of the ineffectiveness of traditional conservation raise a number of important questions. Can we intervene successfully in this dynamic environment, can we neutralise our built heritage in this constantly changing landscape, can we define optimal conditions for preservation? Despite the obvious complexity of sustainability issues that derive from various aspects like site management, resources and tourism, research is obliged to provide solid arguments.

Theoretical research has made serious advances towards the understanding of this aggressive weathering mechanism. These advances though fail to form applications in the preservation of heritage structures. This research aims as well to test the application of thermodynamic theoretical models of salt interaction in the diagnosis of salt weathered structures and the ability to define the optimal conditions for preservation. Additionally, while most of the research in salt damage addresses masonry materials, this project will focus on the particularities of wall paintings. We aim to provide a starting point for further research, since sea spray damage of wall paintings has never been investigated independently of the masonry materials. The objective is to investigate the generation of specific damage patterns that result in the loss of the paint layer and test the hypothesis of salt crystallization between the layers.

Thus the aims of this research can be summarized in the investigation of two kinetic mechanisms corresponding to the interaction of salts and the substrate properties. This two fold investigation will address the following conservation issues:

- Does marine aerosol deposition represent an effective pathway of salt input and which are the main factors that control the contamination degree?
- Is the aggressiveness of the coastal environment attributed to the higher availability of salt aerosols or are there other factors that influence the intensity of damage?
- Do the shelters buffer the external conditions and the deposition of sea spray? Is sheltering alone a sufficient measure for the preservation of wall paintings in the coastal zone?
- Do the paint layers of wall paintings constitute a particularly susceptible and independently weathered element of the structure? Are they more susceptible to salt weathering in the coastal environment and why?
- Can we define the optimal conditions for preservation against salt weathering? Which are the important factors of sustainability in the coastal environment?

5.2 General methodology

As described previously the objective of this study is the investigation of the salt weathering mechanism of wall paintings in the context of the coastal environment. The methodology is designed to address the research questions of this project so that the conclusions will not refer solely to a case particularity but to a more general interest and hopefully application. The variables that directed the investigation methodology have been carefully selected in order to represent adequately the characteristics of the objective and alongside to achieve realistic correlations between them. Each characteristic is composed by many components that can be interpreted in various terms. The accomplishment of the objective should therefore relate to the initial causation, which in this case is the preservation of matter in the context of cultural heritage. It is thus anticipated that the investigation of the weathering mechanism will not comprise an end in itself but it will provide the scientific platform to address sustainability issues. Nonetheless the objective, which dictates the methodology, is strictly limited by theoretical and practical boundaries enforced by heritage ethics. It is thus more realistic to anticipate not a single resultant but a general direction that can be interpreted independently by any application against salt weathering.

Aiming primarily to stay focused on sustainability issues it was considered that in order to serve the objective of this research the methodology of the investigation should converge on a two fold path, comprised by the activation and the consequence of the weathering mechanism. Since conventional conservation invasive treatments have been proven insufficient or uncontrolled, modern conservation ethics suggest passive indirect treatments that focus on prevention rather than remedy. In the case of salt weathering the prevention of damage could be theoretically achieved by various approaches. Most of these approaches are incomplete since they require also the contribution of a direct intervention such as desalination or consolidation. The only absolutely preventive approach is undoubtedly the deactivation of the salts phase transitions by environmental control. On the other hand historic buildings are already weathered and the prevention of further damage alone cannot surpass the need of first aid measures. The pattern of the damage, which dictates its treatment, is characteristic of the material. This project considers that the investigation of the damage pattern in correspondence to the activation of damage supplies the necessary data to access sustainability issues in the context of the aggressive coastal environment.

Although it would be desirable to investigate both the activation of damage and its result simultaneously it was decided that the best ways to access each do not congregate in a single methodology. Whereas more details will be presented on the specific methodology of each assessment this chapter depicts the major characteristics and variables that will dominate the investigation. The first part of this research will address damage activation issues. The approach will consider the thermodynamic potential of salt mixtures found on coastal monuments. It was decided that accessing the activation of damage in-situ, despite the complexity of real conditions and the particularities of each case, would provide more realistic results as well the chance to contribute towards a standard methodological approach. Additionally an evaluation of the source and the pathway of salt contamination will accompany the primary investigation in order to justify completely the coastal context.

The second part will address the generation and the result of damage focusing on the particularities of wall paintings. Alternatively in this case it was considered that the effects of weathering *in situ* are not detectable in the time limitations of a research project. Therefore the assessment will take place in the form of a laboratory accelerated simulation of the damage mechanism in question. This simulation will test the hypothesis that salts crystallise on the interface of the wall paintings layers resulting to the loss of the primary information, which lies on the surface. Both parts of the research although they address different questions, lie under the same objective. Thus they share elements on ways that will be described during the presentation of the results and they will contribute simultaneously to the final discussion.

The complexity of assessing the salt weathering mechanism in-situ can be detected by the fact that the phase transitions of the already existing salts and the enrichment in new salts are two simultaneous processes. In an ideal closed system, in laboratory experiments, the salt input is known and the hydrothermal cycle can be easily controlled, therefore they can be safely correlated. However the complexity of real conditions, introduced by the irregularity of salt enrichment and climatic cycles, has permitted a very limited application of laboratory results in the interpretation of field observations. This project proposes a comparative approach based on field experiments. The comparison between the results of identical and simultaneous *in situ* experiments under variable environmental conditions will serve in the evaluation of its parameter. Comparative studies on salt weathering usually include a number of disparate monuments found in excessively different environments. While this approach indicates one or two major variables that fluctuate significantly from one place to the other, it fails to explain variable weathering of adjacent walls. This project by limiting the climatic variability to a single site and simultaneously expanding the number of the investigated parameters aims to focus on the absolutely essential factors of weathering, instead of regurgitating a self-fulfilling prophecy. The desirable variability of the environmental conditions will correspond in this case to the degree and the aspect of exposure. In this context the major variables that direct the choice of the investigated areas are sheltering and cardinal orientation.

Sheltering creates a microenvironment that corresponds variously to the ambient conditions. This project addresses specifically fluctuations in relative humidity, temperature and wind velocity. The materials of a shelter can either absorb or reflect the ambient heat and can be either permeable or not to atmospheric moisture. Concrete structures specifically, without insulation, absorb heat from solar radiation and release it inside, creating a greenhouse effect in the absence of proper ventilation. Non porous enclosures as well, may protect from atmospheric moisture fluctuations but on the other hand entrap the moisture evaporating from the ground. As a result sheltering may buffer the external hydrothermal conditions, follow them or increase their intensity. Shelters generally reduce wind velocity whether they enclose a structure or not. The fluctuations of wind velocity affect temperature and relative humidity. Additionally the wind might carry water vapour, which increases the absolute humidity. In the Planetary Boundary Layer (the lower atmosphere, approximately 300-700m from the ground) the marine aerosols are following the wind streams and their concentration is linearly related to wind speed (see chapter 3.3). The reduction of wind speed under the shelters theoretically corresponds to lower concentrations. Supposing that marine aerosols are deposited mainly by inertial impaction, fluctuations of their deposition in outdoors and indoors samplers will indicate the efficiency of this pathway. This also will be indicated by the concentration of the species found on the external and internal walls and on the samplers.

Since salt weathering is attributed to salt phase transitions we can safely presume that a stable hydrothermal environment, provided supposedly by an enclosure, suspends the action of salts. By conducting simultaneous stoichiometric experiments on sheltered and exposed wall paintings we can trace the mobility of the systems and correlate it to their thermodynamic potential. By introducing the salt enrichment factor, provided by aerosols sampling in the same sheltered and exposed areas, we can evaluate the degree of its parameter's influence on the decay of the wall paintings, thus how far is the air quality or the hydrothermal conditions responsible for the aggressiveness of the coastal environment.

Orientation is the second general variable of this project. Literature, both on heritage conservation and geomorphology, provides many examples of aspect dependent salt weathering case studies (see chapter 4). Especially on the coastal environment the direction of the wind is of great importance. The coast represents a boundary between the land and the sea, or the continental and the marine environment. In terms of air quality the direction of the wind on the coast controls the composition of atmospheric aerosols. Winds oriented from the sea carry marine aerosols (sea water droplets) and winds oriented from the land carry continental or urban aerosols. The deposition of aerosols on a vertical surface by inertial impaction is much more intense windward, despite the turbulent nature of the wind. Consequently the salt enrichment of either sides of a structure correlated to their orientation and the composition of the salts in each side indicates the source and the deposition mechanism. Wind direction also plays an important role in the fluctuations of relative humidity on the coast. Relative humidity fluctuations in the coastal environment are not always correlated to the fluctuations of temperature. Winds coming from the sea are enriched in water vapour due to evaporation, while winds coming from the land are generally drier.

The *in situ* investigation took place on the archaeological site of Delos Island in the Aegean Sea. This site is restricted in inhabitation, industrial activity or automobiles, thus pollution and human activity, which constitute particularly complicated variables, irrelevant of this study, are presumably eliminated. The archaeological site extends throughout the island so that the coastline is practically its boundary. This provides the opportunity to focus successfully on the dynamics of the coastal environment.

Sheltering introduces a variable with two elements. The criterion is not very strict, since none of the monuments in Delos is completely enclosed by a shelter, and it is restrained to the complete roof sheltering (only natural openings like windows and doors) and not sheltered at all. The orientation of course introduces a very wide variable that usually is limited at least to the four major cardinal directions. Nevertheless for simplicity this project will use only two opposite directions. The most interesting couple is North-South since it compromises 89% of the wind direction in Delos and it is perpendicular to the continental-marine zone of the Mediterranean Sea. The sampling areas that have been selected according to these variables are the House of Hermes (north orientation): rooms G (sheltered) and D (open) and the House of Masks (south orientation): rooms D (sheltered) and atrium (described separately below).

The variables that controlled the *ex situ* experiment do not correspond to those of the field investigation. The salt weathering simulation aimed to address issues of a more general nature irrespectively of aspect and sheltering. Nevertheless it maintains the major characteristics of the research questions. While care has been given to assure the representability of weathering in the coastal environment by implying sea salt spraying instead of impregnation, the primary variable under investigation was the materials properties. Specifically the mortar samples that were subjected to the accelerated weathering imitated the layered nature of wall paintings in order to test the hypothesis of interface crystallisation. The detailed methodology and justification are discussed separately in chapter 11.

5.3 The case study

General description of the site

Delos lies in the middle of the Aegean Sea and belongs to the Northern Cyclades complex (figs 5.1-3). The closest inhabited island is Mykonos, situated 5 miles NE from Delos. It occupies 5km^2, constituted mainly of granite and gneiss as well as a superficial layer of calcareous porous stone, which detains the rainwater and provides potable water. This is also evident by the plethora of ancient wells and cisterns. Unfortunately this also provides a pathway for ground water capillary rise. The highest hill is Kynthos (112m), which lies in the middle of the island, in the SE side of the main archaeological site. There are also smaller hills, not more than 50 m high, which do not offer sufficient protection from the winds. The main archaeological site lies in a small low valley at the northern part of the island (figs 5.4,5).

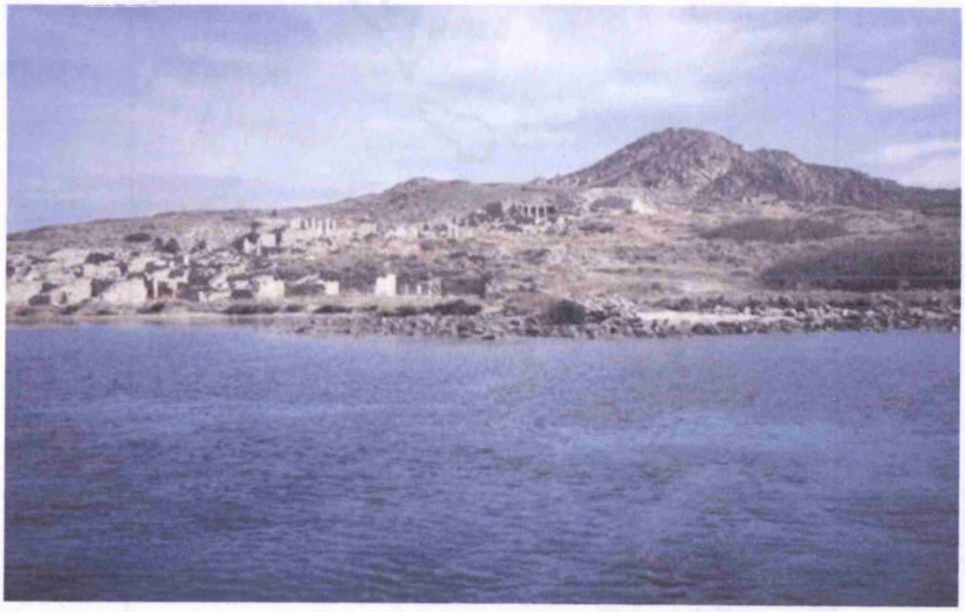

Figure 5.1 Delos island and part of the main archaeological site (view from W)

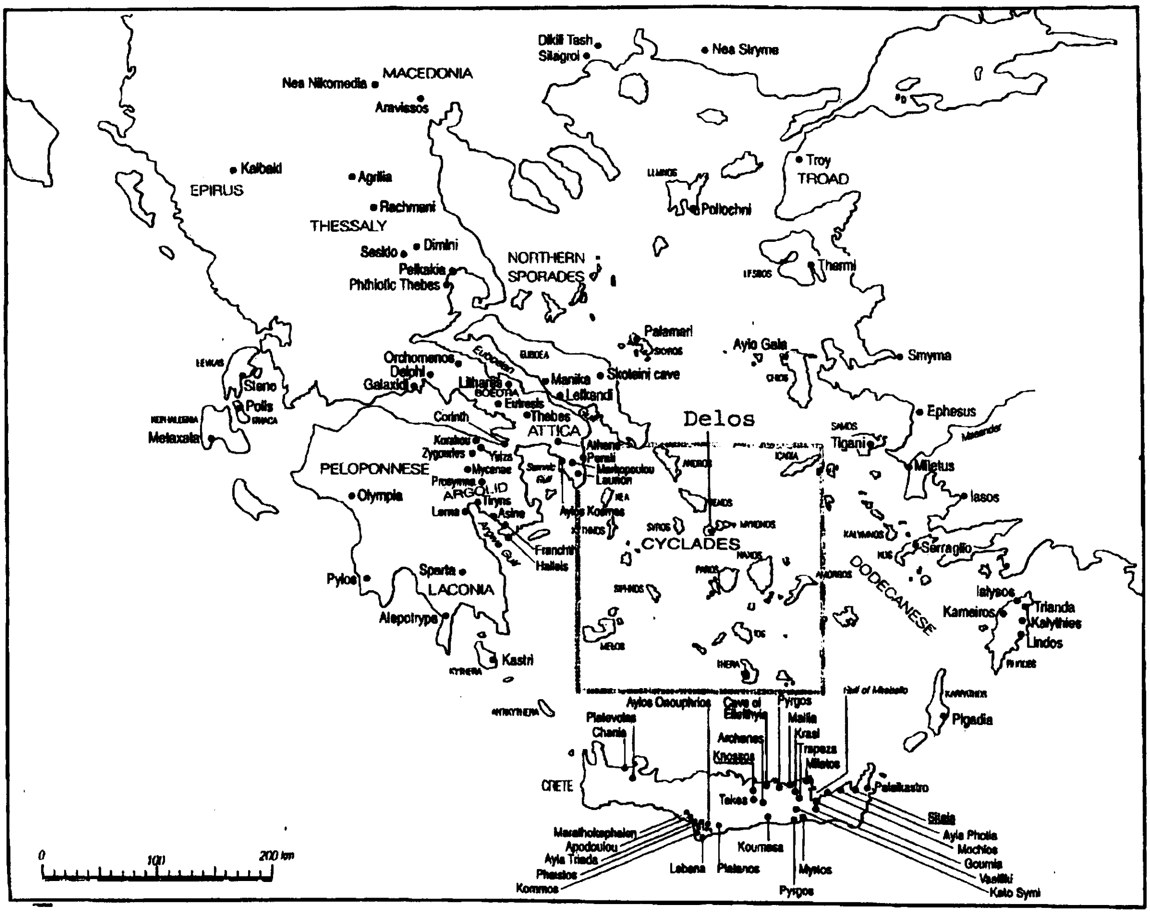

Figure 5.2 Map of Greece depicting sites of archaeological interest. The rectangle marks the Cycladic complex. Delos lies in the middle.

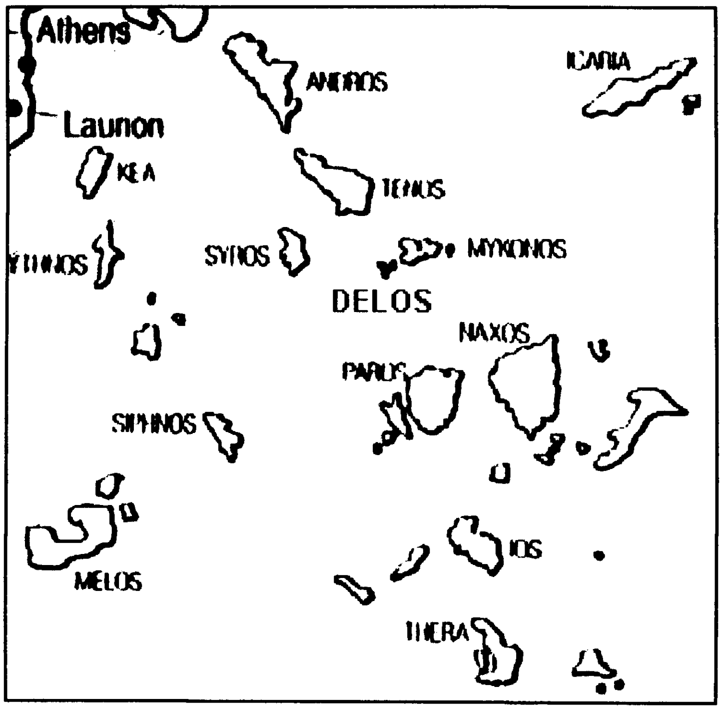

Figure 5.3 Map of Cyclades Islands

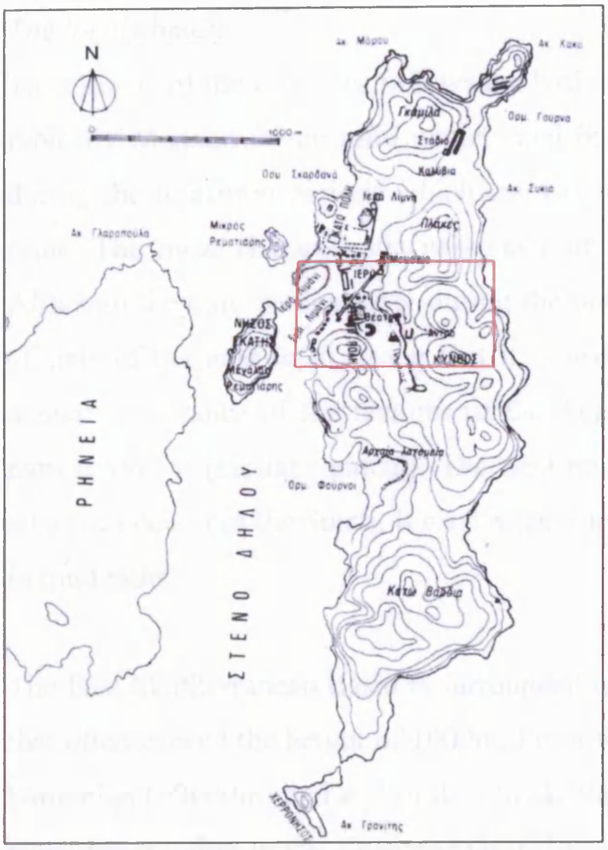

Figure 5.4 Map of Delos (scale 1000m). Red line indicates borders of figure 5 (Zafeiropoulou, 1984)

Figure 5.5 Isometric map of Delos (detail). South part of the archaeological site. Red dot marks top of mount Kynthos (112m), yellow dot marks the port (sea level), blue dot marks House of Hermes (25m), and green dot marks House of Masks (35m). Length of depicted area apx.1km (Zafeiropoulou, 1984)

The local climate

The climate of the Cyclades follows the basic parameters of the Aegean climate, which is typically Mediterranean: mild winters and hot summers, strong hydrothermal variations during the transition periods which can extend for up to 3 months, generally very few rains. The most characteristic parameter of the Aegean climate is the ***etesian*** winds. Although they are present only during the hot months of the year their influence on the climate of the area is so strong that it is usually referred to as "Etesian Climate". The annual appearance of the features of the Aegean climate is so steady that it is actually named after it (etesian=annual). The next most frequently encountered wind is Sirocco, which comes from the South. It carries particles from the African deserts and often results in mud rains.

The East Mediterranean Basin is surrounded in the north and the east by mountain chains that often exceed the height of 1000m. From west to east the Alps are continued from the Dinnarian (>2000m) and end in the Greek Pindos (2917m) and Rodopi (2100m). After a small interruption in the Vosporos Golf that permits the channelisation of the north cold winds towards the Aegean this physical barrier is continued by the Anatolian plateau (>2000) and the Taurus mountains in Turkey. Moving south in the mountain chains of Lebanon (3000m) and Jordan (900m) the height decreases gradually. In the south there are only small hills not exceeding 200m.

The high mountain chains around the East Basin do not permit the exchange of temperature with the surrounding areas. By interrupting the cold invasions from the north, the temperature of the east Mediterranean Sea is kept at a constant of 12°C at 400m depth and actually constitutes a thermal reservoir which maintains a delicate climatic balance in the region. The Aegean Sea represents the northern projection of the eastern Mediterranean basin.

The Etesian winds that influence, apart from the Aegean climate, the entire eastern Mediterranean basin, constituting the only north cold invasion, are present only during the hot months (May-October). They provide a steady weather characterised by very low cloudiness, low relative humidity, dryness and total absence of rain.

Their presence is stronger during the day. Their attenuation and usually total absence during the night is followed naturally by the attenuation of some characteristics. Thus, during the night, the relative humidity is rising again and especially in the islands and the coasts of continental Greece, induced by the rich in vapours sea breeze, it reaches very high values. More rarely the Etesians are followed by fog during the night.

Their direction varies from NE to NW. Their axon is actually bending cyclonically following the coasts of Asia Minor (Metaxas, 1973), but their direction over the Cyclades is always north (Theocharatos, 1978). Southerly they reach the coasts of Egypt and easterly the coasts of Syria and Palestine.

The dryness that characterises the period of the Etesians is attributed to the total absence of rain rather than the low relative humidity of the air. Besides, reaching the coasts of Egypt, enriched in vapours during their long journey over the Mediterranean, they produce very high relative humidity conditions. More specifically the barometric stability of the Etesian stream is binding the appearance of local cyclones, resulting in the total absence of rain (Arseni-Papadimitriou, 1984).

The velocity of the Etesians varies from moderate breeze (4 beaufort, ~6m/sec) to storm (11beaufort, ~30m/sec). Passing through channels, their velocity can reach even higher values. One of these channels is the Tinos-Mykonos channel which directs the wind stream directly on Delos.

Despite the homogeneity of their basic characteristics, the Etesian are divided into seven categories with different features and different influences on the other climatic variables like temperature and relative humidity (Arseni-Papadimitriou, 1984). Furthermore despite the stability of the weather, their appearance is not continuous. Actually it varies from 1 to 29 days. The longer sequences are found in August and July.

The following observations are the result of a large study based on the data collected by the Greek National Meteorological Service between 1894-1970 by fifteen stations located on the islands (Theocharatos, 1978). The atmospheric temperature in the Cyclades follows a simple oscillation with a maximum in July or August and a minimum in January. The sea, which acts as a heat reservoir, offers small fluctuations annually and diurnally. It generally represents lower values from the Ionian complex due to the north invasions, the European and Russian anticyclones during the winter and the Etesians during the summer. Since 1894 the mean fluctuates between 12.5°-15.5° C, the maximum recorded value is 44°C and the minimum –5°C. The temperature of the sea surface is distinctly higher than the air temperature during the cold season, while it is lower during the cold seasons. The influence of the sea surface temperature up to a height of several meters in the atmosphere is evident in the coasts.

The mean relative humidity (RH) values seem to follow the opposite oscillation of the temperature. However a closer look at diurnal fluctuations shows that relative humidity depends strongly on wind direction and speed and frequently presents strong diurnal variations, which are not followed by correspondent temperature fluxes. These disturbances follow the basic pattern: north sector winds and high speed cause a decrease in RH, while south sector winds and lower velocities cause an increase in RH. This phenomenon is global on the coasts due to the enrichment of sea-oriented winds in water vapour as well as the turbulent nature of winds in the PBL.

The annual variation of cloudiness, sunlight and precipitation also follow a simple oscillation with maximum in the cold period and minimum in the hot period. Rain precipitation shows frequently secondary maximum values during the spring, followed by thunderstorm days correspondent maximum values. There is no data for solar radiation in wm^{-2} but generally the Cyclades are considered globally among the regions with the greatest sunshine duration (2700-3100 ha^{-1}). Snowfall and hail are very rare phenomena.

The stability of the Aegean climate, is evident through the many and detailed references to the Etesians winds by ancient writers. Theon in 700 b.c. gives very detailed information on their periodical appearance as well as the origin of their name. Aristotle presents more details. He refers to their diurnal fluctuation, specific dates for their period, their direction and signs that predict their arrival. These signs were also confirmed by modern meteorology. Theophrastos has even categorized the Etesians, a method that was reinvented by modern weather prognosis. The references continue during the Roman and

Byzantine years. More detailed references can be found in several studies (Leivadas, 1973).

Over the last decade however, the climate of the Cyclades is influenced as well by global climate change. The main characteristic of this disturbance is the more frequent appearance of extreme values and storms. Only during the period 2001-2002 the meteorological station in Mykonos recorded the highest and lowest temperature values of the last 50 years. During the summer of 2001 seven scorcher periods were recorded and during January 2002 Delos was covered with snow for 3 days.

Synoptic historic review

The geographical position of Delos contributed to its flourishing as a trade and religious centre (Zapheiropoulou, 1984). The first traces of habitation date to about 2500 B.C. The first flourishing period begins in 1100 BC with the installation of the Ionians. In 478 BC Delos becomes the centre of the Athenian alliance. In 250 BC it is occupied by the Macedonians that diminish the religious role of the island which becomes a major trade centre of the Mediterranean. The luxurious structures, villas and public places decorated entirely with wall paintings date from this period. The acme of Delos stops dramatically in 88 BC, when under Roman occupation, it was destroyed by Mithridates and totally abandoned after a second raid of Mithridate's ally Athinodoros in 69 BC.

From then on Delos plays no important role in the Aegean. In the ensuing period there is still some human activity especially in the granite quarries in the south. Later the island was occupied by Byzantines, Slavs, Arabs and Saracens. Since the 15th century it belongs to the Turkish Empire and serves as a shelter for piracy. It was liberated in 1821 by the Greek Revolution and in 1830 it becomes a part of the first Greek State. The first excavations started in 1872 by the French archaeological school of Athens.

Preservation history

The desperate need to prevent the ongoing damage of the wall paintings is dramatically described in the frequent correspondence of the local archaeological department towards the directorate of conservation since the 1960's. Several treatments have been applied occasionally and somewhat improvisationally, including consolidation, facing and detachment of fragments, which later have been exhibited in the museum of Delos. Unfortunately they are not all documented and those that are, lack essential details. In an attempt to isolate the remaining wall paintings from the harsh coastal environment some areas have been sheltered with concrete slates. The microenvironment in these areas has never been monitored. The disintegration of the wall paintings continued to take place and in 1995 any further conservation treatment was restricted, under suspicions of their contribution to further damages. One year later the Directorate of Conservation, Hellenic Ministry of Culture documented all the wall paintings of the monuments that have been partially sheltered.

Furthermore the French Archaeological School of Athens investigated the aerosols on Delos (Chabas and Lefevre, 1996). This investigation identified seasonal and diurnal changes in the suspended particulate matter, associated with wind speed, as well as a non-negligible presence of pollution. The weathering of the stones on Delos has been reported since then in several studies but the mechanism has not been identified (Sterflinger and Krumbein, 1997; Chatzidakis *et al.*, 1997). A recent study suggests that the local environmental conditions are favouring the deliquescence of NaCl that has been deposited on the marbles by salt spray (Chabas *et al.*, 2000).

Fig. 5.6 The marble lions of Delos

In 1999 the Central Archaeological Council took a historic and very interesting for this study decision about the "marble lions", the symbol and main attraction of Delos. They decided that none of the sheltering propositions was sufficient for the conservation of the statues, so they moved them in the museum and replaced them with replicas.

This tactic of course is not applicable for wall paintings since they represent an integral member of the architectural whole. Exhibited in a museum they lose their aesthetic function and the building loses its identity. Furthermore the detachment is a very destructive technique and moreover it is almost impossible to avoid the environmental shock.

Additionally in 2001 the Conservation Directorate proposed to the Committee for the Conservation of Delos and to the Central Archaeological Council the reburial of a great number of monuments because of lack of appropriate means for their conservation. This proposal has serious implications for the fate of the site since it will affect tourism. The decision has been postponed but this proposal was a clear message for the preservation state of the site as well as for the efficiency of traditional conservation treatments.

House of Masks

The House of Masks lies on the south side of the archaeological site. It is sufficiently protected from the north winds by a small hill. All the openings are facing to the South. It is a Hellenistic luxurious residence constituted by 40 rooms around a large atrium and covering an area of 1320m^2. The total surface of the preserved wall paintings is 162m^2. The rooms G, E, H, L and part of the atrium have been sheltered periodically from the 1950's (fig. 5.7).

Room G is very well preserved despite the large openings facing south. The wall paintings are preserved at the original height of excavation. They suffer from moderate sand disintegration in the lower parts and moderate flaking in the upper parts as well as fluffy efflorescence in the middle and whisker like efflorescence in the upper parts. The atrium's north side, partially sheltered, suffers little weathering and no efflorescence at all. (app. I, II)

It is worth mentioning Room E although it has not been investigated in this project. The wall paintings are severely damaged. In 1965 they have been faced with several layers of gauzes attached with thick acrylic glue. At the start of this project we observed that the inner layers have been pulverised and only the paint layer was still attached on the gauzes. Unfortunately, during February 2002, the south wall remaining renderings (approximately 4m^2) entirely collapsed.

House of Hermes

The House of Hermes is a Hellenistic luxurious structure, probably a men's club, of three gradual floors, which must have covered an area of 600m^2. There are well-preserved wall paintings of 92m^2 approximately. It was partially sheltered in 1952 in order to reconstruct the first floor. It is not protected by any physical barrier from the north winds, while it is built on a north facing hillside which covers its south side (fig. 5.8).

Room D is unsheltered, but surprisingly the wall facing north is in a very good condition. The renderings are preserved to the originally excavated wall height. It is not very clear if the renderings were lime washed. The little remaining of lime wash covered by ochre indicate that if the renderings have been lime washed then all the paint layer is lost although the rest of the mortar is maintained in excellent condition. There is no superficial efflorescence. Room G has been sheltered. Although well protected, with small openings facing east towards the sheltered part of the atrium, suffers from intense superficial flaking at a zone of 1m from the ground, intense sand disintegration in the lower and the upper parts, extending to complete loss of the wall paintings and some efflorescence. (app. I, II)

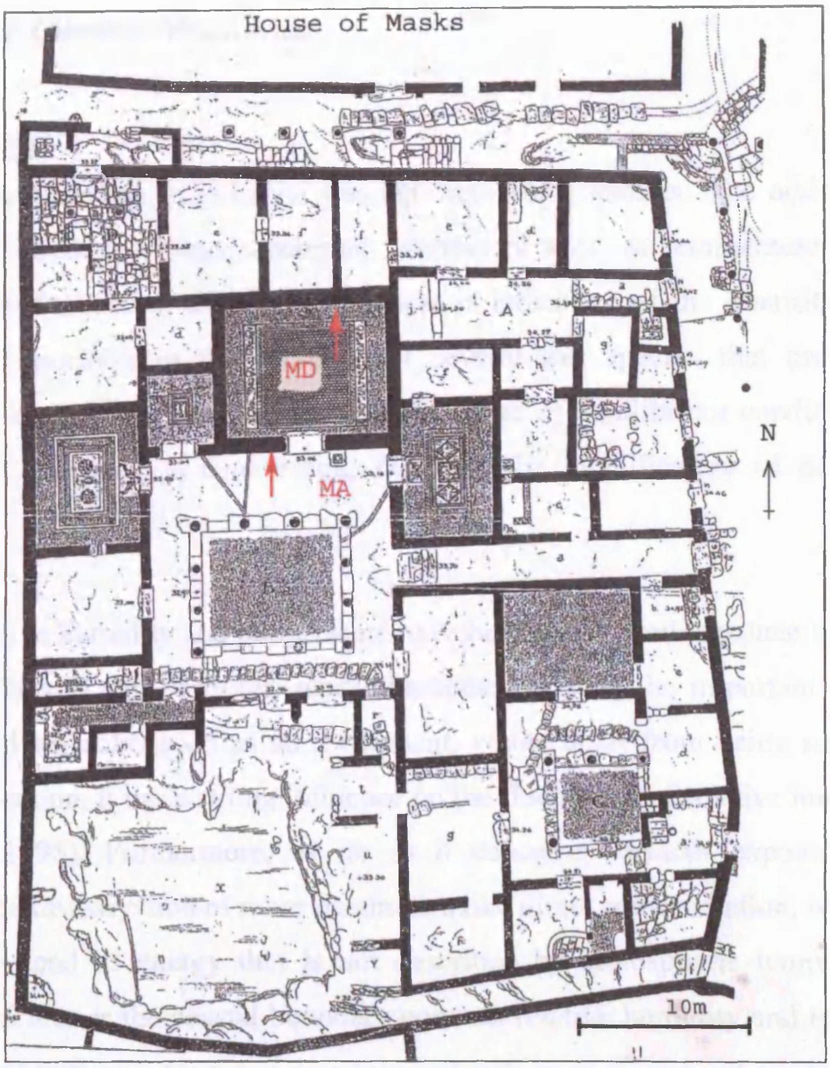

Figure 5.7 House of Masks ground plan. Red arrows mark sampling locations

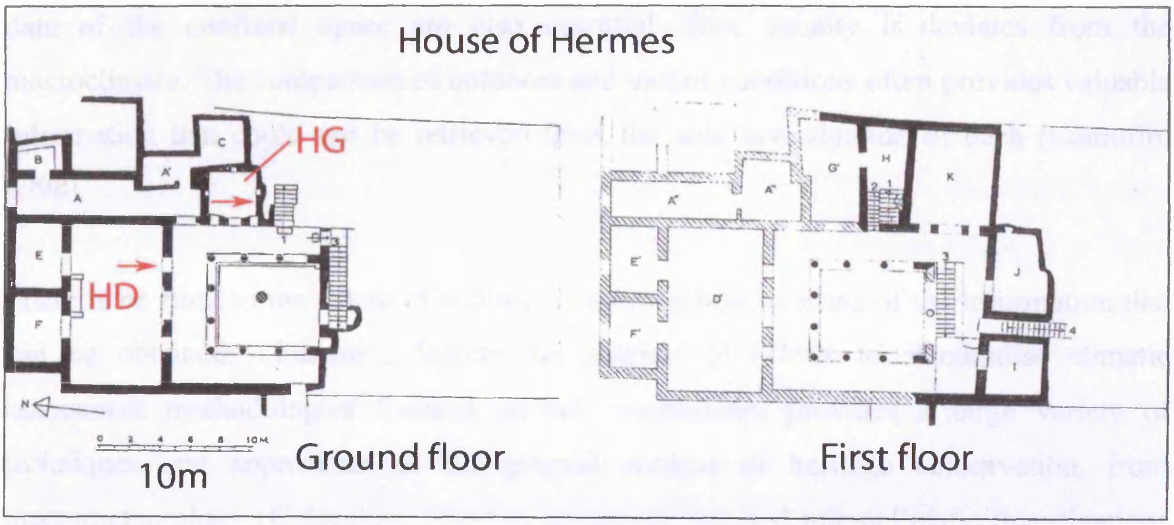

Figure 5.8 House of Hermes ground plan. Red arrows mark sampling locations and microclimate monitoring

CHAPTER 6: Climatic Monitoring

6.1 Introduction

Climatic data recording is essential for salt weathering studies. The activation of salt damage is controlled by environmental parameters such as temperature and relative humidity. The fluctuation of these parameters is indicative of the intensity and rate of weathering. Especially in the presence of several salt species that present a more complicated thermodynamic behaviour with a range of equilibrium conditions, detailed climatic data comprises a determining factor in the identification of the weathering mechanism.

Whereas relative humidity and temperature have been considered adequate to describe the phase transitions of salt mixtures, recent literature revealed the important role of other environmental variables such as air movement, which apart from being responsible for aerosols deposition, it has a strong influence on the fluctuation of relative humidity (Danti and Boddi, 1995). Furthermore, as far as it concerns surfaces exposed to outdoor conditions, the investigation of more parameters like direct solar radiation, which supplies an additional load of energy that is not described by atmospheric temperature, wind direction, which over the coastal boundary controls relative humidity and temperature as well as driving rain, as a source of moisture and salts or as a wash-off agent, is necessary to explain salt weathering phenomena. In the case of sheltered structures microclimatic data of the confined space are also essential since usually it deviates from the macroclimate. The comparison of outdoors and indoor conditions often provides valuable information that could not be retrieved from the sole investigation of each (Camuffo, 1998).

There is no limit to the extent of a climatic investigation in terms of the information that can be obtained. Literature, despite the absence of efforts to standardise climatic assessment methodologies focused on salt weathering, provides a large variety of techniques and approaches in the general context of heritage conservation, from macrometeorology (Colaccino, 1989) to extremely detailed microclimatic investigations (Camuffo and Bernardi, 1995). Nevertheless the climatic assessment frequently overshadows the investigation of the weathering mechanism itself.

Specifically for salt weathering the interest lies in the interaction of the environment and the salts at the proximity of the pores where the damage occurs. Although the complete description of the nanoenvironment of a porous system can be achieved sufficiently, even under the restrictions of cultural heritage (Nappi and Cote, 1997), it lacks the desirable generalisation.

Ideally a combination of every available information that can be collected is useful. Still, climatic monitoring can be very expensive and sometimes the vast amount of data can be more confusing than enlightening. More practically, a sensible choice of the absolutely necessary parameters that correspond to the needs and particularities of each case and address the specific research questions is sufficient to support the primary investigation.

6.2 Methodology-Equipment-Installation-Setup

Frequently climatic measurements for conservation studies are obtained by nearby meteorological stations. The nearest station of the National Meteorological Service to Delos is situated on the island of Mykonos. But since the measurements are taken at significant height inland they could not serve the purposes of this research. Specifically it has been strongly suggested by the Bureau of Meteorological Research, Athens Academy (Metaxas, personal communication) that at least temperature and relative humidity should be recorded on the island of Delos at a height corresponding to that of the monuments in order to acquire accurate measurements.

It was principally requisite to ensure sufficiency and accuracy for the climatic data. The first goal was to define which climatic parameters correspond to the needs of the project. Temperature and relative humidity are by definition necessary since they will be linked to the results of the thermodynamic investigation. Wind speed and direction will be correlated to the aerosols deposition investigation. Solar radiation can not be quantitatively related to either of the field experiments but since its influence is supposedly important for the particular area it has been decided to acquire at least an indication of its intensity. Rainfall and generally meteors are rare in the Cyclades. Although rain events are intense their duration and frequency are very small to be considered important. Thus there is no immediate need for rainfall height measurements in Delos. Nevertheless since exposed surfaces will also be investigated for their salt content it has been considered sensible to acquire an indication of rainfall in terms of "number of days with rain" for the period prior to sampling. The data have been acquired from the meteorological station in Mykonos.

The second immediate goal was to set the type of measurements needed to accompany the field experiments. The thermodynamic investigation of the salt mixtures that exist on the wall of the monuments introduces more demanding needs in terms of precision and accuracy since the climatic data will be correlated to a very complicated range of phase transitions. Furthermore the harsh environment of Delos primarily in terms of sea spray demands specially designed equipment for outdoors use. It was therefore evident that as a principal quality was more crucial than quantity.

In the absence of sufficient funds to purchase the desirable data logging system as well as due to practical difficulties introduced by limitations of the harshness and isolation of the site a less expensive but absolutely adequate solution has been established for monitoring and recording the environmental conditions. The Directory of Conservation, Hellenic Ministry of Culture offered, for the needs of this research, a standard meteorological station that has been used successfully in the past for relevant studies. The station has specially designed for outdoors use, salt solution resistant, temperature and relative humidity probes, wind speed and direction indicators, a pyranometer and a central data logging unit. The specifications of the station and the probes can be found in app. X.C. Temperature has been monitored by a thermistor in Celsius degrees and relative humidity by a thin film hygrometer. The solar radiation has been assessed in terms of energy per surface unit (W/m^2) while wind speed has been monitored by cup anemometer in m/sec and wind direction by a rotating indicator in cardinal degrees.

For practical and ethical reasons the station has not been installed near the monuments. Instead the Museum of Delos offered a convenient and well-positioned site. The central unit has been placed inside a storage room near power supply and the probes on a mast positioned on the terrace of the Museum. Overall the probes were laid at a height of approximately 8 meters from the ground, sufficient for accurate T and RH measurements and simultaneously away from obstacles that affect the general wind particulars.

The storing memory of the unit permitted very frequent observations. In order to monitor the influence of short events, apart form the average conditions, the sampling period has been set to one hour. Data has been collected during all sampling campaigns for a period of 18 months (11/01-06/03). Even though the data is fragmented, because of frequent power cuts, it represents adequately the yearly cycle as well as the average daily deviations.

Although it was suspected that atmospheric temperature and relative humidity might differ from those under the shelters it was not possible to monitor continuously the conditions of the two investigated sheltered rooms. Instead it has been decided to acquire a number of measurements in specific periods as reference. Finally we managed to obtain two small data loggers for the periods 14-28 March 02 and 21 May- 6 June 03 (specifications app. X.C). The loggers have been placed near the investigated wall paintings. Unfortunately these loggers although positioned inside the rooms HG and MD they could not resist salt spray for longer periods. It hasn't been possible to obtain these units during the rest of the sampling campaigns.

6.3 Results and discussion (appendix III)

General description

According to the HNMS (Hellenic National Meteorological Service) annual report the investigated period has not been representative of the usually observed conditions. Although the average values correspond to the standard temperature and relative humidity cycles there were clear deviations of the minimum and maximum values as well as a number of rare short events. Temperature dropped considerably below the average values during the periods 9-20 December 2001 and1-10 January 2002. The temperature dropped below zero for considerable time during the night of January 6th 2002. During this period it snowed and Delos was covered with snow for three days. Only 3 snowfall events have been encountered in the area since 1950. The most characteristic abnormality of the period though was the significantly high rainfall. Cycladic climate is generally considered dry due to absence of rain. Surprisingly rainfall for the year 2002 was much higher than the average value. Both frequency and duration were equally increased.

Another characteristic was the absence of the Etesian winds during the summer. This probably relates to the average decrease of temperature. Nevertheless the sampling periods presented sufficient variability in wind speed in order to be correlated to the deposition rate. Although the *etesians*, due to their north origin, contribute to the dryness of the Cycladic summer, relative humidity maintained the average low values probably due to the intense solar radiation.

Overall the period of study maintained the mild characteristics of the Aegean climate. Temperature fluctuated in daily average values from 7°C in winter to 27°C in summer. Relative humidity follows the temperature's yearly cycle fluctuating from around 80% in the winter to 65% in the summer. Temperature's daily minimum and maximum correspond to the daily average revealing a very balanced daily deviation. Relative humidity on the other hand presents greater variability with a distinct shift from the average towards lower values particularly in the summer. It is absolutely certain that relative humidity and temperature, to a lesser degree, are affected by the wind direction especially when the wind intensity is relatively high. As calculated from the data condensation is unlikely to occur in Delos except under some special circumstances during the coldest period and more likely during the night. The fact that relative humidity deviates daily around the ERH of halite gives a first indication of the weathering rate. Nonetheless although it is expected that halite comprises the dominant contaminant in a coastal environment literature has shown that such assumptions are very premature.

Wind speed fluctuates most of the time between 5 and 10 m/s which corresponds to moderate gales. Short strong gale and storm gale events are frequent, reaching wind speeds up to 20m/s. On the other hand dead calm conditions are very rare. Although the data is sampled, it seems as wind is continuously present on Delos. As expected north wind direction prevails for most of the year. The next most frequently observed wind is south.

Solar radiation follows a smooth curve increasing in the summer and decreasing towards winter. Days with cloud coverage are considerably increased in relation to the average. Overall the solar energy can be considered very high, reaching up to 900 w/m^2 during August. The extremely high radiation is not reflected by atmospheric temperature due to the cooling effect of the wind and the marine location.

Special climatic characteristics linked to salt weathering

The overall decrease of temperature during the investigated period can not be considered sufficient to influence considerably the average characteristics of the weathering mechanism. Both its daily and annual deviation stayed small and therefore representative of the marine environment since the sea, which acts as a heat depot, does not permit extreme fluctuations of temperature. From a remote point of view the marine environment seems less harmful than the continental, which presents more frequent and intense deviations of temperature. Short extreme events however were not absent. The frost conditions encountered in winter might have enhanced condensation. Similarly we can suppose that the scorching events in July (not registered due to extensive power cuts) had an effect on the crystallisation of more soluble and temperature sensitive salts.

RH annual and daily deviation has not proved to be as wide as expected from previous measurements (Minos, 1995). Theoretically though, even in the daily time span, it can be considered sufficient for salts phase transitions. Definitely the very low values encountered in summer should have enhanced crystallisation. Specifically in room MD during summer efflorescence is evident to naked eye. As a first approach the average deviation of relative humidity around 75% gives a promising indication of the rate of salt weathering since the presence of NaCl is strongly expected.

Wind speed despite the absence of the *etesians* remains overall high enough for transport and deposition of sea spray. Although the duration of aggressive events is short the continuous presence of wind in the area predicts that the atmospheric pathway is definitely a major factor of salts input. Similarly we can predict that since the origin of the airborne species is marine, sodium and chloride should be among the major ions expected to be found on the monuments.

Although temp and relative humidity follow a sensible and balanced annual and daily deviation the coastal climate as depicted in the case of Delos introduces another determining factor for salt weathering. The direction of the wind proves to have, as expected, a strong and immediate influence on temperature and relative humidity. Its important role although unnoticed in average values is dramatically depicted in detailed data. In general the coastline comprises a physical boundary between continental and marine air masses. Since the marine winds are enriched in water vapours compared to the continental, the orientation of the wind controls significantly the levels of relative humidity on the wider coastal area. Specifically in Delos and generally the Aegean the continental winds blowing from the north are cold and dry while south winds coming from the Mediterranean are warmer and moist. Looking closely at the first three days of monitoring in Delos (23-25/11/01) we can see the dramatic effect of wind direction on temperature and relative humidity and the even more impressive immediacy of their response (charts IIIA.2,4,5). During the 23rd temperature fluctuated between 16° and 19.7° C and relative humidity between 84% and 100% under warm and moist south winds. At 14.00 on the 24th the wind direction shifted suddenly to south. Temperature decreased immediately down to 12.5°C and later at around midnight it reached 8.7°C, where it continued fluctuate on the 25th. Relative humidity instead of increasing as expected as a response to the decrease of temperature, decreased as well with a small delay. It reached 54% by midnight and continued fluctuating between 46% and 57% on the 25th. It is quite obvious that the balance between temperature and relative humidity is disturbed on the coasts under the influence of marine or continental winds. Despite the fact that a sufficient wind speed is needed for noticeable effects the standard conversely proportional relation of temperature and relative humidity cannot be held for granted in the coastal environment. This case underlines the importance of absolute humidity and the investigation of atmospheric moisture sources and transport which are frequently neglected. We suspect that frequent fluctuation of wind direction could be more aggressive than the average relative humidity deviations themselves. At least it is evident that even detailed temperature and relative humidity data cannot adequately describe the environmental particularities that activate salt weathering.

It was anticipated that the deposition of marine aerosols would be significantly increased during summer because of the unique intensity of the *etesian* winds. Overall the average annual wind speed was decreased due to the absence of the *etesiasns*. Nevertheless the wind speeds encountered in Delos during monitoring are considered sufficient to transport and deposit suspended particles on vertical surfaces. Unboubtedly similar wind conditions in Delos, as described by Chabas and Lefevre (1996), increase the presence of sea spray in the atmospheric particulate.

The implications of the increased rainfall height for salt weathering can be summarised to an additional source of moisture. In this respect we should expect that since rain is rare in Delos these frequent events probably washed off superficial deposits from exposed walls or transported the salts deeper in the masonry while on the same time increased the supply of water and probably the transport of salts from the ground.

Certainly direct solar radiation induces crystallisation. In this respect it might increase the frequency of phase transition cycles when relative humidity does not fluctuate sufficiently. On the other hand we can suppose that by accelerating crystallisation it does not permit to the deposited sea spray to penetrate inside the pores reducing the potential of damage. The latter corresponds conveniently to the better state of preservation of the exposed wall paintings.

Sheltered areas microclimatic evaluation

The microclimate under the shelters follows in general the outdoors trends of temperature and relative humidity. Although wind speed was not measured indoors we can safely assume that in both cases the shelters, positioned directly on the structure, block significantly the circulation of air. As for solar radiation it is evident that it does not affect directly the sheltered areas.

The indoor temperature daily deviations correspond closely to the outdoors values. The only exception is the maximum values, which are slightly higher outdoors probably as a result of the intense solar radiation. As expected due to the good heat conductivity of concrete and the absence of insulation the shelters do not buffer the fluctuations of temperature.

Relative humidity follows the average fluctuation of outdoors but at a much wider daily deviation range. The shift towards higher values can be explained by the absence of direct solar radiation and air movement. The lower values though cannot be interpreted adequately. On the contrary it was expected for the above reasons that relative humidity would be lower outdoors. Although both instruments have been recently calibrated and both relative humidity probes work on the same principle we cannot exclude the case of inaccurate measurements. Especially under sea spray contamination relative humidity probes do not work properly. Nonetheless in this case we would expect extreme fragmented values or a shift towards higher values – as the deposited salts would attract moisture – and not corresponding wider deviations. Furthermore both data loggers in rooms HG and MA presented the same deviation and thus it is very unlikely that both recorded the same inaccurate measurements. The only variable that could be related to the low relative humidity indoors is the absence of sea spray. It might be true although not absolutely justified that sea spray, as a source of water vapour, continuously present on the site does not permit very low values of relative humidity outdoors. In terms of salt weathering the wider deviations of relative humidity in the sheltered areas corresponds conveniently to their poorer state of preservation.

Although the shelters block significantly the wind, the influence of its direction on temperature and relative humidity is reflected in the indoor microclimate. More specifically as can be seen in charts IIIB.1,2 at 18-19 March the intense north winds lowered temperature and relative humidity, while at 20-22 March the wind shifted progressively towards south driving simultaneously temperature and relative humidity towards higher values.

The comparison between the two sheltered rooms reveals a slight shift towards higher relative humidity and lower temperature in room HG. Both rooms were evenly affected by the wind direction. Since orientation does not play a significant part the only sensible explanation is that room MA is better ventilated. It is far more spacious than HG and with exceedingly larger openings. The better circulation of air probably enhances evaporation prohibiting the built of high relative humidity. Nevertheless since relative humidity depends on absolute humidity apart from temperature we might as well seek more sources of moisture in room HG (charts IIIB.3,4). Alternatively we can mention that the floor of room MD has been insulated as a conservation treatment for the floor mosaics. Indoors monitoring during May reveals the same large deviations as in March. Temperature follows the outdoors rise while relative humidity sustains the same high values.

Climatic interpretation in the detail needed for salt weathering studies proves to be very difficult and complicated. Especially in the case of coastal areas that introduce more complex boundary parameters, the identification of the interaction between the environment, the structures and the salts becomes problematic.

Evidently solid conclusions cannot be drawn solely from climatic data. Even assumptions seem somehow perilous in the absence of information for the composition and the distribution of salts as well as their source and transport particulars. Although the climatic data holds a supportive role in the investigation of salt weathering, in the next chapters it will become an indispensable reference.

CHAPTER 7: Aerosols deposition

7.1 Methodology

The marine location of the investigated site does not necessarily indicate the salt contamination particulars. Sea spray apart from depositing by inertial impaction, also sediments on the ground and can be transported by ground water capillary rise. The contribution of each pathway of salts transport as well as the identification of its source cannot be investigated solely through correlations between the concentrations of the species found on the renderings. At least a discrete evaluation of one pathway is necessary. In this case the easiest and most reliable neat assessment is the dry deposition of the aerosols. The deposition measurements, following the same general variables of aspect and sheltering, will indicate the efficacy and the trends of the atmospheric pathway. It is however important to assure that this assessment will not describe the ambient concentrations but the actual deposition on the wall paintings.

The deposition process should therefore be representative of the studied particularities. The common methods of aerosols sampling that involve air pumping through a filter, do not correspond at all to the needs of this assessment. Therefore the material that has been used as a deposition sampler was identical to the one studied. This approach, using identical materials as samplers, introduced to overcome the weak representation of deposition velocities by ambient concentrations, has been successfully used for a number of different disciplines, from the corrosion of telephony wires (Klassen and Roberge, 1999) to pine forests decline (Gustafsson and Franzen, 1996) due to sea spray. Especially for metals and alloys the process has been standardized (ISO 9225). Morcillo *et al.* (2000) used this standard to identify a very close relation between deposition, wind direction, velocity and duration over the coast. They noticed however that this relation becomes negligible for wind speeds under 3m/s. In conservation studies this approach has been used by Behlen *et al.* (1997) to quantify sea spray deposition on stones, Grossi and Murray (1999) for acidic gases deposition and Hoffman *et al.* (1998), who used mortar plates to investigate deposition on renderings. But while for stones, freshly cut specimens, extracted from the same quarry as the studied materials, can be used as samplers ensuring a relative similarity, for mortars this approach introduces a basic limitation since they are man made. On the other hand mortar samples coming from the same matrix present a desirable higher degree of homogeneity than the stone samples, ensuring reliable results in simultaneous sampling experiments. Nevertheless a further limitation, not only for mortars, is that while industrial research addresses damage as an exception, in conservation studies the investigated materials are already weathered. Still, the structural damages (asperities), that could affect the results, are not considered important for the needs of this research since the questions do not address the conservation state of the particular renderings but correlations between variables of a more general interest.

In order to control parameters that affect directly or indirectly deposition such as porosity and surface roughness different types of mortars can be used as samplers. Porosity should normally affect condensation development on the surface of a mortar and consequently the deposition and adhesion of dry particles as well as gases, but as discussed previously marine aerosols are more likely to be present in the liquid state. Therefore relative humidity does not represent the primary variable for the deposition assessment. However porosity controls the penetration of the sea droplets, which overall might affect the eventual enrichment.

The composition of the mortar samplers that have been used in Delos for the aerosols deposition assessment was relevant to the first two external layers of wall paintings in Delos. The porosity and roughness of the exposed surface has been controlled by the percentage of aggregates since it was lime washed for type I mortars and plain for type II. A fat lime putty and sharp sand in 1:3 ratio have been used for the mortar matrix. The lime wash has been applied before the complete drying of the mortars by a soft brush. In order to control the net input of salts by aerosols deposition the aggregates were washed by deionised water before the preparation of the samples and the extract has been analysed. The samples remained in an airtight chamber, packed with dry ice, to accelerate their carbonation, for several days. The samples were tested daily with phenolphthalein and after they were seemingly carbonated they were transported to the site of sampling in airtight boxes. Furthermore blank samples were analysed after their preparation and carbonation.

A parameter that has been given attention was the positioning of the samplers. Inertial impaction is influenced by the angle between the air stream and the collecting surface. In this project specially designed holders have been used to attach the mortar samplers vertically on the walls of the monuments, as close as possible to the area where the drills have been extracted, facing the investigated wind direction in order to describe the actual process. Additionally the vertical positioning minimised the deposition due to gravitational settling, which ensures the orientation correlations validity. The holders were rain sheltered to ensure the evaluation of dry deposition only.

The exposure time has been 15 days, a relative minimum assessed by the literature, in order to ensure detectability of the salt species and simultaneously minimise the complexity of climatic conditions and specially wind speed and direction, which is essential to correlate them safely. This method apparently does not permit diurnal or individual events investigation. The size of the samplers collecting surface that must be related to the exposure time, was 2.5 x 2.5 cm for ethical reasons, so that it does not compete with the architectural and painted features of the adjusting walls and practical reasons of transport, storage and analysis preparation. The size of the samplers does not influence the process since the collecting surface is flat (size affects deposition on cylindrical surfaces but not on plates (Zimon, 1982)). The rest of the surfaces were enclosed by the holder's chambers. The salt input in each sample has been assessed by aqueous analysis. The mortars were immersed in deionised water (10ml) and the extract was analysed by Ion Chromatography (IC) and Inductive Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

Further analysis included Scanning Electron Microscopy for the identification of individual crystals on the deposition samplers. This complementary analysis served as a control tool to correspond the ionic concentrations to salt species. The porosity of the samplers introduces a limitation for surface imaging and analysis. It was suspected that if the solutions will penetrate the sampler some species will crystallise on the surfaces while others will crystallise inside the pores resulting to low representability of the deposited particulate. Therefore supplementary samplers which were non-porous and adhesive accompanied the primary investigation. The adhesive tape was attached on the reference mortar samplers to avoid any influence of the mounting panel and they were placed on it accordingly. It was anticipated that the tape would collect more particles than the mortar samplers providing the chance to separate and study individual salt particles as well as a more complete picture of the atmospheric species including non dissolved as well organic material that might influence the deposition process. Analysis was limited to semi-quantitative results of individual particles. Both EDAX spot analysis and mapping have been used to identify the composition of multicomponent crystals.

Nevertheless SEM identification of individual crystals cannot assure that the marine aerosols were modified before reaching the surface of the samplers, and therefore correlate them to wind direction. However the quantitative results of the aqueous analysis and their correlation to wind direction will indicate the deposition pathway and process because if the aerosols were modified before impaction on the samplers than the chloride concentrations would not correspond to those of sodium in respect to seawater. The concentration and composition of the marine aerosol might not be totally identical globally, because of the contribution of minor elements due to local sources, but the Na/Cl ratio is well established (Riley and Chester, 1971). Any disturbance in this ratio means that the aerosols have been modified after their production and not before. Fluctuations of sulphate and nitrate from the average concentrations in seawater are usually used by several disciplines to describe enrichment or deficiency. The concentration of Na however is used as an indicator element for the contribution of seawater (Torffs and Van Grieken, 1997). The only way that the concentration of marine aerosol Cl can be depleted against Na is by replacement by atmospheric sulphate or nitrate (Seinfeld and Pandis, 1998). The contribution of elements due to sea spray has been assessed by the enrichment factor (EF) according to the following equation, using Na as the marine origin indicator element:

$$EF_{marine}(X)= (X/Na)_{aerosol} / (X/Na)_{seawater}$$

where $(X/Na)_{aerosol}$ is the ratio of the concentrations of an element X and Na in the aerosol and $(X/Na)_{seawater}$ is the ratio of their concentrations in bulk sea water. The $(X/Na)_{seawater}$ for the Aegean sea has been provided by the National Center of Marine Research.

The contribution of wet deposition and run off water were not assessed in this project due to lack of appropriate instrumentation and limited sampling intervals. Although rain events are not absent in the Cyclades their frequency, duration and intensity are so low that they cannot be considered as a major factor of deposition or wash off of the exposed surfaces, especially in relation to the constant presence of sea spray. Nonetheless since rain acts as an atmospheric wash-off mechanism its composition mirrors the suspended species. Therefore rain samples have been collected and analysed as a supplementary indication of the air quality. Additionally reference samples of ground water were collected by two evident sources of moisture, the well in the House of Masks and the stream of Scardanas which flows on the east side of the monuments (fig. I.5).

7.2 Results and discussion

The results of the deposition experiment are summarised in appendix IV. Aerosols samples have been collected during 4 periods of 15 days in March 2002, August 2002, January 2003 and May 2003. Whereas the investigation of the wall paintings salt content had to follow a sensible annual climatic cycle the deposition data has been collected at random periods since its major variables (wind speed and direction) fluctuate randomly throughout the year. Although it was desirable to include an etesian wind event in the summer and at least one south wind event it was not possible to predict their appearance accurately. The above-mentioned months were chosen to match those of drills extraction for practical reasons only.

During the first period 14-28 March 2002 the deposition results are in good accordance with the climatic data. The samplers oriented towards the north (House of Hermes, HD) collected far more aerosols than those oriented towards the south (House of Masks, MA). The specimens positioned inside the sheltered rooms HG and MD collected a very small amount of aerosols (chart IV.1). Although north winds prevailed during this period the percentage of south winds does not correspond to the relatively high concentration of species found on the south collector (charts III.5-6). This can be explained by the fact that the south wind event although of short duration was relatively intense while north winds fluctuated in intensity including periods of almost dead calm (<5m/s). Since the sampling was continuous unfortunately we cannot establish a linear relationship between the wind speed, aspect and concentration. Nevertheless the basic trends of deposition are clearly described.

Qualitatively Na and Cl dominate the deposited dissolved species indicating the marine origin of the aerosols (chart IV.2). The enrichment factors for SO_4 indicate a secondary source which is probably anthropogenic (table IV.7). These results are in accordance with the finds of Chabas *et al.* (2000), which specified excess anthropogenic sulphur in air masses passing from Delos and originating in the North. Whereas this preliminary study depicts the presence of anthropogenic species in atmospheric concentrations far from any relevant source, in a supposedly "clean" environment, the present experiment proves that these species are actually deposited on the surface of the wall paintings.

On the other hand the chlorides are depleted against Na. We can assume that some sulphur was not deposited in the gas form of SO_2 but it was already incorporated in the sea spray before deposition, replacing the missing chlorides as sulphate according to Eriksson's reaction (see chapter 3.3). Although excess sulphur has been related to north winds it is evident that the samples facing south collected more sulphate despite their low concentrations. During this period there was only one very brief south wind event. In the absence of appropriate data we cannot relate the air masses of this event to any source. In general south winds in this area are supposedly clean of anthropogenic sources. Nevertheless sulphur enriched air masses coming from the south-eastern Mediterranean basin have been correlated to biogenic sources (Ganor *et al.*, 2000). Another explanation for the origin of sulphur might be the fact that gases do not present such strong orientation dependence as larger particles and can be deposited on surfaces in the lee of the wind through turbulence. The samples facing north are slightly depleted in chloride pointing to the strong influence of sea spray originating from nearby. Evidently north winds prevailed during this period. As a result the pure sea spray, which mainly originates from the nearby waters screens the depleted spray if of course there was any. In this case the excess sulphur (almost double of that of sea water) seems to deposit as gas.

Sheltered samples also present high EF values for sulphate followed by chloride depletion (table IV.7). In this case it is plausible to assume that the enclosed shelter buffers the larger particles as sea spray whils permitting smaller particles as gases to flow around it and enter through openings. Another interesting explanation for the presence of excess sulphur is the redistribution of gypsum from weathered areas. Unfortunately this assumption cannot be investigated without results for Ca. It is though true that Chabas and Jeannette (2001) identified individual gypsum particles in air masses collected near weathered areas in Delos. This new insight in the redistribution of gypsum provides an additional explanation when its dissolution is not favoured by the environmental conditions. It must however be stated that in the case of the south and sheltered areas the concentrations were very low and therefore more susceptible to faults during handling and fluctuations corresponding to the analytical method's accuracy and precision.

The absence of the intense Etesian winds in summer 2002 is reflected in the deposition results (table IV.2, charts IV.3,4). As can be seen in charts IIIC.7-8 the wind speed for the period 9-22 August is the lowest of all the sampling periods and so is the total deposition concentration. The deposition rate between the two major aspects is also in accordance with the climatic data. The low percentage of south winds corresponds to the deposition rate of MA and is similar to the one of March. The composition of the aerosol though is slightly different. There is a clear shift of the EF values towards pure seawater. Both chloride and sulphate seem to originate from seawater for the exposed north and south areas. The only case that maintains its high values for excess sulphate is the sheltered area MD. This finding strengthens the assumption of gypsum redistribution through the atmospheric pathway. The absence of excess sulphate, although possibly coincidental, could be initially interpreted as a deactivation of sources or a blocking of the pathway. Since it is not possible to access accurately the back trajectories of all the air masses that passed from Delos for such a long period we can only rely on the general north origin of the winds which has been related to anthropogenic pollution.

Contrary to the findings of the present project, Chabas *et al.* (2000) reported more anthropogenic sulphate in August than March, which they attributed to more intense photochemical activity and absence of rainfall. Although during the latter investigation (July-August 1995) the intensity of the wind was much higher than August 2002, which might affect the ability of the atmospheric pathway to carry particulate matter, one should consider the nature of the samplers used in each case as a far more important variable. In the investigation carried out in 1995 nuclepore membrane filters have been used to describe atmospheric concentrations rather than deposition. In the present investigation the nature of the sampler is directly related to species that deposit on the surface of similar materials without necessarily describing other species which might at the time be present in the surrounding atmosphere. It is quite clear that the deposition mechanism presents particularities that cannot be interpreted solely by means of sources and pathways. Even if we accept the local origin of the winds during August 2002 against the remote origin of the air masses during March we cannot neglect the local sources of pollutants and mainly marine traffic, which is much higher during August.

Evidently there are three variables that could be related to the sampler's particularities, each leading to a different interpretation. The density of the mortar sampler, which contrary to the filter, forces the wind to flow around it, permitting only the heavier particles to detach from the trajectory and deposit, does not provide an adequate explanation since it contradicts the results of March investigation. The affinity of calcareous materials to sulphur gases is another characteristic which also contradicts the results. Accepting the presence of more particulate sulphur during the warmer months there is only one possible explanation for the absence of excess sulphur during August and it relies on the fluctuation of relative humidity. During March the higher levels of relative humidity probably enhance the deposition of sulphur in the gas form. During August the very low relative humidity and the intense direct solar radiation "dries" the mortar samplers reducing the ability of gases to deposit. On the same way gas to particle conversion is also decreased. The latter alternatively does not effect the deposition of sea spray, which maintains a very adhesive brine form even at very low relative humidity percentages.

Deposition of aerosols during the third sampling campaign 19 January – 2 February 2003 returns to the higher values equivalent to those of March (table IV.3, charts IV5-6). The results are in accordance with the climatic data since the average wind speed is slightly higher than March with less dead calm events. Nevertheless the aspect variable does not agree with the percentage wind direction. Although the samplers oriented towards north collected significantly more particles than the south samplers, the percentage of north wind events was evidently smaller. More specifically there are two small periods of N winds, a large period of NE, E, and SE winds and a large period of persisting SW winds (charts IIIC.9-10). The dominance of south winds during this period was not depicted by the deposition concentrations. The higher intensity of the SW wind is also in conflict with the results. This conflict raises another limitation. The production of sea spray and thus its availability for deposition is not directly related to wind speed. It would be more accurate to measure the atmospheric concentrations simultaneously with the deposition rate.

Nevertheless similar case studies have shown that the absence of marine aerosols under these conditions and such proximity to the sea is very unlikely. We should then attribute this disturbance to other causes. The most profound explanation can be found in micromorphological elements of the building hosting the samplers and its surrounding environment. Probably these features play a more important role in deposition than what was expected by creating turbulent phenomena near the ground and around walls.

Similar phenomena have also been reported at this scale. Hoffman *et al.* (1998) observed decreasing particulate deposition on renderings on parts of a wall screened by vegetation. The climatic data collected at a certain distance from the monuments and at a significant height from the ground, offered information for the general wind direction neglecting disturbances caused by geomorphologic or built features. Ideally the wind speed and direction should have been measured by oriented hot wire anemometers positioned at the sampling spot. In the absence of this data we can only depict some features that might have caused this disturbance, namely the high walls blocking the south sampler from east and west and the deep slope of the water reservoir found in front of it. Although the samplers could have been positioned more ideally, it was essential for the purpose of this research to measure atmospheric deposition in the same area where the wall paintings samples have been extracted, in order to correlate it to their salt content and composition.

The EF values for this period also return to the March trends. Specifically there is clearly excess sulphate corresponding probably to anthropogenic sources while chloride is slightly depleted. This find reinforces the role of relative humidity in deposition. The presence of excess sulphur is most probably related to the enhanced deposition of sulphur dioxide gases due to increased relative humidity and possibly condensation on the surface of the porous mortar samplers.

The fourth sampling period 23 May – 6 June 2003 was marked by the presence of two very aggressive north wind events that reached storm gale conditions with more than 15 m/s in speed (charts IIIC.11-12). The average wind speed is the highest of all the sampling periods and the deposition is accordingly high (chart IV.7-8). Despite the presence of a clear and persistent south wind event between 23-26 May the deposition on the south sampler reaches approximately the ¼ of the north sampler concentration. This can be adequately explained by the low intensity of the south wind event. Moreover apart from the two very intense but short events the wind stayed north for the rest of the period. The composition of the aerosol corresponds again to sea spray. Chloride is not depleted while the sulphate EF values do not indicate any other origin apart from marine aerosols for the exposed samplers. Excess sulphate has been found only in the sheltered area MD that has already been associated with redistribution of gypsum. Although temperature is still lower than August relative humidity has reached the low values of summer, corresponding to the assumption that sulphur dioxide deposition is diminished during the "drier" months.

Supplementary sampling

In order to evaluate the sites of sampling in terms of distance from the coastline and its influence on the deposition rate a supplementary set of samplers has been installed at two different locations of the island. The small dimensions of Delos did not permit a more elaborate set up so the areas of sampling represent two extreme cases and the results are only indicative. The value of these samples is more likely a reference that can be used in terms of control rather than correlation.

Unfortunately some of the samples were lost because these areas are untended. The results from the remaining samples can be found in table IV.5. The samples named EXP were positioned at the port of Delos (fig I.5), only 3 meters from the breakwater and at a height of approximately 3 meters from the ground, oriented towards north. EXK samples have been installed at the "Andron", near the top of Kynthos hill, positioned on the ground at the edge of the slope and oriented north as well.

Not surprisingly the deposition on the EXP samplers was immensely higher than that of HD although its distance from the port is only 300 meters. This exponential relation as described in Gustafson and Franzen (2000) can be explained by the fact that the samplers on the port were inside the range of spume drops as well. The difference does not correspond to particle numbers but mass since droplets directly detached from the sea by wind or wave break are much larger than the typical marine aerosol (see chapter 3.3). As it was testified by microscopic observations EXP samplers carried round crystal clusters of around 0.5 mm in diameter, which were not present on the HD samplers. We can assume that the preservation of monuments found within proximity of spume drops cannot be safely correlated to climatic data since the influence of direct spraying is far more important. On the other hand the position on the monuments investigated in the present project is more representative of the average conditions ensuring a generalisation potential. It is also interesting to notice that the EF values for EXP indicate a clear marine origin of the aerosols. It is quite clear that the immense mass of spume drops would obscure any other source if present. It would also be very tempting to relate the clear difference between types I and II concentrations - which was not evident in the other sampling locations - to hydraulic discontinuity, since the layered sample maintained lower values but the limited number of samples does not permit such assumptions. On the contrary EXK samplers collected almost the same amount of aerosols as HG whereas they lay at a much higher spot from the coast. Although theoretically there exists a clear exponential relation between height from the sea and marine spray deposition, it has not been depicted between HD and EXK. Nevertheless it is evident that the HD position offers a clear unblocked spot, safe for correlation with the climatic data.

Additionally apart from the short 15 days periods, a set of samples have been left on the island for longer intermediate periods. These samples also served as reference since it would not be possible to correlate them to climatic data. The results (Table IV.5) are not exactly proportional to the time of exposure because of variable climatic conditions. Nevertheless they maintain the deposition rates between the different sampling locations. These samples were designed to serve as well for depth distribution investigation through thin sections but unfortunately most of the samples were lost or they were displaced and therefore considered unsuitable.

Rain samples have been collected on several occasions during the sampling campaigns (table IV.6). The results reflect the atmospheric concentrations at the time and can be assessed only qualitatively since the samples have been acquired randomly during the event. As rain washes-off the particulates from the atmosphere their concentration progressively decreases. The EF values for samples from Delos show clearly a marine origin of the dissolved particulates. In one case (July 22) there is excess sulphate as well. The samples collected in Athens at approximately the same period as a reference reveal a totally different composition, enriched particularly in sulphate, potassium and calcium.

The extremely high concentrations of sulphate reflect the urban environment while calcium indicates terrigenous origin. Whether the rain acts as a wash-off or enrichment factor of salts is a matter of the duration and the intensity of the event (Steiger *et al.*, 1997). We can definitely assume a large influence of the properties of the sample. Lime washed mortars will more likely let the rain flow over the surface while porous rough surfaces will capture and absorb it.

Two more water samples, not representative of the atmospheric quality, have been collected from Scardanas stream and House of Hermes atrium well and they are presented here for reference purposes (table IV.6). Surprisingly the stream does not present the usual river water composition. On the contrary the EF values indicate clearly marine origin. This is attributed to the fact that the flow of the stream is controlled by rainfall, which reflects the atmospheric concentrations, and moreover the absence of frequent rain does not permit the dissolution of the bedrock, which characterises the river water composition. The water from the well in HD is also rich in marine species, which probably are transferred there by rainwater. Seawater infiltration is not very likely on the granitic ground of Delos. Ca and Mg are nonetheless enriched indicating dissolution of the bedrock as well as nitrate which probably signifies biological activity.

<u>*Microscopy and qualitative analysis of individual atmospheric particulates*</u>

It has proven very difficult and time consuming to trace deposited particles on the mortar samples partly because sea droplets have been absorbed in the pores and partly because the surface of the samplers was uneven obscuring precise imaging. The few particles that have been identified are primarily composed of Na and Cl and as can be seen in figures IV.1-6, originate from the crystallisation of a droplet spread on the surface. Smaller Na-Cl particles that have also been detected (20μm) maintain a cubic form (fig. IV.7).

The detection of particles on the adhesive films was far easier mainly because of the marked difference in brightness between the particles and the reference surface. In all 33 particles have been documented and analysed with SEM-EDAX. The film that has been placed in the sheltered room HG collected far less particles than those of the exposed areas HD and MA. The distribution of particles especially in site HD was particularly dense (fig. IV.8) The composition of the particles varies a lot. It must be stated that less particles than those observed on the films are expected to deposit on the wall paintings. Since the films are adhesive they also collected larger and insoluble particles, like pollen and sand, irrelevant to this research. The vast majority of the inorganic particles can be safely identified as sea salt. Spot analysis revealed the presence of other salts apart from NaCl that crystallise from the brine in various shapes, mainly composed of Ca-S, Mg-Cl and Mg-S. NaCl usually maintains the cubic form (fig. IV.7-8,21).

The sea salt clusters are frequently accompanied by spherical particles, rich in phosphorus and sulphur, probably of biological origin (fig. IV.9,19-20). In some cases there evidences that these particles preexisted in the sea water droplets (fig. IV.23). Calcareous particles rich in sulphur probably weathering products (gypsum) were identified in both sheltered and exposed samplers (fig. IV.15). Aggregate amorphous particles containing Si and Al were found either single or around the sea salt brines (fig. IV.13). Other terrigenous particles contained mainly Ca and Mg (probably dolomitic).

<u>*Summary*</u>

The first field experiment testified principally to the deposition of suspended particles on mortars through inertial impaction. It is therefore anticipated that this process represents an effective pathway of salt contamination on the wall paintings in Delos. The second most important observation is that this process is dominated by marine aerosols and thus the sea is the primary source of salts deposited by the atmospheric pathway. The composition of the aerosol, reflecting marine concentrations, is mainly comprised of Na and Cl. We therefore expect a strong presence of halite even in the higher parts of the masonry, which cannot be contaminated through ground water capillary rise. On the other hand it was revealed that the excess anthropogenic sulphur that was detected in the atmospheric species on Delos actually deposits on vertical mortar surfaces. Although chloride depletion was found on the aerosol it was not possible to quantify the ratio of deposition between sulphuric gases and sulphate incorporated in the sea spray. Either way we can expect the presence of thenardite and possibly gypsum as a weathering product of the calcareous matrix. The presence of excess sulphur in the aerosol also complicates its thermodynamic behaviour. We assume that the absorption of the spray in the mortars will be fractionated leaving the less soluble salts closer to the surface. Since there were no significant differences between the two types of mortar we can assume that the surface properties of the wall paintings do not represent an important variable for deposition.

Wind speed was the most important variable controlling the deposition of sea spray proportionally. In this respect the shelters provide sufficient buffering by decreasing deposition at a rate between 1/3 and 1/6. The final product of deposition is a resultant of wind duration and speed. The extended time of exposure needed for this experiment did not permit the establishment of an absolute relationship. It was however suspected from average wind speed calculations that there must be a non-linear relationship curving between 5m/s and 10m/s (chart IV.9). We can presume that deposition is insignificant under 5m/s while it increases substantially over 10m/s. Theoretically this curve is not open towards higher values (see chapter 3.3). The wind direction indicators were placed at a distance from the monuments, which proved to be more significant than was expected. Micromorphological features of the built and the natural environment around the samplers caused conflicting results between deposition and aspect. Future research should also include atmospheric concentration measurements, gas collectors, rain exposed samplers and run-off water analysis in order to investigate all the atmospheric input parameters simultaneously.

We must finally state that the presence of the other ions that comprise seawater could not be accurately quantified because of their small concentrations - in relation to the analytical accuracy. It is however quite clear that the wall paintings in Delos are being contaminated by a multi-salt solution with a more complicated thermodynamic behaviour than pure halite. Moreover since the contamination is not the result of a random event but is rather a continuous process, the concentrations of salts in the wall paintings will be constantly changing, complicating their thermodynamic behaviour further.

CHAPTER 8: Stoichiometry

8.1 Methodology

The decay rate of wall paintings, due to the action of salts, can be expressed by the frequency and the intensity of the deliquescence cycles of the salts present. Salt weathering in the coastal environment has been particularly associated with the presence of halite. The investigation of aerosol deposition in Delos showed that the contamination from the atmospheric pathway alone comprises a salt mixture whose hygroscopic behaviour is far more complicated, despite the dominance of halite. It was also evident that, even in this remote marine environment, the aerosol included other species apart from sea salt, of anthropogenic, terrestrial and biogenic origin, as well as weathering products. If, as expected, other sources and pathways of salts are also active in Delos, the salt content of the wall paintings might constitute a multi-salt system with potential for more than one outcome.

As described earlier this project follows a comparative approach considering a number of general variables. In the same context the activation of salt weathering has been investigated in response to the particular stoichiometric composition of the salt mixtures found in each of the four cases corresponding to aspect and exposure. The following methodology describes the type and the amount of data required for the purposes of this investigation.

In order to assess the thermodynamic behaviour of salt mixtures it is necessary to know the concentration of each constituent. Thus in principle the method of investigation must lead to quantitative data. Moreover, the concentration of each ion might change in time due to automigration and enrichment with new salts and consequently one random sampling campaign cannot represent accurately the potential for weathering. Alternatively periodical sampling can serve not only as a richer stoichiometric evaluation but as a control tool for the correlation of the thermodynamic potential to climatic cycles as well. In this respect each sample, replicated under different environmental conditions, apart from its individual value will also represent a particular reference of the system's evolution.

It is apparent that ideally the periodicity of sampling should follow a certain climatic cycle. Although laboratory and in situ experiments reveal that phase transitions may occur within seconds (see ch.2.6) the time limits of traceable quantitative fluctuations caused by liquid state salts capillary transport are not known. Despite the potential of diurnal phase transitions, that will be assessed theoretically, the present investigation addressed the annual climatic cycle by four sampling campaigns corresponding to the winter and summer peaks and the two intermediate periods. Whether the particular year is representative of the average local conditions or a particular day of sampling is representative of the season is not important since the results were derived after correlation with the particular climatic conditions, which have been monitored simultaneously. Accepting that salt weathering is more likely a periodic rather than a random phenomenon the decay rate can be expressed by the average period of phase transitions. Nonetheless, due to material particularities, the annual cycle does not always represent a maximum limit within which damage will occur. Periodical sampling should be directed by visual observations, not necessarily weathering effects that are not always evident, but also indirect effects like salt efflorescence or debris release. In the case of Delos similar observations justified the sufficiency of the annual cycle as a minimum period of traceable changes. On the other hand there is no potency to any reasonable argument supporting the extension of the sampling period or the frequency of sampling campaigns since ethical and time restrictions restrict collection to a very limited number of samples during a limited period. Furthermore this project evaluates the fluctuations of environmental parameters over a period of time, much longer than laboratory experiments have indicated as sufficient for detectable changes.

Salt weathering takes place inside the pores of the material. Superficial salt efflorescence although thermodynamically important as a part of the salt system, can be considered harmless in terms of weathering. Thus superficial efflorescence sampling underrepresents the weathering potential of a structure. Unfortunately non-destructive techniques of salt extraction like the application of poultices do not offer comparative results and lack the desired accuracy due to solubility fractionation. The latter is also enhanced in the case of wall paintings due to hydraulic discontinuity between the layers. The needs of this project directed the extraction of core drills from the wall paintings in order to use the samples′

ent as a comparative measure and ensure the simultaneous extraction of all the species.

The size of the tools usually used for extracting cores however, is not ethically acceptable for wall paintings. Therefore a special drill 1mm in diameter has been used to extract mortar debris instead of undisturbed cores from the renderings. Although this technique presents difficulties in execution, it causes less damage to the wall paintings while being governed by the same principals of core drilling. A limitation of this method derives from the fact that the holes left behind by drilling might act as a new evaporation surface influencing the results of the next campaign. It has been considered that it was favourable to risk the reproducibility of the samples by extending the distance between them as far they seemingly belong to the same area than sacrifice the accuracy of the results.

In order to ensure the spatial representation of the samples two more variables have been introduced, depth and height. It is not thought that the aerosol deposition is significantly influenced by height although deposition velocity is expected to be less at the lower parts of a wall because of the turbulence caused by the ground. However the height is very significant for ground capillary rise because of the well-accepted fractionation of salt species in response to their solubility. At least two samples in height are necessary to describe the average fluctuation of a vertical system.

The research interests of this project do not direct a further representation of the areas of sampling. Statistically acceptable methods like grid-sampling cannot be applied because of Heritage deontology. Besides, statistical significance is not always in agreement with the particularities of the research questions. Unbiased sampling undermines the importance of valuable subjective information. The concept of sampling incorporates by definition a certain degree of argument. In this case it is considered important to test the extent of salt content fluctuation between the lowest and the highest damage zone of the wall painting. The lower zone represents qualitatively a sink of all the species that originate from the ground as well as species that accumulate superficially in higher parts and are transported by diffusion to the lower zone. Quantitatively the lower damage zone signifies the first fractionation step of the less soluble species of the system. The higher damage zone represents the limit of vertical capillary transport and thus the accumulation of the less soluble salts. Nevertheless in coastal areas damage might extent well above the ground moisture height due the deposition of sea spray. The qualitative and quantitative comparison between exposed and sheltered areas where the deposition of aerosols varies significantly will reveal the importance of sampling location. The above arguments derive from the review of similar case studies as presented and justified in a previous chapter (chapter 4).

Sawdy (2001) argues in terms of the spatial representability of samples taken from vertical surfaces that since significant fluctuations can be found horizontally as well, it is preferable to sample according to the observed deterioration phenomena. Although comparison between areas of similar or different weathering patterns can definitely provide vital information this approach is not always applicable since deterioration is not always evident and the weathering mechanism is not necessarily active on already weathered areas. Although it is true that significant variations might be found between adjacent samples it is expected that a sample set taken from an area under different environmental conditions will be representative of the potential of this specific system and thus a sufficient comparative measure between areas of different exposure.

The sampling areas are depicted on figures 1,3,6,9 in appendix II. In room HD the area 1 represents the only evident zone of damage (sand disintegration) extending from the ground to 20cm above (fig 8.1). Area 2 represents the highest zone of preserved renderings at around 180cm where there is no evident damage although it is suspected that the rendering was covered by a thin lime wash layer which is probably entirely lost. This mortar is generally well preserved apart from the lower zone. Area 1 in room HG also represents the lower zone of damage and area 2 lies within a zone of superficial flaking and periodic efflorescence at around 1m from the ground (fig 8.4). Room MA presents the same patterns as the other exposed room HD with a few crates of sand disintegration at the higher part and more intense weathering near the ground. Area 1 represents the lower zone of sand disintegration and area 3 the higher damage zone which lays near the limit of preserved material at approximately 190cm from the ground (fig. 8.3). In room MD three damage zones were clearly distinguished and thus area 1 represented the lower zone of sand disintegration starting a few cm above the ground, area 2 represents a large zone continuous efflorescence and limited sand disintegration and area 3 the highest preservation zone where efflorescence is evident during the warmer period and suffers from superficial flaking (fig. 8.2).

Figure 8.1. Room HG, south wall

Figure 8.2. Room MD, north wall

Figure 8.3. Room MA, north wall

Figure 8.4. Room HG, south wall

Furthermore the drills have been extracted in depth sequence in order to evaluate the depth distribution of the species in relation to time and environmental conditions. The small depth of the investigated material could be considered as a single hydraulic system. Thus it would be expected that the salts would either crystallise externally as efflorescence or internally as subflorescence. Similar studies on masonry stone have shown that significant fluctuations lie beyond this depth (Steiger, 1996). Nevertheless as described by Sawdy (1995; 2001) wall paintings present a significant fractionation of salt concentrations between their layers and thus it essential to sample in depth according to the layers distribution. Although this distribution is not exactly known, in order to represent at least the external lime wash layer the first two samples have been extracted from a depth of 1mm and the rest of the samples every 3mm. The limitation of this method is that the samples were not as undisturbed as they would be with the use of core drilling tools. Special attention has been given during sampling in order to ensure that only the material attached in the drivers of the drill was sampled while both the drill and the sampling area were carefully cleaned of debris before each sample.

Although some of the sampling areas represent damage zones it was considered that samples taken from damage lacunae might not carry the evidence of the mechanism that caused them. Accepting that damage expands spatially under the same mechanism it was decided to sample from the edge of the lacunae in order to represent the material in its entirety. Thus sampling always included all the investigated layers of the rendering in all areas, damaged or not. Although it was essential to sample from the external layer of the painting the areas that bear pigments were excluded for ethical reasons.

The samples were analysed by aqueous analysis after extraction of the dissolved species by deionised water. The analytical methods that have been used are Ion Chromatography for the anions and Inductive Coupled Plasma-Atomic Emission Spectroscopy for the cations (specifications in app.X.A). The salt content was expressed as %weight of salt per unit weight of the sample (mortar) in order to represent a comparative measure. The ionic concentrations provided by these analytical techniques do not supply crystallographic information. In order to verify the identification of salts that derived from the thermodynamic assessment supplementary samples were analysed qualitatively by SEM-EDAX. The amount of sample needed for crystallographic identification (XRD) and the fragile state of the material did not permit sampling for this purpose.

Fluctuations in the ionic composition over depth and height indicated the mobility of the system. The correlation to the ambient conditions showed whether the distributions follow the thermodynamic predictions for the present species or if they are purely coincidental. The complexity of the simultaneous salt enrichment by various pathways limits considerably the potential of this stoichiometric approach. The evaluation of the salt input that preceded was therefore necessary to control the correlations between the areas of sampling.

The following presentation of the results is accompanied by a preliminary discussion based solely on stoichiometric data. The height and depth distributions of the % ionic and total salt concentration have been correlated against aspect and degree of exposure. The evolution of these values in time is discussed in correlation to the fluctuation of the environmental conditions. The purpose of this discussion is to evaluate the amount and the quality of information that can be gained in the absence of thermodynamic calculations. The methodology of the thermodynamic analysis, the results and the discussion on the optimal conditions for preservation will follow in a later chapter.

8.2 Results and discussion

The core drills have been extracted from the wall paintings according to the initial sampling programme, following the major variables of sheltering and aspect as described in the general methodology. The exact areas of sampling are marked on drawings in appendix II. The walls of the unsheltered rooms HD and MA are facing the corresponding wind orientation while the sheltered walls of rooms HG and MD are irrelevant to this variable. The monuments that have been selected were not under any conservation project during the hole period of sampling. Rooms HD, HG and MA were open to visitors while access to room MD was restricted only to personnel.

Unavoidable technical and bureaucratic obstacles forced minor changes both in terms of time and location. After the first two sampling sets (11/2001 and 3/2002) the sampling area on the east wall in room HG was replaced by the south wall. The reason was that the upper part of the wall adjacent to the ceiling was badly damaged permitting rainwater to run-off on to the wall paintings and thus it was not considered representative of sheltered conditions. Likewise it was decided after the analysis of the first sampling set that a third intermediate sample in height would represent better the height distribution. The renewal of the sampling license that was necessary caused some minor delay. Additionally the winter period sampling was postponed until January 2003 because it was impossible to reach the island, due to bad weather, during the scheduled visit on January 2002. Also a technical problem that occurred during the sampling campaign of March did not permit samples colection from room MD. In order to obtain more representative and balanced set of samples the sampling periods were increased to five. The supplementary period of sampling occured in May 2003. Finally the large number of samples required by this project did not permit the colletion of replicates.

The samples were always extracted around noon when the highest temperature and the lowest relative humidity were observed in order to avoid condensation effects. The depth of the drills remained generally constant around 1-1.5cm although in some cases fewer samples could be extracted from a drill because of technical problems. The samples were extracted manually without the help of a mechanical rotor, which might have caused damage to the very brittle mortars, thus the drill frequently stuck to large aggregates that could not be penetrated. This problem was minimised by using an extra flexible but hard enough drill that bent around the obstacles (specifications app.X.B).

Figure 8.5. Sampling with drill

The drill had very deep corrugations, relative to its diameter, to encapsulate the drilled material without just pushing it aside. Since it was not possible to use a core drill because of its large diameter (2.5cm the smallest available in the market) the exact sequence of the samples in depth could not be thoroughly ensured. Extra care was taken in order to clear the drilled hole of debris before proceeding to the next depth and additionally to sample only the material captured inside the drill corrugations. Although we cannot assure that the sequence of the extracted samples is representative of the layers of the wall painting extra care was taken in order to assure the distinction of at least the first two layers or alternatively the interface between the lime wash and the underlying porous layer. Additionally in order to avoid contamination the samples were stored in an air tight sealed sampling tube immediately after extraction. The process has been tested and practiced in the lab on much harder mortar samples and despite the difficulties that usually occur in the field the sampling campaigns were completed without any particular inconvenience or limitation. Table 8.1 depicts the number of samples extracted from each area at each sampling campaign.

Room	HG			HD			MD			MA		
Height	I	II	III	I	II	III	I	II	III	I	II	III
Nov ‘01	2	n.a.	5	5	n.a.	6	4	3	4	n.a.	n.a.	3
Mar ‘02	3	n.a.	4	3	n.a.	4	n.a.	n.a.	n.a.	n.a.	n.a.	4
Aug ‘02	3	5	5	3	5	5	5	5	5	5	5	5
Jan ‘03	3	4	4	4	4	4	3	2	3	3	3	3
May ‘03	4	5	4	3	3	4	4	5	5	4	5	5

Table 8.1 Number of samples extracted from each location

The mortar samples have been weighted and diluted in 20ml of distilled water for the first three campaigns and in 10ml for the rest. The water extract was then analysed by IC and ICP-AES at the laboratories of the Geology Department, Royal Holloway College, University of London. The results (raw in app. V.A), representing the ionic concentration of the water extract in ppm (weight) were calculated in order to obtain the percent weight concentration of each ion in the initial mortar sample. The total salt content of each sample was calculated as the sum of the major ionic species percent concentration to the sum of the weights consisting each drill while the drill's percent content of each ion was recalculated as the sum ionic concentration to the sum of all the samples weights of all the drill's set. The depth distribution of total salt content was simply calculated as the sum of the major ions percent concentrations and the depth distribution of each ion represents the percent concentration to the samples weight.

The analytical percent concentrations tables can be found in app. V.B and they are summarised in charts (app. V.D).The concentratins of the fist three campaigns as presented in the tables have been recalculated as 10ml dissolution for correlation purposes. It must be mentioned that the results as presented in the charts offer limited information and cannot be studied independently. A combination of the three charts describing the total salt content per height, the concentration of each ion per drill, and the total distribution of salt per depth is considered adequate enough in order to read and interpret the results.

The highest average concentrations were undoubtedly observed in room MD. This does not correspond to the findings of the aerosol investigation according to which this room received the lowest amount of sea spray. This simple fact alone is adequate to verify the existence of an alternative source or at least pathway of contamination. Indeed the average concentrations of each species affirm the dominance of gypsum throughout the year and only a periodic appearance of halite during the warmer months which is not necessarily related to direct sea spray. On the contrary sea spray deposition during August was the lowest of the four sampling campaigns. It is not quite clear whether gypsum is a by-product of the cementious materials that have been used in past conservation treatments but from a first approach it seems very likely.

The height distribution of the total salt content in MD reveals an interesting periodic trend (charts V.1,22,43,46). While the average concentration stays relatively constant the absolute salt content decreases with height during the warmer months and it increases during the colder months. This periodicity was also evident through visual observations. The superficial salt efflorescence was visible in the upper parts of the wall only during the summer and in the lower parts during the winter while thick crusts covered the mid section throughout the year. This unusual behaviour can not be interpreted by the simplistic point, frequently quoted in the literature that efflorescence is visible during low relative humidity and disappears when relative humidity increases. A view of the absolute concentrations of each species reveals a strong fractionation with height, which clarifies this trend.

Stoichiometrically, the samples collected during November 2002 show that Ca and SO_4 concentration decreases with height while Na and Cl remains constant but in significantly lower concentration (chart V.2). During August 2002 the concentration of sulphate decreases considerably in the lower part of the wall and it remains constant at the upper section (chart V.23). At the same time the concentration of Na and Cl increases in the upper part. In January 2003 the height distribution returns to the November trend while in May 2003 the trend of August is already present (charts V.44,47). The depth distributions do not correspond to the above periodicity but it must be stated that the environmental conditions of November and May do not correspond to those of January and August (charts V.3,24,45,48). More likely they comprise an outrider of the peak conditions.

Additionally the depth distribution represents the superficial part of the wall since it was not possible to sample from the deeper sections of the masonry. We must keep in mind that the salts could move under the suitable conditions in deeper parts, which will not necessarily follow the observed pattern. This is also true for the concentration of each ion since salts might fractionate in depth as well.

In this sense we can assume that during the lowest peak of relative humidity halite is drawn to the surface of the upper part where it crystallises as efflorescence while in the presence of higher relative humidity it dissolves and moves to deeper parts. The very low concentrations of halite in the mid and low section might be related to the presence of ground capillary moisture. As mentioned earlier the central floor mosaics section of room MD has undergone a major restoration work including the isolation of the mosaic from the concrete support by nylon sheets spreading to 20cm from the edge of the wall. This treatment does not permit ground moisture to rise to the surface. Alternatively moisture is driven towards the walls where it is allowed to rise through the foundations, which are not isolated as well. It is very obvious that the suppressed moisture that should evaporate from the floor increases the availability of water supply at the edges of the room, near the walls. It is visibly evident that the edges around the room are constantly damp. It is possible that rising moisture distributes halite in the lower section deeper inside the wall. This can be supported by the homogenous distribution trend of halite in the lower and mid parts. We can suppose that the lower zone represents a solution tank, which supplies the upper parts with chlorides. The moisture supply though fluctuates during the year as a result of temperature and rain events. The morphology of halite crystals on the upper edge of the rendering supports this point. SEM revealed that the crystals have whisker shape usually a result of low water supply (fig. VI.2,3,4). Contrarily halite found on the dense crusts covering the lower parts maintains its cubic shape (fig. VI.1).

Although it is not possible to quantify the contribution of each pathway for chlorides it is very likely that the excess sulphate found on MD originates from ground capillary rise. The concentration is so high that we cannot relate it to sea spray depleted or not. Supplementary samples taken from the concrete mortars used for the mosaic conservation on the floor around the walls support this point (MDmos, MDgr/ app.V.B). The height distribution of gypsum during the cold period shows a clear influence of capillary rise.

We would expect that during the warm period the withdrawing moisture level leaves gypsum behind to crystallise. The constancy of gypsum concentration in the mid sections can be interpreted as insufficient ground water supply for gypsum dissolution. The much higher concentration observed in the lower part during winter disappears almost completely during summer. In this case we can assume that ground water supplies dissolved gypsum in the mid section during high capillary rise and withdraws it from the lower parts during summer. This can sufficiently explain the absence of crusts in the lower parts but not the intense weathering that is probably related to the dissolution and recrystallisation of gypsum, unless the salt is withdrawn along with the debris.

This trend where the less soluble salts crystallise in the lower part of the wall and the more soluble ones crystallise in the upper parts has been frequently observed and signifies that salt input prevails through capillary rise. This observation corresponds to the site variable (indoor environment) of this site since salt aerosols do not reach it as easily. Nonetheless this trend cannot sufficiently explain the high concentrations of chloride and sodium on the upper section of the wall. Supposing that ground moisture can reach the upper parts supplying halite while leaving gypsum behind in the lower sections underestimates the interaction between the salts. Should not halite, if present deeper in the lower sections, influence the phase transitions of gypsum? Accepting that halite undergoes phase transitions in the upper part as a result of fluctuating humidity we should also accept that it interacts with gypsum in the lower parts. On the other hand although the deposition of sea spray is very low in this room some halite has been found in the superficial gypsum crusts also supported by microscopic investigation (fig. VI.5,13). Even if salt supply from the ground fractionates the deposition of species in a manner that they do not interact should not sea spray influence the constancy of gypsum in the mid section? In order to obtain a clearer view thermodynamic calculations linked to the environmental conditions are definitely needed. Furthermore apart from halite and gypsum that dominate in this case, other species have also been identified by SEM, containing Mg-Cl, Mg-S (fig. VI.9,11) Ca-Cl and K-Mg-Cl (fig. VI.7). Although quantitatively insignificant, these species, probably corresponding to very soluble salts, might interact with the major salts altering their thermodynamic properties.

Surprisingly the concentration of salts in MA was much lower than that of MD throughout the year (charts V.10,19,25,40,49). One would expect that since outdoors, MA should be more susceptible to sea spray. Nevertheless as was identified in the previous chapter, probably due to micromorphological features of the building and the surrounding environment, sea spray does not reach this room even during intense south winds. In this sense the results from the drills correspond to the aerosols deposition investigation. Chlorides dominate as expected in most of the samples (charts V.11,20,26,41,50). The small fluctuations might depend on atmospheric deposition and detachment. Sulphates are also present probably in the form of gypsum reaching their highest concentration during January as in MD. The appearance of gypsum in the colder months is most probably related to the presence of moisture. This relation can be interpreted both as gypsum migration from other parts rich in sulphates such as the anastylosis concrete and the conservation mortars or as generation of gypsum from the authentic material due to sulphuric acid chemical dissolution. Both mechanisms result to intense weathering although according to the climatic data none should be activated in Delos exposed areas. We can however associate the presence of moisture to ground water capillary rise and sea spray.

The absence of salts from the lower parts during August might signify some influence of ground capillary moisture as well. In the first case a vertical fractionation of the species would serve as a strong indication but it cannot be depicted in MA as clearly as in MD. On the other hand the influence of sea spray, as described by the deposition investigation, is not very strong but the homogenous vertical distribution of the salts favours this option. Another fact that reduces the potential of ground contamination is the absence of sulphates from the floor of MA (sample MAgr, app.V.B).

The most tempting interpretation is undoubtedly the interaction between the species. The presence of hygroscopic salts has been held responsible for the increase of phase transitions of gypsum and other less soluble salts but could it also generate the appropriate conditions for chemical dissolution of calcium carbonate? As in MD thermodynamic investigation is again needed in order to read the results. The stoichiometric approach alone seems to create more questions than answers.

In general although the total salt content is much less than in MD there are clear signs of weathering, mainly superficial, on the wall paintings. The mixture of salts in MA is more complicated than in MD with all species relatively present and maybe that is where the causes of weathering should be traced in this case. Depth distribution is homogenous during the colder months while as the temperature increases the salts are withdrawn towards the surface. Despite this there were no visible salt crusts on the wall paintings surface at any time of the year. SEM investigation on superficial samples though revealed sea spray deposits (fig VI.25-27).

Room HG has seemingly undergone the most serious weathering of the investigated areas. The lower and upper zone of weathering, adjacent correspondingly to the floor and the ceiling, has suffered significant to complete material loss while the median zone presents lime wash exfoliation. Large parts of the wall paintings are covered by algae and thick salt crusts, identified in SEM as Na-Cl columnar crystals (fig. 27,29) and Ca-S in various forms (fig.VI.17-24).

The samples extracted initially from the east wall reveal the presence of sodium chloride and calcium sulphate as well as some nitrate (Charts V.8,17). Sulphates dominate in the lower part of the wall and chlorides at the upper one. Both drills depth distribution shows significantly higher concentrations in the external samples (Charts V.9,18) . However it is obvious that the concentration of sodium does not correspond exactly to chloride. During the same sampling campaign powdery sodium sulphate efflorescence has been detected on the floor near the wall. SEM revealed two crystalline forms of Na-S containing species, an aggregate like that was found on the floor in large amounts and a whisker like found scarcely on the upper part (fig. VI.31).

The fractionated height distribution implies the contribution of ground moisture capillary rise. There is certainly some sea spray contribution as the deposition investigation revealed. Gypsum probably originates from the cementitious mortars used for the conservation of the floor mosaics. The origin of sodium sulphate is not quite clear. As a first indication the complexity of the mixture in relation to the wide range of relative humidity daily deviation seems to be responsible of the intense weathering. The thermodynamic investigation will probably reveal more details of both the origin of sodium sulphate as well as for the conditions of weathering.

During the second campaign the concentrations in both areas decreased exceedingly. Before attempting any other explanation we must acknowledge the influence of a serious limitation that was testified during the campaign. Rainwater was freely entering from the ceiling right above the sampling areas running off on the walls. This detail that has not been detected from the start represents a serious limitation for the sampling methodology and forced the modification of the sampling areas for the future campaigns since the variable of sheltering was not thoroughly satisfied. It is suspected that the run off water dissolved and washed away the external salt efflorescence. The depth distribution reveals that the deeper concentrations have not changed significantly.

The east wall sampling areas were replaced by a new set on the north wall during the August campaign. The new licence permitted another drill in height. Since the particular wall was preserved to its authentic height the extra sample was taken from a higher area representing the intense weathering of the renderings near the concrete ceiling. The height distribution presents higher salt content in both the upper and the lower part (Chart V.31-33). The composition of these areas is dominated by calcium, corresponding mainly to chloride and secondly to sulphate, while the median zone is completely composed of sodium and chloride corresponding precisely to halite. The depth distribution follows the usual summer fractionation with exceedingly high concentrations within the first two samples. SEM crusts investigation detected whisker like Na-Cl efflorescence in the median zone while a dense Ca-S crust covered the upper and lower areas.

The dramatic alterations of the salt distributions during the January campaign correspond to the rise of relative humidity (Charts V.34,35). The most manifest sign of the dominating presence of moisture is depicted by the depth distribution (Chart V.36). It is obvious that the wide curve of August has been replaced by an even distribution, which can be interpreted as dissolution and transport of salts deeper in the masonry. Although there is an overall significant increase of the total salt content the internal samples have been more influenced than the external. The lowest area corresponds stoichiometrically to calcium and sulphate, which has been found as efflorescence during the last campaign. In the median zone halite has been replaced mainly by calcium and chloride followed by a relative increase of sulphate, sodium and nitrate. The upper part is dominated by calcium and sulphate, in much larger concentration than the lower zone, while chloride and nitrate are also present. It is interesting to observe that the height distribution of sulphate is inversely proportional to that of MD during the same campaign. Since both rooms represent indoor conditions where aerosol deposition constitutes a minor contamination pathway, we can assume that while in MD sulphates originate primarily from the floor conservation cements in HG they originate from the concrete ceiling as well. The difference between these rooms is that the shelter in HG is adjacent to the authentic masonry while in MD the shelter lies on the restored masonry several meters higher than the authentic wall. In both cases the goal of anastylosis was to restore the authentic height of the masonry but in one case it is favourable for preservation while on the other it is not. It is quite interesting to argue whether the authenticity could be sacrificed with an extra set of building stones separating the wall paintings from the concrete slab in favour of preservation.

In May the concentrations in all three areas return to the low values of the August campaign (Charts V.55-57). The composition retains the average characteristics with more sulphates in the upper area and more chlorides in the median. The climatic variables, in a purely statistical interpretation, correspond to this fluctuation (charts III.1-4). Nevertheless while in room MD a sensible explanation was at hand in this case the interpretation of the concentration fluxes is more challenging. Since the height distribution of the total salt content presented a downward scale it is quite tempting to relate salt migration to infiltration of rainwater. The concrete slab that shelters room HG is poorly preserved and it was evident in the case of the east wall that rain does flow freely inside the room. A similar case might occur for the south wall only not so evident and much slower. As for the composition of the contamination since rain was primarily composed of sea salt we can assume that the rainwater dissolves and transports sulphates from the concrete slate. In the same context the chlorides found on the median zone might also originate from the same path under an opposite thermodynamic fragmentation than that occurring from ground capillary rise. This assumption does not of course exclude the possibility of supplementary contamination from the ground.

The decrease of the concentrations during the warmer and drier months might be interpreted as withdrawal of the salts towards the surface and crystallisations as efflorescence, which was not sampled. This assumption is supported by the depth distribution which, as in MD, curves towards the exterior samples.

Another interesting observation is the presence of excess calcium. The origin of dissolved calcium might be ground water. Its presence was testified by analysis of the well water, which is found only a few meters from room HG. In the absence of data for HCO_3^- it is very difficult to trace the cycle of calcium. We can only assume that calcium originates, apart from ground water, from seawater, conservation mortars, a well as weathering products of authentic calcareous materials. Especially the latter could be easily identified in the absence of other external sources for calcium.

The potentiality of dissolved calcium is rather intriguing. We have seen that calcium coexist with either chlorides, sulphates, nitrates or mixtures of them, corresponding to salts of variable behaviour from the extremely soluble $CaCl_2$ to the barely soluble gypsum. It would be also interesting to investigate whether thermodynamically the presence of excess calcium can be related to the withdrawal of sodium as Na_2SO_4 efflorescence, which was detected in large amounts during the first campaign.

The aqueous analysis corresponds to the qualitative results of SEM that separates different efflorescence zones. The correlation of this zonation to according weathered areas is however too convenient to explain the periodicity of weathering especially in the presence of other salt species that might influence the transition process. It is evident that the situation is much more complicated than in MD. The interpretation is again problematic in the absence of thermodynamic data. Nevertheless there is an evident similarity between rooms MD and HG that distinguish the indoor environment from the exposed areas. Due to the absence of direct solar radiation and wind, which enhance evaporation in the exposed areas, relative humidity reaches and maintains higher values. Thus ground moisture is permitted to rise higher in the masonry and transport the more soluble species. Additionally it permits the mixture of species that originate from the ground with species that deposit from the atmosphere. On the other hand, beyond the evaporation zone, deliquescence conditions are reached more easily and more frequently even for the less soluble salts like gypsum.

The sampling area in room HD received the highest deposition of aerosols. However the average salt content of the wall paintings was lower than that of the sheltered rooms. The average composition of the drills signifies a predominant marine origin of the salts although sulphates and nitrates were not absent. The first sampling campaign of November 2001 reveals non-fractionated height distribution with higher concentrations in the upper part indicating the atmospheric pathway as the primary salt enrichment (Charts V.4-6). The even depth distribution in the lower zone could be interpreted as a supplementary influence of ground moisture. At the next sampling campaign after the rainy season the chlorides are slightly reduced retaining the height distribution of the previous campaign (Charts V.13-15). The concentration of Ca in significantly increased without any corresponding concentration of sulphates. We already traced the origin of the excess Ca in ground water and its transport to the masonry through capillary rise induced by the elevation of the water table due to rainfall. In this case Ca probably corresponds to HCO_3 and recrystallises as $CaCO_3$. In contrast with the sheltered rooms that have undergone conservation treatments the ground capillary moisture does not contain sulphates as well. The finds of the next campaigns as well as the samples from the floor that will be presented separately support this assumption.

During August the total salt content is significantly decreased probably due to superficial crystallisation (Charts V.28-30). Excess Ca is still dominant in the upper part. The next campaign of January, after a long period of heavy rainfall, reveals that even if the concentrations of the other species are slightly increased, remaining in very low values in relation to the sheltered rooms, the concentration of Ca has significantly increased in all zones (Charts V.37-39). Sulphates are slightly increased in the lower zone, chlorides in the median and nitrate in the upper one. We can assume that driving rain washed-off the superficial deposits while simultaneously enhanced capillary rise. The elevation of the water table reached in January the surface, flooding room HD.

In May while excess Ca is still present in much lower concentration than January sodium, and chloride dominate in the median zone indicating sea spray deposition (Charts V.55-

57). The depth distribution of chloride is also concentrated in the external samples. It is evident that rainfall constitutes a determining factor for the preservation of the unsheltered wall paintings in Delos. Room HG although exposed to the main wind direction is better preserved than the sheltered rooms. There are two variables that preliminarily might be responsible for this, the lower salt content and the smaller relative humidity fluctuation. Although this room suffers the highest sea spray deposition we can assume that the direct solar radiation forces the salts to crystallise on the surface without penetrating the mortars where they are later washed off by rain. On the other hand the absence of sulphate sources restricts the production of gypsum that was abundant in the sheltered areas. Nevertheless if the mortars were covered by lime wash as well, we must speculate a very fast loss of this layer during the first years of exposure.

Although the daily deviation of relative humidity is very small and shifted towards lower values we cannot estimate the behaviour of the mixtures found on the wall paintings of HG without thermodynamic calculations. The role of excess calcium that has been found in the other rooms as well, primarily during the colder periods, must be given specific attention. The stoichiometric correspondence of Ca to Cl in relation to the precipitation of Na_2SO4 that has been depicted previously raises a serious query for the expected thermodynamic behaviour of the Na-Cl-Ca-SO_4 mixture.

Before closing the description of the stoichiometric results we must depict a phenomenon that was deliberately not mentioned earlier in order to access it en bloc. During the last sampling campaign of May 2003 exceedingly large concentrations of nitrate appeared in rooms HG, MD and MA while it was totally absent from HD. Initially there are no obvious connections between these rooms that can distinguish them from room HD. Room MA is exposed contrary to HG and MD. The simultaneous as well as the previous aerosols sampling campaigns did not indicate the presence of airborne nitrate and thus we should exclude the atmospheric pathway. Nitrate is usually related to biological products. If the presence of nitrate in ground water is linked to a biological cycle it should have been traced in the earlier campaigns as well. More likely it originates from a random phenomenon. During the previous campaign of January it has been observed that the sheep that move freely on the island had found shelter from the intense rainfall in room HG. It was testified by the large amount of excrement that the sheep stayed for a long time in room HG. Although some nitrate has also been detected in January we can assume that its dissolution from the organic deposits and its transport to the masonry through capillary rise was enhanced by the elevation of water table and it was thus delayed to reach the exceeding concentrations that were traced in May.

Although room MD is locked by bars and thus the sheep could not find shelter there other adjacent rooms are accessible. As for the area MA, which is not sheltered, we can state that the wall under investigation although exposed represents the external side of a sheltered room. Room HD on the other hand is not adjacent to any sheltered area. The potential of contamination during handling is rather unlikely due to the normality of the results. Although this is a highly assuming explanation it signifies the importance of random events that cannot be predicted. *In situ* sampling brings with it the risk of misrepresenting the investigated population and although salt weathering is more likely allegiant to a periodicity it is evident that open systems are more unpredictable than we assume. Wherever might the nitrates originate from there can be no doubt that they were present in this campaign. The extent of the influence of this random salt enrichment is not simply stoichiometric. Statistically the occurrence of nitrate could be considered "accidental" and of minor significance against the constancy of the other ions. Nonetheless, nitrate seems to correspond to $CaNO_3$, a very soluble salt that in relation to the rest of the species that were found on the wall paintings might result in a totally different thermodynamic result than what was justified by the previous campaigns. In the next chapter the significance of this random find will be investigated in terms of weathering potential through thermodynamic calculations.

So far the fluctuation of the ionic concentrations has been interpreted in terms of salts mobility. It was thus possible to identify sources and pathways of contamination and estimate the contribution of each. By relating the climatic data to the variables of exposure, aspect, height and depth a rough model of salt transition cycles and transport has been attempted. Trying to exploit the most of a strictly stoichiometric data set it becomes inevitably challenging to attempt as well a correlation of the analytical results to weathering. We argued previously for the multiple potential of weathering as the continuous salt input, the automigration and the thermodynamic fractionation as well as the pore properties of the material, like hydraulic discontinuity in the case of wall paintings, which change constantly the stoichiometric balance of the content. It has been decided that instead of abstracting the data in order to focus on a single potential it would be preferable to exploit the diversities produced by the complexity of the data to compose a more realistic model. Although the same argument stands for the mechanism of weathering it is not quite clear so far whether the type and the amount of the data that has been collected are adequate to interpret salt concentrations in terms of weathering effects.

Following the comparative approach that directed the sampling strategy we can initially assess the weathering patterns of the wall paintings that have been sampled. A first indication of different weathering mechanisms is the strong localisation of two distinct patterns. Flaking of the superficial wall painting layer (white wash) is observed only in the sheltered areas. In MD this pattern is located at the upper part of the rendering while in HG at the median zone (approximately at the same height as in MD). Both zones are mainly associated with NaCl, which specifically in these two cases has been found in the form of whiskers during the August campaign. We can assume that low moisture supply forces the halite crystals to grow perpendicularly to the wall painting surface causing this flaking appearance of the external layer. Although other species have been found deeper in the mortar NaCl prevail in the externals samples and efflorescence. The final damage is probably a resultant of several factors including pore properties, moisture supply and crystal morphology but we cannot disregard the distinctively dominant presence of halite.

Sand disintegration on the other hand, corresponding to loss of pulverised material, is observed both indoors and outdoors. This pattern extends from shallow areas of a few millimetres to large areas of several square meters that expand to total loss of the rendering exposing the masonry. Although it appears in several zones it distinctly affects the lower zone of the wall from the floor to 10-20cm above. In some cases it has also been observed that sand disintegration affects only the internal layers of the rendering leaving the external ones intact. The lower zones of all rooms as well as another distinct zone of disintegration in the upper part of room HG are mainly associated to Ca-SO_4. Gypsum is sparingly soluble and thus it is very unlikely to undergo hygroscopic deliquescence. We can assume that the lower damage zone represents the limit of gypsum rise through ground moisture. Fluctuating ground moisture supply might also trigger gypsum cycles in the lower zones. In this case we must accept that the decay rate follows a long annual periodicity. The same pattern is also encountered in the case of sulphur dioxide attack but in this case gypsum is the product rather than the cause of damage. However sand disintegration due to sulphation of the original material is associated to rain wash-off and thus it cannot be encountered indoors. Nevertheless we cannot exclude the possibility of progressive mechanical weakening of the material.

Another weathering pattern, not always evident, is the lateral detachment between the layers of the rendering or between the rendering and the masonry. Although similar scaling patterns are encountered on many porous materials this particular damage is probably distinctive of layered materials and has been attributed to preferential crystallisation at the interface of the layers due to hydraulic discontinuity. The documentation of 1995 identified very extensive areas that had been detached from the masonry. Although the method of this investigation is not known we can attribute certain validity to this report. Large pieces of rendering have been witnessed on the site standing in a pretty good state of preservation completely detached from the masonry. Nevertheless in the sheltered areas the damage mechanism can be more accurately described as sand disintegration of the underlying layer while for the exposed areas the term detachment fits rather the description of the pattern. The depth distribution of salts did not offer any particular insight of fractionation between the layers apart from the usual larger concentrations of the first two samples that represented the white wash layer. There is not any evident association of this pattern to the stoichiometric data. We could however distinguish the area HD where although the mortar stands in a surprisingly good state of preservation, a large gap between the rendering and the masonry has been witnessed during drilling. Contrary to the sheltered areas the underlying layers were not pulverised and the rendering has been detached in one piece. Although the evidence might have been lost the results of the present project cannot link this pattern to salt weathering. It was true however that the first sampling campaigns, before the intense rain period that affected primarily this area, revealed significantly high concentrations in the deeper samples. We could assume that during the long arid periods that are normally encountered in Delos the superficial deposits supply slowly the material with solution, which fractionates at the interfaces until it reaches a threshold of damage. Probably this process is much slower than the deliquescent cycles that can be achieved frequently indoors due to the built of higher relative humidity and does not follow a certain periodicity.

<u>*Supplementary samples*</u>

A few additional samples were required in order to investigate other potential sources of salts. Sampling focused on the conservation mortars that have been used in the past for the wall paintings peripheral consolidation, the floor mosaics restoration as well as the concrete shelters. The samples were extracted by drill but not in depth sequence. They were analysed by the same technique described for the rendering drills. The results as presented in app.V.B represent the percent concentration of each ion to the total sample weight.

The largest concentrations of salts have been observed in the floor mosaics conservation mortars of the sheltered rooms HG and MD. They were composed mainly of Ca and SO_4 and contained as well Na, Cl and NO_3. Thus ground moisture capillary rise is very likely an additional source of salts and primarily gypsum in these rooms. An additional sample taken from the area that has been isolated in room MD showed significantly lower concentrations. The floor of the exposed rooms HD and MA that have not been treated contained very small concentrations of soluble species, primarily Ca which more likely originates from ground water. In both cases chlorides were higher than sulphates. Specifically room HD floor contained almost no sulphates at all. The low concentrations of sulphates on the wall paintings of this room support the above assumption for the origin of sulphates. An additional sample that has been extracted from HG floor after the removal of the animal excrements revealed an increase in Na, Cl and NO3.

The consolidation mortars of the wall paintings also contained significant concentrations of salts. In the absence of an evident source of moisture however, apart from condensation, which should not be a frequent possibility in Delos, we cannot consider them a very likely source. The mortars of HD contained the lower concentrations, probably due to rain-off. Chlorides were higher than sulphates, possibly as a result of sea spray deposition. Two seemingly different mortars have been sampled from room HG. The grey cementitious mortar contained more sulphates than the white one. The largest concentration, composed mainly by sulphates, has been observed in the mortars of room MA which had been applied more recently (1995).

Two samples have also been extracted from the inner side of the concrete shelters of rooms HG and MD. The MD shelter contained almost no soluble species while HG that has been related to rain-off contamination contained significant concentrations, mainly sulphates and nitrates. The two shelters have been installed in different periods and maybe they are made of different cements. The poor preservation of the HG shelter is indicative of its lower quality. Apart from a possible source of salts this shelter also comprises a source of moisture since rain might penetrate the intensely weathered material.

<u>*Summary*</u>

Summarising the stoichiometric results of aqueous analysis we can draw some preliminary conclusions for salt weathering in Delos. The most striking observation is definitely the abundant presence of sulphates that probably correspond to gypsum. As far as it concerns its origin only assumptions can be made. In the previous chapter the methodology permitted the use of enrichment factors that quantitatively indicated the origin of each ion. But while in the deposition investigation the sample represented an absolute value in the case of the drills the sample comprises a relative measure. Each sample described a particular resultant of depth and height but the sum of the samples cannot be assumed as representative of the whole system. The fractionated automigration and the continuous enrichment in new salts complicate things further. Although the drills represented in depth the whole of the rendering we cannot be certain that both quantitatively and qualitatively the salts system did not extend to the masonry as well. We can argue that the difference in porosity limits the transport of salts towards the building stones but we certainly cannot use each drill as an absolute system. As far as it concerns height the limited number of samples supplies only indications of the salts fractions. Nevertheless there is no doubt that these indications are valid for a preliminary discussion. From a first point of view the large sulphate concentrations do not correspond to sea spray alone. Similarly the deposition of excess atmospheric sulphate either remote or local was insignificant. There must be another source, which should be traced irrespectively of the atmospheric pathway. The height distribution supports the assumption that sulphate is primarily transported from the ground. In this case the most obvious source is the conservation mortars that have been applied to the floor mosaics. Similar cementious mortars have also been applied to a smaller extent on the wall paintings and of course we cannot exclude the concrete slabs. Nevertheless it was evident that the transport of sulphate was strongly linked to the presence of moisture. Thus the most effective pathway is ground capillary rise followed by runoff rainwater and probably to a lesser extent condensation.

The presence of gypsum in the coastal environment is considered a serious weathering factor. The importance lies primarily in the thermodynamic behaviour of its mixture with halite leading to more frequent and intense phase transition cycles. Additionally we should mention that sulphate has been associated to other salts as $MgSO_4$ in MD as well as $NaSO_4$ in HG whose mixtures with halite have not been investigated (fig. VI.37-44). On the other hand the stoichiometric investigation indicated the coexistence of gypsum with other salts even more soluble than halite such as $CaCl_2$, $CaNO_3$ and $MgCl_2$.

The presence of gypsum raises also another very important aspect. We assume so far the sulphate contaminates the wall paintings either in the form of gypsum or other salts. We should however investigate the possibility of gypsum as a weathering product of the authentic material. The chemical dissolution of calcareous materials by H_2SO_4 has been linked to urban and industrialised environments where sulphur is abundant in the form of SO_2 gases. It is not possible to correlate quantitatively the cycles of Ca and SO_4 from the present results but we cannot exclude the possibility of a similar chemical attack from sulphates that originate from remote pollution or even sea salt alone. Strong indications of chemical attack come from SEM imaging that reveal sulphation of the original material (fig. VI.33-35). Although the extent cannot be assessed quantitatively the mechanism will be investigated as well through the weathering simulation that will be presented in Chapter 11.

The most solid conclusion that can be drawn solely from this approach is the variety of the contamination pathways. The deposition of aerosols has been quantified in the previous chapter. The present investigation revealed the presence of other effective pathways. The height distribution proved to be very helpful in identifying ground moisture rise. Furthermore the fractionated distribution of reference elements indicated as well alternative sources. We must mention that Arnold's model of height fractionation underestimates the interaction between the salts, thus we should consider that a certain amount of the less soluble salts that fractionate at lower zone might be transported higher in the masonry. Accordingly due to insufficient supply of moisture in the higher zones the less soluble salts will probably crystallise and build in time significant concentrations. Similarly the less soluble salts might, due to a concentration gradient, diffuse back to lower zones. On the other hand in the case of the coastal environment sea spray supplies irrespectively of height a complicated mixture containing other salts apart from halite. The depth distribution of reference elements also showed that the unsheltered areas present higher concentrations of sea salt on the external areas. Nevertheless in the sheltered areas the higher relative humidity might enhance the deliquescence and absorption of the more soluble constituents of sea water leaving the less soluble ones on the surface. It was not however quite clear whether there was a fractionation in depth as well. The external samples definitely presented the higher concentrations but although the efflorescence were not sampled we can assume that the percent concentration of these samples do not represent exclusively subflorescence. Both height and depth distributions proved to be essential for the correlation of the stoichiometric results to the climatic data.

The comparative approach that was followed in this investigation proved to be essential for the understanding of the concentration fluctuations. The variable of exposure offered the desirable reference to distinguish the damage potential of the sheltered and the exposed areas. It was evident that although deposition is significantly lower in the sheltered areas their salt content was higher. Irrespectively of this variable we could presume the existence of a critical threshold of salt content for damage. This difference along with the variation of the salt composition was distinctive of two different pathways of contamination which might as well be responsible for different weathering mechanisms. Aspect on the other hand does not comprise a determining factor for weathering. Since the honeycomb damage patterns that have been observed on the granite masses in Delos were strongly oriented towards the main wind direction we can assume that a totally different mechanism acts on the wall paintings.

Deposition was higher in HD (north) than in MA (south) and so was the salt content although to a lesser degree. The fluctuation of the salt content in time follows a similar curve in both cases. The slightly better state of preservation of room HD can only be attributed to the different salt composition. HD is primarily influenced by sea spray while in MA the salt mixture is more complicated. Another observation is that the salt content decreases more in HD during the rainy season. Probably aspect might play a role in the case of driving rain. Surfaces on the lee of the main wind direction receive less direct wetting by rain than those windward. In the absence of run-off experiments however it has not been possible to explain under which conditions rain deposits or washes-off salts. On the other hand if room HD has already suffered complete loss of the external layer the aspect criterion is just satisfied but distinctive of a particular pattern as well.

Another interesting observation deriving from the stoichiometric approach is the complexity of the salt mixtures. Even if we accept a limited number of sources and species that contaminate the masonry, automigration and fractionation due to thermodynamic properties and kinetic effects of the support result in ion exchanges and mixing of the contaminants that introduce a multiple potentiality that could not be predicted even if we knew precisely the particulars of contamination. SEM investigation also presented a surprisingly wide variety of salt species either in the form of single crystals and crusts or coexisting in mixed precipitates. The most striking example is chloride which, accepting that it originates exclusively from sea salt, has been found to correspond quantitatively to other ions apart from sodium, like calcium, magnesium and potassium, in several occasions. Nonetheless the origin and the fate of these mixtures can only be assessed thermodynamically.

The quantitative and qualitative deviations of the salt content in time suggested the mobility of the system. During the presentation of the results a preliminary correlation to the climatic conditions has been attempted. The discussion leads to the acceptance of the serious omissions that ensue in the absence of thermodynamic calculations. The stoichiometric approach required crude assumptions on the identity of the salts, their hygroscopic behaviour and the interaction between them while minor species were totally neglected. In some cases sensible models have been attempted while in others even assumptions were not plausible. From another point of view these deviations might as well be coincidental. Periodical sampling might be considered, under a certain convention, as a kind of replicating. As long as this convention can be tested and confirmed the validity of the sample is not at stake. Unconventional sampling replicas exist only in theoretical approaches since in real conditions each sample is unique and cannot be replicated. Even if the periodic samples do not represent the investigated area they hold a certain value in respect to the conditions under which they were extracted.

Sampling from materials that are already weathered raises serious queries that were encountered in the present case as well. The *in situ* stoichiometric investigation of salt weathering has a two-fold aim: explain the observed damage that the material has already suffered and estimate the mechanism that will cause further weathering. One could argue that these two uses of the stoichiometric data are not necessarily in accordance. Can we assume that the mechanism that caused the observed damage is still active? Even if we accept that this mechanism left behind traces in the form of stoichiometric data to what extent are they indicative of potential further damage? On the other hand the damage itself might influence the weathering process. While in other decay mechanisms the weathering product is inactive in salt weathering damage might reduce or accelerate decay. This is even more complicated in the case of layered or inhomogeneous materials. For example sampling from an area that has been detached from the bulk of the material might indicate the mechanism that produced it but does not ensures that the same mechanism will cause further damage to this area or the one underlying. Similarly sampling from a lacuna of sand disintegration or honeycomb weathering, which are both characterised by material loss, might indicate the potential of weathering but does not ensures the evidence of the mechanism that caused them.

Especially in the case of wall paintings the loss of the external white wash layer might activate a different mechanism by exposing the underlying more porous layer. Although seeming patterns offer a reference to weathering it is not quite clear whether sampling from weathered areas is accurate. As mentioned earlier it was decided to sample from the vicinity of the damage assuming that the spatial evolution of salt weathering follows certain normality. Was this assumption accurate? *In situ* stoichiometric investigations for wall paintings are scarce in order to build solid conclusions for sampling strategies. Although the comparative approach and the variables that directed it proved very helpful we must not underestimate the fact that it was highly biased by the specific conditions encountered in Delos. We can definitely accept that sampling must be designed to address specific needs but we should simultaneously be aware of the danger of the self-fulfilling prophecy. The most important convention that was accepted by this project is thus the continuity of weathering. The next chapter will assess the capability of thermodynamic calculations not only to define optimal conditions for preservation but as a tool to explain previous damage as well.

CHAPTER 9: Thermodynamic approach

9.1 Introduction – The application of ECOS programme

The purpose of the stoichiometric approach was limited to correlations between ion concentrations and their response to the investigated variables. Although this approach proved to be useful for several aspects of salt weathering it was evidently not adequate to explain the triggering mechanism of damage or to evaluate the optimal condition for preservation. The iterative sampling methodology supplied valuable information on the periodic character and the multiple potential of salt weathering but the correlation of the stoichiometric data to the climatic fluctuations was very limited and sometimes controversial. In every occasion the need for thermodynamic considerations was evident.

Single salts undergo phase transitions under specific hygrothermal conditions, which are well established for single salts. These conditions though change dramatically when two or more salts interact. The investigation of salt mixtures hygroscopic behaviour requires complicated thermodynamic calculations. Although several models have been attempted in various disciplines only a few authors tried to confront this problem in the context of cultural heritage conservation (Price and Brimblecombe, 1994; Steiger and Zeunert, 1996). The end product of their efforts is a computer-based model (ECOS) that calculates salt crystal volumes for given ionic concentrations and hygrothermal conditions (Price, 2000). This model is based on Pitzer's thermodynamic approach (Pitzer, 1973), which is widely accepted and applied in atmospheric chemistry studies (Clegg and Whitfield, 1991).

As described in chapter 4 conservation literature contains several examples of thermodynamic considerations based on single salts equilibrium conditions. During the last decade there has been a growing appreciation of the importance of salt mixtures hygroscopic behaviour. The equilibrium model of halite and gypsum described by Price and Brimblecombe (1994) is mentioned in almost every publication on salt weathering proving that the thermodynamic approach is becoming more and more essential. Nevertheless there isn't a single publication up to now applying thermodynamic calculations on specific case studies of salt weathering. In situ investigations are limited in crude assumptions of salts interaction, usually based on published theoretical work (Lubelli *et al.*, 2004).

The only extended work on ECOS application is included in the unpublished PhD thesis of Sawdy (2001). This work investigates the dynamics of salt weathering by applying thermodynamic calculations *in situ*. This application sets some standards for the methodological approach of thermodynamics in salt weathering and demonstrates the multiple functions of ECOS by adding presuming amounts of efflorescence salts to the mixture in order to investigate potential interactions. Confronting though the problem of electrochemical balance, instead of risking fictional results it considers only a small and highly biased number of balanced samples limiting the use of ECOS to a single result. A few conservation projects, incorporating ECOS applications, have been published so far in non-refereed media but their results are very limited and lack the critical perspective (Bionda, 2004; Stormeyer and Franz, 2002).

From a very optimistic point of view ECOS signifies a triumph for preventive conservation. Traditional treatments can be easily condemned but up to now the alternatives were plausible within the context and for the purpose of research. ECOS most attractive feature is that it can easily and quickly execute complicated calculations, which were a researcher's privilege, through a user-friendly computer interface. In the same way it offers unlimited application of the data to a wide range of real or hypothetical environmental conditions. The input demands are easily met by anyone who has accessibility to simple chemical analysis and climatic monitoring. The results that it provides, seen from a very simplistic point of view, address directly conservation issues by defining the optimal conditions for preservation. On the other hand ECOS simplicity, giving the conservator the chance to wash his hands of the burden of salt weathering, comprises the most significant limitation or even hazard of its use.

It is obvious that unsophisticated use of ECOS might result in very hazardous conclusions. The danger lies in the application of environmental control which if used improvisationally might not be simply ineffective but might cause further damage by accelerating the weathering rate or trigger a new weathering mechanism. Moreover the external factors that influence salt weathering and consequently the application of environmental control are incorrectly restricted to fluctuations of the ambient temperature and relative humidity. Thus the results of ECOS, although addressing solely temperature and relative humidity, should be accessed under a wider prism of environmental factors such as wind movement, direct solar radiation, air quality and of course salt and moisture sources and contamination pathways.

The limitations of ECOS are clearly described by the developers (Price, 2000). Although it was intended to include in the model every system that can be encountered in practice the end product considers only a limited number of ions: Ca^{++}, Na^{+}, Mg^{++}, K^{+}, Cl^{-}, NO_3^{-}, SO_4^{--}. Practical limitations relate to the sampling and the analytical methodology. Non equilibrium limitations relate to kinetic deviations that derive from the nucleation process, the rate of phase transitions, the degree of disparity between the measured and the ambient climatic conditions, pore structure properties, solubility fractionations and the influence of other parameters like ground moisture and atmospheric deposition. There is no doubt that these limitations might play a determining role in the outcome and make the use of ECOS in decision-making investigations insufficient if not perilous. From a pessimistic point of view these limitations seem overwelming.

Undeniably there is a clear need for thermodynamic approaches to salt weathering and ECOS offers a promising even if compromising approach. Before condemning ECOS as another elaborate tool that wishes too much, we should first investigate its function. In other words learn how to use it. Primarily one should learn how to pose questions to ECOS instead of anticipating fast and easy answers. But although the developers have clearly described the limitations of ECOS they do not elucidate its "judicious" use.

In order to apply thermodynamic considerations for the purpose of this research we had to accept certain conventions described in the methodological approach of the *in situ* investigation. ECOS *in situ* application has been used to investigate the extent that these conventions limit the application of thermodynamic calculations. Thus ECOS resultants in comparison with climatic data have been used to explain previous damage and to investigate whether this damage is ongoing. The results of periodic sampling should therefore follow a reasonable continuity upon which we attempted to construct a weathering model. The purpose was to investigate the ability to produce a reasonable model out of the specific data and under the mentioned limitations and propose a flexible methodology of thermodynamic approaches *in situ*.

The variables that have been described in the previous chapter determine the practical limitations of sampling methodology. We have already challenged the previous simplistic approach to salt weathering in the coastal environment. We have seen that although the investigated site represents a remote marine location the different pathways and sources of contamination resulted in complicated salt mixtures. Likewise other factors like automigration and solubility fractionation deprive the structure of a single thermodynamic potential. The setting of the damage triggering mechanism to the ERH of halite was thus questionable even when halite is the only efflorescence. On the other hand, even when sea spray was evidently the predominant source of salts, we had to question the influence of the minor species. While the discussion of whether halite alone causes damage and more or less than other salts seems completely unessential, under he challenge of salts interactions, the sampling strategy set a solid background for the thermodynamic investigation of the present salt mixtures.

The phenomenological investigation, both in terms of salt efflorescence and weathering patterns, served also as a control of ECOS results while other parameters like ground moisture and atmospheric deposition have been taken into account. The comparative approach certainly offered the liberty to correlate the results in accordance with the variables that we considered significant for this research. Although this investigation has been carried out irrespectively of kinetics we attempted to define the optimal conditions for preservation as well. The outcome will be additionally criticised through the prism of some kinetic considerations in the next chapter.

The present study considers each drill as a system where each salt might exist in either the solid or the liquid state. Thus the input data of ECOS is comprised by the sum of each ion's molar concentrations of all the samples that constituted the whole drill. The resultant of each individual sample might also present an interest in respect to the extent that automigration and solubility fractionation influences the potential of the mixture but the small depth of wall paintings allows us to consider all the samples as components of a unique system. Nevertheless the depth distribution as presented in the previous chapter has been considered in the discussion. On the other hand the interaction of species in height is likely to be influenced from ground moisture, which is independent of deliquescence cycles triggered by atmospheric humidity.

Usually analytical investigations use heavy statistical manipulations of the data like balancing, averaging and excluding extreme values. This project considers that the manipulation of the results leads to omissions that might be statistically acceptable but deprive significant elements from the purpose of this research, which lies in the identification of every potential damage mechanism through the spectrum of salt interactions. Thus the data has not been statistically manipulated before the thermodynamic analysis.

The multiple potential of the ECOS resultants has been discussed in three ways: the ionic composition in response to sources and contamination pathways, the weathering mechanism as reflected by the damage patterns and the weathering rate in response to daily or annual transitions. Potential relations between the variables of sampling have also been investigated in order to trace differences or similarities that respectively distinguish localised particularities or characterise the wider context of the coastal environment.

Before proceeding to the thermodynamic assessment however it was essential to test the electrochemical balance of the data. The weight concentrations have thus been calculated as molar concentrations and the ratio between the sums of the positive and the negative charges has been calculated for all the samples. The results are presented in appendix V.C. As expected due to analytical errors and arithmetic approximations the balance of the molar concentrations was seldom unity. Nonetheless in many cases the ionic imbalance was so extreme that we must assume the existence of other ions that have not been investigated. The electrochemical imbalance is always shifted towards the positive charge. Evidently there is also a relation between the imbalanced samples and the extreme presence of Calcium. This find indicates the hypothesis of HCO_3 infiltration through ground moisture capillary rise.

ECOS programme offers the option of balancing the data input by adding or abstracting ionic quantities. The autobalance feature also offers a helpful option but it should be used very cautiously and only when the imbalance is very small because otherwise the results become highly speculative. It was quite clear that the manipulation of the data should follow a reasonable and justified hypothesis. By abstracting or adding a small percentage of one or more components the desirable electrochemical balance does not alter significantly the quantitative relation of the ions. Nevertheless ECOS demanded a balance of 10^{-17}, in order to perform the calculations, which has been proven extremely difficult and time consuming to achieve. On the other hand when the imbalance was quite severe the data manipulation, by adding or abstracting an amount of the observed efflorescence seldom followed a unique hypothesis. On the contrary in some cases the assumptions were conflicting. Also the assumptions have to follow reasonably the environmental conditions under which the samples have been extracted otherwise the convention of periodic sampling is not justified.

Although we have accepted the multiple potentiality of salt weathering it was essential in order to avoid large estimations to establish a global treatment of the data and justify it in accordance with the climatic data as well. It has been found through trial and error that by abstracting a larger or smaller amount of calcium all the samples balance without any other manipulation. We have thus to accept the hypothesis that Ca^{++} is extracted from the thermodynamic potential of each sample in the form of $Ca(HCO_3)_2$ which is scarcely soluble and presumably precipitates first. Still, even if the samples are balanced ECOS presented a difficulty in calculating the results in the presence of sufficient amounts of Ca^{++} and SO_4^{--}. This could be overcome by extracting all the amount of gypsum leaving an surplus of either sulphate or calcium. We can assume that since gypsum is slightly soluble its presence does not influence significantly the results. Evidently gypsum was the most abundant efflorescence along with halite. On the other hand the presence of more soluble salts influences the solubility of gypsum. We can presume that the amount of gypsum found in the mixtures might represent a fraction of the total gypsum content that was actually dissolved and transported by the solution. Since it was impossible to overcome this difficulty the amount of gypsum that was extracted was recorded in order to include it in the discussion and assume its participation in relation to the amount of the other species as described by ECOS (table 9.1).

Room	HG			HD			MD			MA		
Height	I	II	III	I	II	III	I	II	III	I	II	III
Nov	0.18	n.a.	0.0	0.03	n.a.	0.0	1.1	0.5	0.01	n.a.	n.a.	0.17
Mar	0.05	n.a.	0.0	0.08	n.a.	0.14	n.a.	n.a.	n.a.	n.a.	n.a.	0.29
Aug	0.07	0.6	0.1	0.06	0.09	0.09	0.12	0.5	0.08	0.24	0.1	0.15
Jan	0.06	0.06	0.18	0.1	0.02	0.01	0.2	1.1	0.3	0.14	0.01	0.1
May	0.13	0.1	0.18	0.02	0.003	0.02	0.15	2.0	0.05	0.07	0.04	0.1

Table 9.1 Gypsum extracted from each mixture (mol)

Although some of the sampling campaigns were not complete all the samples have been investigated with ECOS. The reference temperature represents the daily average of the month of sampling while the full range of RH has been used (15%-98%). While the daily deviation of temperature is small in Delos we had to consider the annual transition between the sampling campaigns. According to ECOS temperature is very important for the less soluble salts as well as hydrates. Thus individual hypothetical calculations have also been performed and incorporated in the discussion. In some cases the discussion also includes fictional predictions concerning the response of single salts or fictional mixtures presumably produced by fractionation. Accordingly hypothetical environmental conditions reflecting the influence of direct solar radiation, air movement and ground moisture rise have been attempted in order to enhance the discussion and the conclusions.

9.2 Results and discussion

Room MD

The first sampling campaign of November indicates quite a balanced resultant for room MD (charts VII.1-3). The lower zone (1) is dominated by the presence of gypsum. By extracting 1.1 mol of gypsum the significant surplus of sulphate results in hydrated salts of Na, Mg and K. According to ECOS mirabilite is the first salt that precipitates from the mixture at 87,8%RH, significantly lower than its ERH (95%) as a single salt. The next step at 71.7%RH indicates the major equilibrium point of the system where four species precipitate simultaneously and reach quite sharply their highest volumes. Mirabilite dehydrates to thernadite while simultaneously bonding with magnesium and potassium sulphates to form bloedite and aphthitalite respectively. Chloride is entirely consumed in halite, which is also slightly delayed from its ERH as single salt. Nitrate bonds as $NaNO_3$ with $NaSO_4$ to darapskite at 68.5%RH and as niter at 40.9%. The latter represents the last step of the system.

The mid zone (2) presents a slightly different resultant. The initial calcium extract and gypsum are both decreased to less than half quantity of the lower zone. The equilibrium of mirabilite is thus shifted slightly lower to 86.5%RH and the next step exactly as presented above to 71%RH. The most significant change is the shift of niter towards higher values (63%) closer to its ERH.

Gypsum is sparingly present in the higher zone (3). The dominance of chloride primarily as halite and secondly as sylvite does not permit the precipitation of mirabilite or thernadite. Alternatively sulphate is consumed to aphthitalite, which precipitates along with halite at 72%RH, bloedite, which is slightly delayed and picromerite. Sylvite equilibrium is significantly decreased (46.4%RH). The consumption of sodium as halite permits also the presence of Mg-SO_4 independently from bloedite as hexahydrite (62%), starkeyite (58%) and kieserite (22.4%).

The height distribution and the potential of the salt mixtures present a very interesting fractionation, which probably relates to the presence of ground moisture. As the moisture content assumingly decreases with height the composition of the salt mixtures leads to more soluble species. The presence of moisture at the lower and mid zones permits the precipitation of mirabilite, which is absent in the higher zone. Gypsum also decreases with height permitting eventually the thermodynamic dominance of halite at the upper zone. Although this first campaign represents more likely a reference we can attempt an initial correlation of the predicted potential to the environmental conditions. Obviously the fluctuation of RH is not the only parameter that governs deliquescence and crystallisation cycles. The variable of height distinguishes the presence of ground moisture as another parameter that generates phase transitions.

Autumn represents in Delos a long period of transition from the dry and hot summer to the mild winter. The time of sampling can be detected at a mid point of atmospheric temperature and relative humidity and at the starting point of the rainy season. The fluctuation of RH over the period of sampling indicates diurnal phase transitions of mirabilite while the other salts probably stay in solution. The forthcoming period of very high relative humidity, which reached condensation during December and January might have caused deliquescence of gypsum as well. After the small frost period, temperature returns to the values of November and relative humidity is slightly decreased. From the end of January until the next sampling period of March RH rarely surpasses the ERH of mirabilite but drops frequently below the ERH of halite. As can be seen by the climatic data the sudden drops of RH are diurnal. On the other hand several rain events have occurred in Delos by the time of sampling. We can assume that mirabilite is more likely to crystallise at the mid zone that at the lower one. The presence of ground moisture probably delays the precipitation of mirabilite. Gypsum should precipitate as well at the mid zone. It is not clear whether the very fast drops of RH permit the crystallisation of halite. It is very interesting to notice that the less soluble species of the higher zone are kept in solution under conditions where they should crystallise as single salts. We can assume that this is favourable for preservation. As the average RH decreases towards the summer the diurnal fluctuations pass more frequently from the ERH of the salts found in the upper part.

Unfortunately it was not possible to sample from room MD during the March campaign. After a long period of warm and dry weather, which started spontaneously around May, the sampling campaign of August revealed a totally different thermodynamic potential (charts VII.4-6). Gypsum has significantly decreased in the lower zone (0.1 mol) while thenardite is totally absent. Chlorides respond primarily to halite, sulphates to starkeyite and nitrates to niter. The presence though of the very soluble carnallite and nitromagnesite shift the equilibrium towards much lower values. Thus halite precipitates at 59.2%RH while due to the higher temperature and the absence of ground moisture starkeyite precipitates immediately at the same value without the prior presence of epsomite. Niter precipitates slightly later at 55%RH. The next significant step at 30.4%RH dehydrates starkeyite to kieserite while part of niter dilutes and recrystallises as carnallite and nitromagnesite.

Similarly the mid zone presents a different potential dominated by more soluble salts. Contrary to the lower zone gypsum maintains the high concentration of November. Halite crystallises at 61.5%RH due to the presence of the very soluble carnallite, bischofite, nitromagnesite and anhydrous nitrocalcite. In the upper zone the dominant presence of halite maintains its ERH close to the normal values (71.4%) despite the presence of the same very soluble salts.

Obviously the withdrawal of ground moisture governs the alterations observed in MD from the previous campaign. The potential of November is absolutely justified. Mirabilite is probably withdrawn from the mixture as efflorescence. Gypsum precipitates in the mid zone while it is dissolved by ground moisture and probably diffused back to the foundations in the lower zone. This can be supported by the constant presence of gypsum crust that has been observed in the mid zone and the periodic efflorescence in the lower zone. As expected ground moisture supplies sulphates that crystallise slowly in the mid part while simultaneously causes phase transitions of less soluble salts in the lower zones. The presence of moisture in the deeper parts is probably responsible for the sand disintegration of the lower zone. The external efflorescence of gypsum in the mid zone during the warm months probably avoids damage. On the other hand deliquescence plays the primary role in the upper zone where halite is withdrawn slowly towards the surface and crystallises as efflorescence. Furthermore the diurnal fluctuations of RH during the warm months probably cause transitions of halite, which might be responsible for the flaking damage of the external layer. The low supply of moisture is presumably the cause of the whisker like appearance of the halite efflorescence. The rest of the species in the lower and the mid zone stay more likely in solution since their extremely low ERH is not reached in the sheltered areas. The evident marine origin of the species in the upper zone indicate that sea spray dominates as contaminant in the absence of ground moisture.

The next sampling campaign of January confirms the ground moisture origin of sulphates (charts VII.7-9). In the lower part, where damage was probably deactivated during summer, the rising ground moisture offers the appropriate conditions for the generation of hydrated salts. It is quite clear that the thermodynamic potential of August, which permitted the crystallisation of starkeyite, has altered in a more aggressive form favouring the production of epsomite and hexahydrite as well. Thus as predicted by ECOS the first salt that precipitates is epsomite 89.4%RH followed by hexahydrite at 84.5%RH. Potentially at lower values the dehydration of hexahydrite should occur at 52% (starkeyite) and 20% (kieserite). Halite found in very small concentration is kept at very low ERH (58%) as are the rest of the very soluble salts such as carnallite and bischofite. Gypsum is also present at almost the double proportion than August.

The most interesting observation is that the species found in August in the lower parts have been transported to the mid zone altering again the thermodynamic potential. The slower supply of moisture however does not favour the generation of epsomite as in the lower zone. Thus the mixture crystallises initially as hexahydrite (71%) followed by halite (67%). The lower concentration of magnesium and sulphates not only restricts the generation of Epsomite but also lowers significantly the ERH of hexahydrite. The less soluble salts dominate again the potential of the mid zone. Alternatively the higher zone, which as presumed so far is mainly influenced by atmospheric RH deliquescence, does not present any particular alteration.

The fluctuations of RH during this period favour phase transitions only at the lower part and specifically between Epsomite and Hexahydrite. The mid zone represents again the height of gypsum accumulation with the rest of the species probably in solution. At the upper part halite is progressively dissolved and withdrawal to the deeper parts. It is very interesting to observe that the exfoliation of the upper zone is particularly observed during winter. We can assume that the withdrawn of halite releases the white wash flakes that have been generated by diurnal fluctuations during summer.

The stoichiometric results of May indicated a peculiar phenomenon of salt contamination, which was expected to influence significantly the thermodynamic potential (charts VII.10-12). Indeed as predicted by ECOS the contamination of nitrates, although not periodic, alters the behaviour of the mixtures dramatically. As expected since the contamination was induced by ground moisture uptake the upper zone is not significantly influenced. Nitrates are present in the form of dehydrated nitrocalcite but their low concentration does not effect the ERH of halite which is again dominant. As confirmed by the depth distribution halite has already started to move towards the surface as last August. In the mid and the lower zones however the generation of the very soluble nitrocalcite retrains the crystallisation of the other species, lowering their ERH to extremely low values. Gypsum is again dominant but probably influenced by the dissolved species. The most dramatic effect in this zone is the disturbance of the less soluble salts, which up to now have been presumed to crystallise on the surface without frequent phase transitions. The new potential might generate deliquescence and recrystallisation of these species. At the lower part as already predicted by the previous samplings sulphates have withdrawn to the surface or the foundations. For the moment the only effect seems to be the lowering of halite's ERH but later during the return of rising moisture we can presume that the presence of nitrocalcite might expand the sulphate salts vertical transport. Alternatively if gypsum, which during the warm period is reduced, becomes dissolved as well, the potential of damage might alter significantly by more frequent summer phase transitions of gypsum. This random phenomenon, although insignificant in relation to the strong stoichiometric periodicity of this room, proved to be thermodynamically extremely important.

Room MA

The predicted salt species that derive from ECOS investigation for room MA indicate that the marine origin prevails on this exposed area. During August the lower zone in MA contains, apart from a small amount of gypsum (0.24mol), several species that we should expect to crystallise from sea spray along with nitrate salts. The presence of very soluble salts like nitromagnesite and nitrocalcite shifts the equilibrium of halite, which precipitates first, at 67.8%RH. Both niter and sylvite, which follow at 56.4% and 51.7% respectively, are more severely deviated from their ERH as single salts. The mid and upper zones, less affected by ground moisture, present reflect more closely sea spray precipitations. In the absence of the less soluble niter and sylvite the ERH of halite drops significantly to 58,6% in the mid zone and 57,6% in the upper zone. The rest of the salts in these zones present equilibrium below 30%RH.

The average daily deviation of RH in August appears between 69%-75%. We can thus assume that since phase transitions are not plausible, damage is deactivated during this period. According to the results of ECOS all the salts should be in solution. Nevertheless due to direct solar radiation on the exposed surfaces we can presume that the spray deposited on the surface might crystallise during the day. As temperature slowly decreases towards winter the daily deviation of RH increases, reaching in November an average fluctuation between 76%-81%. The species found in August should thus stay in solution. On the other hand as ground moisture rises again the mixtures are enriched by sulphates, which alter significantly the equilibrium.

Indeed the thermodynamic investigation of the mixtures found in January reveals an alternative situation. Sulphates and nitrates probably transported through capillary rise dominate the potential of both the lower and the mid zone, indicating the height of moisture rise, while the upper zone presents a similar behaviour to August. In contrast with the sheltered area MD gypsum has decreased. The lower zone presents a complicated potential with halite still dominant and in equilibrium closer to its single salt behaviour at 69,7%RH. Sulphate is present as hexahydrite at 62%, dehydrated to starkeyite at 52%. Nitrate is consumed in nitratine (62%) and niter (59%), which are both severely deviated from their single salt equilibrium. It is very interesting to observe that in this case the deviations are not enhanced by the presence of very soluble species but due to the presence of hydrated salts. In contrast with the sheltered MD despite the enrichment from the ground halite is dominant probably due to continuous sea spray deposition.

The salt mixture found in the mid zone presents an even more complicated potential. Again the presence of halite is very strong and presents the same ERH as in the mid zone shifted towards higher values than August probably due to the presence of less soluble species. The low temperature favours initially the precipitation of mirabilite at 89,1%RH, slightly lower than its single salt equilibrium. The next step between 69.4% and 64.2%RH is composed by sharp and alternate precipitations of halite, aphthitalite, bloedite, niter and nitratine. Below 64%RH hexahydrite dehydrates to starkeyite and kieserite. The upper zone is slightly enriched in halite probably from sea spray. Although the same species as in August precipitate from the mixture the equilibrium of halite has shifted closer to single salt conditions at 68.1%. The rest of the species present very low ERH below 33%.

The environmental conditions of January do not favour phase transitions in the lower zone. We have thus failed to explain the severe damage encountered as sand disintegration at this height. Both the potentials of August and January indicate that the salts stay in solution. We can only assume that damage probably occurs during the decrease of temperature towards the warm period due precipitation of the les soluble sulphates and nitrates that accumulate by ground moisture rise during winter. Unfortunately the sample set was not as complete as in MD since we obtained samples from the upper part only during the November and March campaigns.

In the mid zone the daily deviation of RH does not favour phase transitions of the present salts. Mirabilite is probably the only salt that precipitates while the other salts stay in solution. We can assume that external damage observed in this zone derives from the precipitation of mirabilite during ground moisture uptake. It is very interesting to notice that damage in the mid zone presents horizontal patterns at different heights, which might reflect the limit of moisture rise.

The salt mixture of the upper zone stays again in solution as in August. This behaviour is in accordance with the good preservation state of this zone. Nevertheless we should mention here that both of the exposed locations under investigation despite their good state of preservation present extended detachments from the masonry. Accepting that most of the salts found in MA should stay in solution for long periods we can assume that the solutions supply slowly with salts the deeper part of the renderings. It is very tempting to presume that this potential is also responsible for the detachments. The hypothesis that can be drawn is that since the environmental conditions do not favour phase transitions the solution can be transported freely in the rendering until the hydraulic boundary between layers of different pore properties where crystallisation is triggered by moisture supply deceleration. An alternative hypothesis that can be drawn is that during evaporation the receding moisture front leaves at the interface solution islands that reach the superaturation threshold for crystallisation. This potential as described by ECOS also supports the absence of efflorescence on the surface of the exposed areas despite the prevailing atmospheric pathway of contamination. The depth distribution as described in a previous chapter provides the information that salts are withdrawn towards the surface only in the mid zone during August while they are more evenly distributed in all zones during January.

As in the case of MD the nitrate contamination observed in May affects severely the thermodynamic resultant of all the zones in MA. Initially we can observe that the sulphates have withdrawn from the system, which returns approximately to the composition of August. Thus we assume that the sulphate contamination in both MD and MA is a periodic event probably controlled by ground moisture rise during the rainy season. The less soluble salts that were present in January either diffused back to the foundations along with the receding water table or crystallised as efflorescence, which was washed-off by rain. Contrarily to the sheltered area MD where gypsum along with other sulphates form a crust on the surface of the mid zone the salts that effloresce on the surface of MA are probably subjected to redistribution by rain or wind.

The composition of salts during May indicates, apart from the nitrates, marine origin. In contrast to the results of August the thermodynamic behaviour of the salt mixture is governed by the presence of the very soluble nitrocalcite. In the mid and lower zones the predicted ERH of halite is extremely lowered to 36% and in the upper zone to 30%. Although the potential of the previous periods also indicated that the salts stay in solution we can assume that the presence of Nitrocalcite might cause phase transitions of gypsum as well as other less soluble sulphates in the future.

During the first two sampling campaigns of November 2001 and March 2002 only one sample was taken from MA because of a bureaucratic misunderstanding about the sampling license. In both cases the sample has been extracted from the upper zone. Halite is dominant as in the other campaigns and its equilibrium slightly deviates from the single salt behaviour at 71.7% in November and 71.4% in March.

Room HG

As described in the previous chapter the sheltered area HG presented corresponding fractionations of damage and salt efflorescence. The results of ECOS indicated whether this phenomenological relation is thermodynamically justified or coincidental. The resultant of the lower zone, as represented by the samples extracted in August, reveals that the significant presence of very soluble salts like bischofite and nitromagnesite influence severely the ERH of halite and magnesium sulphate. Consequently hexahydrite and epsomite are excluded from the thermodynamic possibility of the mixture, which initially precipitates as starkeyite at 59.6%RH followed by Halite at 50.7%RH.

We can assume that the amount of gypsum that was extracted (0.07mol) is quantitatively important and probably plays a role in the system's equilibrium. According to ECOS the double amount of bischofite lowers slightly the ERH of gypsum but affects significantly the dehydration equilibrium of anhydrite, which as a result affects the ERH of halite. Although the addition of magnesium and excess sulphate disturbs the function of ECOS we can presume from individual calculations for the Ca-Mg-SO_4 system that the presence of gypsum favours the precipitation of epsomite and hexahydrite as well.

The mid zone, dominated clearly by halite, presents a less complicated resultant. The small amounts of more soluble salts can influence significantly the ERH of halite, which precipitates sharply at 73.7%RH. According to ECOS calculations even in this ratio (halite:gypsum=20:1) the ERH of gypsum is slightly lowered to 94%RH. We should also mention that the large amount of halite was concentrated in the external sample and might reflect the whisker efflorescence that was witnessed during this period in this zone and verified as Na-Cl by SEM. Thus the ERH of halite more likely corresponds to the external efflorescence while the internal halite deposits might be more influenced by the other very soluble salts. The upper zone is again dominated by gypsum. By extracting it from the mixture (0.1mol) the resultant is governed by the very soluble nitrocalcite, antarctite and tachydrite that shift the ERH of halite to 48.4%. Presumably gypsum is not affected by these salts due to its quantitative predominance.

According to ECOS results the mid zone represents the upper limit for halite capillary rise and precipitation. Obviously halite remains in solution in both the upper and lower zones. Accepting the solubility fractionation of capillary rise we should attribute the presence of gypsum in the upper zone to source and pathway other than ground moisture. Presumably gypsum accumulates at this height during the rainy season through penetrating moisture from the concrete ceiling. According to the climatic data the mixture stays inactive at this height during August. Similarly there must be no phase transitions of any of the salts found in the lower zone during this period. All the salts appear to stay in solution apart from gypsum, which probably precipitates from ground moisture during winter and is not affected by relative humidity fluctuations. Alternatively the ERH of halite in the mid zone as predicted by ECOS favours phase transitions not only in seasonal but also in diurnal rate. There can be no doubt that the flaking damage of the external layer in the mid zone is related to the whiskery precipitation of halite during summer. We can assume that the particular crystal morphology is attributed to the limited supply of deliquescence moisture in contrast to the cubic halite, which precipitates by sea spray and ground moisture.

The next sampling campaign of January verifies the accuracy of ECOS calculations for the previous campaign. The different resultants are obviously a sensible function of proportional fluctuations and environmental conditions. The enrichment in sulphates and nitrates results in the addition of niter (70%RH) in the resultant of the lower zone as well as the generation of hexahydrite (81.4%RH) which was not favourable in August. The presence of soluble salts is still strong keeping the ERH of halite at the low levels encountered in the previous campaign. Similarly the slight increase of very soluble species in the mid zone lowers significantly the equilibrium of halite at 69.4%RH. A small amount of niter is also present in the mid zone probably transported by capillary rise. Alternatively the upper zone does not present any significant changes. The small shift of halite's ERH to 54.3% is attributed to the drop of temperature since the composition of the mixture is almost identical with the one of August. Gypsum stays constant in the lower zone, decreases significantly in the mid, probably withdrawn as efflorescence, and increases almost to double in the upper zone probably due to the increasing rain height.

The environmental conditions favour phase transitions of hexahydrite in the lower zone, which is probably responsible for the sand disintegration. Halite is deactivated in the mid zone, staying more likely in solution. No phase transitions are favoured in the upper zone as in August. Probably the intense damage observed in this part is attributed to the crystallisation of gypsum transported by rainwater and not relative humidity fluctuations.

As in the previous cases of rooms MA and MD the contamination of nitrate during May influences the equilibrium annual cycle severely. Nitrate appears in the form of nitratine and nitrocalcite. The dominance of the latter in all the zones lowers the ERH of the mixtures, which should stay in solution according to the environmental conditions throughout the year. Although this appears to be in favour of preservation, deactivating the phase transitions that have been held responsible for weathering, we should consider the new potential that will be introduced by the addition of new sulphates and of course the equilibrium of gypsum. Independent ECOS calculations for the system Ca-SO_4-NO_3 reveal however that the influence of nitrocalcite on gypsum's ERH is minimal. Nevertheless we also have to consider the dehydration of gypsum, which has not been mentioned so far. The presence of other salts can influence the ERH of anhydrite but as predicted by ECOS the strongest influence is attributed to temperature. Thus the only period that actually phase transitions of anhydrite can occur is the summer. At the average August temperature of 26C anhydrite's ERH rises to 70%, which according to the climatic data is diurnally encountered.

Concluding the investigation of room HG we must mention the cases of the east wall which was sampled only in November and March for reasons that were previously explained. ECOS resultant indicates the presence of sulphate salts both in the upper and the lower sampling zone. The dominant salts at the lower part are halite and mirabilite. Mirabilite initially precipitates at 93,8%RH slightly deviated from its equilibrium as a single salt while halite and thernadite precipitate simultaneously at 71.4%RH. The upper part is clearly dominated by halite. The lower concentration of mirabilite must be responsible for the large deviation from its equilibrium. Thus mirabilite precipitates at 85.7%RH and halite along with thernadite at 71.7%RH. The height distribution indicates that mirabilite originates from the ground. Indeed ECOS predictions justify the phenomenological observations for this case. During this campaign a thick powdery efflorescence has been sampled from the ground adjacent to this wall and whiskery efflorescence has been sampled from the top of the preserved rendering. Both cases revealed by SEM-EDAX analysis the presence of sodium and sulphur (fig. VI.31). Thus we can assume that Na-S salts are transported from the ground to the rendering where they precipitate in amorphous form in the lower part and as whiskers in the upper part due to a lower supply of moisture. The climatic data also justifies these finds.

The concentration of mirabilite is reduced in relation to halite at the next campaign of March. Accepting that moisture capillary rise is enhanced by rainfall it is rather strange that after the rainy season the amount of sulphates that probably contaminate the renderings by ground moisture is not increased respectively. The only explanation is the fact that rainwater was entering freely from the concrete ceiling right above the sampling locations and probably washed off the superficial deposits. This fact comprises as well the reason for the change of sampling location since the sheltered environment was not represented sufficiently. Nevertheless this assumption is contradicted by the constancy of halite. We can initially argue that since halite primarily originates from sea spray it might as well continue to contaminate the wall by atmospheric deposition independently of the rain-off. An alternative argument derives from ECOS predictions. According to the climatic data and the depth distribution mirabilite is the only salt that crystallises during this period. We can thus assume that rain-off affects only this superficial deposit and not halite, which is probably drawn deeper in the masonry in solution. Rain-off might also explain the absence of gypsum, which was abundant as efflorescence in the south wall. One way or the other the presence of mirabilite comprises according to ECOS a serious threat for the preservation of the rendering since it is subjected to phase transitions both diurnal and annual.

On the other hand the change of sampling location that was forced by practical reasons provided the chance to study the multiple potential of adjacent walls. We cannot explain why sulphate resulted in epsomite instead of mirabilite nor why there was not halite efflorescence in the mid zone along with the damaging results observed on the south wall but in both cases the resultants were well balanced and justified. The fact that we did not have samples from August when damage occurred might be a determining factor but on the other hand there were not any phenomenological indications of flaking either. It is evident that predictions from such a small samples population are endangered but clearly the resultants for the two walls were different although the contamination particulars should be quite similar.

Room HD

The thermodynamic resultant of HD is in most cases totally dominated by halite. This finding is in agreement with the aspect and exposure variables of this site. The deposition investigation indicated that HD is more subjected to sea spray than the other locations. Furthermore the absence of conservation cementitious mortars on the floor justifies the low presence of sulphates. Nevertheless in order to explain the good preservation state of this site, in contrast with its obvious susceptibility to weathering factors, we need to investigate more closely the thermodynamic resultant of ECOS in relation to the environmental conditions that govern it.

During November and March samples have been extracted only from the lower and the upper zone. ECOS resultant for the lower zone in November indicates the dominant presence of halite along with much smaller quantities of gypsum and other sulphates and nitrates. The precipitation of mirabilite is not favoured and thus thernadite precipitates simultaneously with halite and bloedite at 71.4%RH. A very similar resultant is predicted by ECOS for the upper zone. Halite precipitates at 71.7%RH followed by thernadite at 69.4%RH. The dominance of halite and the similarity of the potential in both zones indicates that sea spray prevails as source and pathway of contamination. During the next sampling campaign of March although halite is still dominant the composition of the minor species has changed significantly. Sulphates have been withdrawn from the potential replaced mainly by chlorides. As a result the ERH of halite is slightly reduced to 69.7%RH in both zones. The most sensible explanation for the withdrawal of the sulphates is that they precipitated as efflorescence and washed off by rain. This explanation though does not comply with ECOS predictions and the climatic data according to which all the species should stay in solution during March. On the other hand the concentration of all the species is significantly reduced to almost ¼ from November to March. This fact signifies the influence of a reducing factor on the exposed surfaces of HD. We can thus assume that all species have been washed off by rain and the salt mixture of March reflects sea spray deposition.

During the next campaign of August sulphates are again present but only in the lower zone. Halite is still dominant but precipitates at a lower ERH (67.8%) due to the presence of the very soluble bischofite, nitromagnesite and carnallite. In the mid zone halite precipitating at 68.1% deviates as well from its ERH as a single salt. The most significant deviation though can be observed at the upper zone where the ERH of halite drops to 55%. The same phenomenon has been observed at the upper zone of the other exposed room MA. Probably during the warm period halite crystallises as efflorescence at the upper part as a result of the intense solar radiation and the absence of ground moisture. The remaining halite is then subjected to the influence of the other very soluble salts and stays in solution. According to the climatic data the salt mixtures of the lower and the mid zone must stay in solution as well.

During January halite's ERH drops even lower (61.2%) than that predicted for August. It is obvious that the proportion between halite and the more soluble species has changed while the sulphates have withdrawn from the system. Although the environmental conditions did not predict precipitation for any salt in the lower zone in August we can assume that due to the intense solar radiation the less soluble sulphates along with some halite might have crystallised on the surface. On the other hand the continuous supply of sea spray might have altered the potential that was predicted for August permitting the precipitation of the less soluble species. The withdrawal of the salts that presumably precipitated could have been achieved by rain-off since the rainy period had already started during the sampling campaign of January.

A slightly similar case is predicted by ECOS for the mid zone. Halite is significantly reduced while bischofite, present in the form of tachydrite in the previous campaign, has retained its volume. As a result halite deviates to 71.4%RH. A similar assumption of halite precipitation and rain-off is plausible in this case although it contradicts the environmental conditions, according to which halite should stay in solution. Another fact, which indicates the influence of rain, is the reduction of gypsum during January in the upper and the mid zone.

The upper zone presents a considerably altered resultant mainly characterised by sulphate and nitrate enrichment. Thus halite's ERH is still kept very low while niter and hexahydrite precipitate at 69.7% and 64.7% respectively. We can presume that sulphate is washed off from the conservation cements that are in contact with the wall painting's upper zone. Nevertheless the climatic data does not favour the precipitation of any salt.

As mentioned in the stoichiometric approach room HD has not been enriched in nitrates during May. Thus in contrast with the other rooms HD does not present considerable alterations in the salt mixture composition. Halite is dominant in all zones while small amounts of sulphates are again present in the lower and the middle zones. We can presume that after the rainy season sea spray is not washed off by rain and thus enriches primarily with halite all the zones. In contrast however with August when temperature and solar radiation reach their peaks halite does not precipitate as efflorescence and is thus traceable in the drills.

In general ECOS predictions for HD presented some contradictions between the potential of the mixtures and the climatic conditions. According to these predictions all species should stay in solution throughout the sampling period. From a first point of view this presumption is in accordance with the good preservation state of the wall paintings. On the other hand in order to explain the fluctuations of the species concentrations we had to assume that at least during the warm period some salts should crystallise due to direct solar radiation. Ground moisture, although not a significant source of sulphates in HD, might have affected the equilibrium as well. As in MA, which is also exposed, the most severe weathering in HD, apart from some minor white wash exfoliations in the upper zone and sand disintegration at the lower zone, is the detachment of the rendering from the masonry which has been witnessed in the lower and the mid zones during drilling. As already described for MA the low ERH which retains the salts dissolved has been suspected responsible for the transport and the accumulation of the solution to the rendering-masonry interface. On the other hand we cannot explain the entire loss of the paint layer (presuming that there was one). Again we can only presume that lime washes are particularly susceptible to direct sea spray due to interface phenomena that override our thermodynamic predictions.

Although there is no evidence to support this assumption the similar finds for HD provide a strong indication that the exposed surfaces detachments are related to the equilibrium conditions of the salt mixtures and interface phenomena. Although this weathering pattern is not as dramatic as sand disintegration or honeycomb weathering it results in severe damage. Indeed a large piece of rendering has been detached and fallen-off in 1996 from the upper zone of HD just a few meters from the sampling location. Surprisingly although this piece was slightly damaged from the fall it stood in a pretty good condition indicating that there was no other mechanism affecting it apart from detachment.

It is very difficult to define the rate of this mechanism. ECOS resultant in relation to the climatic data did not indicate clearly when phase transitions are triggered. The only indication of crystallisation is the reduction of salts during the warm period. We can assume that the cold season represents a period of slow salts accumulation and transport to the interface disturbed by rain-off. After the rainy season sea spray deposits on the surface undisturbed building slowly a crust. During this period the superficial deposits supply with solution the deeper parts. According to the data relative humidity is still fluctuating higher than the ERH of the mixtures building significant concentrations on the interface due to hydraulic discontinuity. The transition from the winter to summer is very fast in the Aegean. The climatic data reveals that during the warm period solar radiation reaches at noon $900w/m^2$ on a horizontal surface. Presumably the fast evaporation, enhanced by the solar radiation leaves at the interface solution islands that cannot follow the withdrawn of moisture to the surface.

As described by Scherer (2004) for a random case of variable pore size distribution, the liquid pockets trapped between small radius pores, will eventually dry up when the local RH becomes low enough for the menisci to pass through the pore entries. In the case of layered structures we suppose that this mechanism is localised on the interface. The isolated liquid pockets will eventually generate localised damage on the interface separating the layers. Progressively this mechanism will produce a gap, which will act as a crystallisation surface. The gap that has been witnessed in HD during drilling might be responsible for the loss of the less soluble salts and part of halite in the summer. According to ECOS the resulting mixture composed by more soluble salts stays in solution. We could then assume that the presence of this mobile solution influences the salts that have been presumably crystallised at the interface generating diurnal transitions but more likely this mechanism follows an annual cycle triggered by the fast transition from winter to summer since diurnal fluctuations of RH are relatively small.

9.3 Optimal conditions for preservation

In general the thermodynamic resultants of the particular cases have been clearly described and justified with the use of ECOS. It was very intriguing to witness the plethora of information provided by the thermodynamic approach which does not solely lead to an abstract prediction of damage conditions but describes a sensible model between the variables of time and location. Since the convention that was followed is absolutely verified we can definitely state that the thermodynamic approach, if applied appropriately, holds a particular value for salt weathering investigations. The outcome, which could not be predicted by stoichiometric calculations, underlined in most cases the importance of salts interactions.

The variables that directed the sampling strategy played an essential role in understanding and interpreting the results of the thermodynamic approach. The variable of sheltering offered the opportunity to distinguish two different models of weathering acting independently under the same context of coastal environment. The variable of height revealed and justified the multiple potential encountered on the same wall due to various sources of salts and contamination pathways.

Similarly periodic sampling proved to be essential to verify thermodynamic predictions. The variability of environmental conditions under which the samples have been extracted revealed the significant periods for weathering during which phase transitions could be achieved and in some cases indicated indirectly the rate of weathering by distinguishing diurnal and annual cycles. It was clear that a single sampling period would have resulted in omissions and more importantly misunderstandings that might have jeopardised the credibility of the investigation. Besides although the stoichiometric approach had provided indications of possible relations between specific weathering patterns and ion concentrations we managed through the thermodynamic approach to justify them. It was evident that damage was not solely related to specific ions but to the predicted interactions between the salts and the resulting equilibrium.

The thermodynamic manipulation of fewer samples is probably more revealing than an absolutely accurate and statistically acceptable stoichiometric representation. The acceptance of a multiple potential is much closer to reality than an abstracted global resultant. This is verified by the relations generated between the spatial and time variables. Thus the thermodynamic approach can limit the number of samples needed to describe adequately a particular case. We must also mention that apart from the extraction of more or less calcium there was no other manipulation of the data. Furthermore the drills have been represented by the sum and not the average of the sample set thus the data used for the thermodynamic approach reflects the absolute values obtained by analysis. On the other hand we assumed that each drill represents a continuous system. If this is not true we should expect that salt distribution is fractionated and thus the species do not interact. The depth distribution as described in a previous chapter provided the information needed to verify the predictions. Nevertheless in most cases we had to accept the continuity of our predictions in the time intervals between the sampling campaigns.

On the other hand cyclic weathering and simultaneous contamination obstructed the interpretation of the resultants. It was obvious that the deposition investigation did not supply all the information needed and in some cases crude assumptions had to be made concerning both contamination and removal to explain the resultants, without whatsoever any controversial conclusions. There is no doubt that more elaborate investigation of the contamination particulars would have supported significantly the thermodynamic approach. Similarly the limited climatic data left in some cases significant doubts. Although the wider context has been adequately described more information on localised conditions like surface temperature and air movement at the sampling sites would have been very helpful. Additionally the correlation of thermodynamic predictions to specific weathering forms would have been much enhanced if we had more frequent and elaborate documentations from the site.

Another aspect that has not been adequately accessed is the possibility of other weathering mechanisms, acting simultaneously on the mortars, as biological decay and most importantly sulphation of the original material. We tried to explain damage that has already occurred by means of chemical analysis of the present salts. Evidently there was an interpretation problem in the lower areas of sand disintegration patterns. The presence of gypsum was assuming to be related to it, but not in terms of phase transitions. Alternatively gypsum fluctuations have been interpreted as removal and contamination. But we did not clarify if gypsum has been transported to the masonry or if it comprised sulphation product of the authentic material. On the one hand the presence of ground moisture in the lower parts must have restricted phase transitions and on the other it might have provided the necessary conditions for sulphation. Still in this case, although a combined approach with other investigations would have been preferable, the thermodynamic investigation achieved the quantification of gypsum, which is more than enough information for the purpose of this project.

Nevertheless can we expect that the generation of a reasonable model ensures the definition of optimal conditions for preservation? The thermodynamic approach offers the means to delimit a range of hygrothermal conditions under which damage is deactivated. From a first point of view this sounds very easy and achievable. ECOS predicts the combination of solid minerals under equilibrium conditions that result at least to an upper limit of phase transitions. This upper limit signifies the boundary of permitted relative humidity fluctuations. By applying environmental control techniques triggered on the boundaries defined by ECOS we could thus ensure sustainability. The results though of this project, signifying the multiple potential of weathering, proved that this approach is too simplistic.

ECOS periodical *in situ* application provided the opportunity to investigate open systems under real conditions of continuous and varied contamination, which along with automigration and solubility fractionations resulted in multiple thermodynamic potentials. Different sampling locations even on the same wall presented different results. To what extent can we thus apply a unique environmental control approach? The height variable although limited to three components revealed significant variation. Especially in rooms HG and MD the relation of sulphate salts to ground moisture produced an interesting fractionation which resulted to varied equilibrium conditions in height. But in the exposed rooms as well fractionated efflorescence and varying deposition frequently resulted in discrepancies. We could thus estimate the maximum upper limit as a boundary for optimal conditions. On the other hand the presence of ground moisture does not only transport salts in the masonry but controls their phase transitions as well. Environmental control seems more plausible for the parts of the masonry that are not influenced by ground moisture. Nevertheless we can argue that according to Lewin's model (1982) RH controls the height of moisture rise and the crystallisation location. *Ex-situ* experiments have shown that controlled ambient conditions can force superficial crystallisation or restrain the moisture rise to a preferred height. Although the resultant is a function of many parameters ECOS predictions can support *in situ* environmental control projects by setting the upper boundaries.

Still even if we manage to ensure stable hygrothermal conditions at a unique optimal range the continuous sea spray deposition and differential contamination might shift the equilibrium from the initial predictions. The periodic investigation revealed that the ERH changes significantly during the year as a result of salt input and removal. There is no doubt that a combined approach implying elimination of one or more sources and blocking of contamination pathways along with desalination techniques would have more effective results. Again the thermodynamic approach is essential in controlling such operations by predicting hypothetical conditions of preservation.

It would be really helpful to repeat the thermodynamic investigation after or during the application of environmental control. Unfortunately the proposed sampling methodology, requiring destructive extraction of samples, is not repeatable. Sawdy (2001) had the chance to investigate simultaneously areas that have been previously desalinated with intriguing results. Although this is not always feasible it underlines the multiple function of thermodynamic analysis, which can provide insight in various questions. On the other hand phenomenological approaches in combination with no destructive techniques can also provide sufficient information based on which we can predict hypothetical equilibrium conditions. The proposed thermodynamic approach provides the platform for future investigations on various maintenance or invasive problems.

As mentioned by the developers ECOS predictions can be more likely interpreted as an upper limit of phase transitions (Steiger *et al.*, 2000). It is thus preferable and less perilous to place the optimal conditions range above this limit than below, keeping the species in solution. Temperature control is more feasible than relative humidity conditioning, which requires elaborate, expensive and difficult to install humidifying equipment. Nevertheless according to ECOS dramatic shifts from the average might have important effects on the equilibrium of the more soluble and hydrated salts. Furthermore the response of solid materials to temperature changes is much slower than that of the air. Thus the discrepancy between the measured values and the ambient temperature inside the pores of the material might cause further problems. On the other hand although salts react quite sharply to relative humidity changes the hygroscopic properties of the solution are dramatically affected by the properties of the pore that hosts it. Environmental control is more realistic by means of a long-term slow transition towards the optimal conditions rather than alarm triggered air-conditioning. The stability of the environmental condition at the optimal range can also be achieved by alternative means of insulation, which can buffer the macroclimatic fluctuations.

Nonetheless the environmental control hould not only focus on hygrothermal conditions stability. The air movement probably plays a determining role as well. Although research has not produced clear evidence we should reasonably expect that evaporation is enhanced by air movement. It was clear that relative humidity fluctuations were smaller outdoors while the maximum values were higher in sheltered room HG than MD, which was better ventilated. On the other hand the upper zones of the sheltered areas that were contaminated solely by marine originated species, although less susceptible to atmospheric deposition than the exposed sites, presented more intense weathering, which was attributed, as justified by ECOS, to the microenvironment's fluctuations. Direct solar radiation, which was a significant factor in the particular case of Mediterranean climate, can influence the transition process also without traceable indications in the ambient temperature. In many cases the intense solar radiation was the only reasonable explanation for evaporation. Although from a first point of view this restricted sea spray penetration, it might have induced fast evaporation of entrapped solution pockets inside the mortars. Furthermore rainfall comprises another important environmental parameter. The absence of efflorescence on the exposed surfaces has been partly attributed to rain-off while ground moisture infiltration was increased during the rainy season.

But what is the purpose of the optimal conditions investigation for the exposed sites? There is no doubt that sheltering provides the only means to control the environmental conditions. The particular cases investigated by this project were somehow biased by the fact that the sheltered rooms have also been treated with mortars, which apparently supplied the sulphates salts. While this could not have been predicted we cannot override the fact that the microenvironment created under the shelters was responsible for the phase transitions of the particular mixtures. Even if the particular exposed cases present a better preservation state than the sheltered the damage that they have undergone is unacceptable since it affected the paint layer. The methodology proposed by this project can help in the determination of the new artificial environment in order to prevent the mistakes that lead to the intense weathering of the already sheltered areas.

Keeping the relative humidity higher than the upper limit of phase transitions might induce other problems like biological damage or gases deposition. While ECOS provides the chance to investigate hypothetical conditions for preservation with varied temperature and relative humidity we must state clearly that combined approaches are absolutely necessary in decision-making investigations. This way we could construct a theoretical model of annual and diurnal fluctuations in order to test potential solutions in relation with other weathering mechanisms.

According to the previous discussion we can draw a number of conclusions for the preservation of the investigated monuments in Delos. Primarily it is evident that despite the slower weathering rate, preservation is impossible in outdoor conditions. Sea spray can cause severe damage to paint layers, especially in combination with direct solar radiation. Room HD which receives the larger amount of sea spray presented a critical relative humidity near the ERH of halite. During the winter months we presume that the salts stay in solution. Damage, probably in diurnal rate, more likely occurs during the warmer months under the influence of direct solar radiation. Sheltering in this case will definitely provide both protection against sea spray deposition and solar radiation. Considering the state of the adjacent sheltered room HG special care should be given to avoid undesirable effects caused by the lack of insulation, the insufficient ventilation, the poor quality of the shelter and the addition of salt rich conservation materials.

Although room MA is also dominated by halite, the enrichment of the lower and the mid zones in sulphates during the winter months complicates the definition of optimal conditions for preservation. Again the critical point of relative humidity is a bit lower than 70% throughout the year. In contrast with room HD the addition of sulphates, which is probably related to ground moisture rise, causes the crystallisation of mirabilite in a range of relative humidity between 70-90%. The latter is probably the cause of sand disintegration in the mid zone. Since the semi-sheltered conditions of room MA offer a relatively suitable environment for minimal deposition and deactivation of phase transitions the efforts should focus on the elimination of the sulphates source and the decrease of ground moisture supply. We presume that any other environmental intervention might alter the ground moisture evaporation height causing further damage.

The strong presence of gypsum and halite along with other sulphates constitutes a very complicated situation in room MD, difficult to confront by means of environmental control. Simple interventions like the insulation of the shelter should therefore be accompanied by ground moisture control and desalination of the floor mosaics which probably constitute the source of sulphates. A similar situation has been predicted for room HG, enhanced by the poor preservation of the shelter and the lack of proper ventilation. In both cases we predicted a multiple weathering potential for the three investigated zones. Thus any intervention in favour of one zone might be unfavourable for another. In both cases insulation could help maintain higher relative humidity during summer which would prevent the crystallisation of halite and the consequent paint layer flaking in the mid and the high zone of rooms HG and MD respectively. The lower zones of MD and the low and high zone of HG presented a very wide range of phase transitions especially during the colder months. This complicated behaviour could not have been predicted without ECOS calculations.

Nonetheless we must keep in mind that the potential of salt mixtures is not consumed in thermodynamic considerations. Kinetic factors can change significantly the resultants. But to what extent are the in situ predictions subjected to kinetic deviations? Are kinetics simply a minor consideration or do they absolutely override the optimal conditions for preservation described by the thermodynamic approach? In the next chapters we will attempt to reassign the optimal conditions for preservation under the prism of some kinetic considerations in order to clarify further the "judicious" use of thermodynamic predictions.

CHAPTER 10: Kinetic considerations

10.1 Methodology

The extensive *in-situ* campaigns and analysis of this project lead to the identification of the dissolved species present on the wall paintings in Delos as well as the investigation of the salt system's evolution in time, with respect to a number of parameters, implicit in describing the weathering environment in general terms. The next immediate goal was the application of the analytical results to a theoretical thermodynamic model, using the ECOS program, in order to determine the hygroscopic behaviour of the salts mixtures and relate it to the evolution of the salts system in time and the ambient conditions. Eventually this correlation resulted in the identification of suitable conditions for preservation, as depicted in the previous chapter, and consequently in a solid basis for the concluding discussion on sustainability.

Nevertheless, despite the known limitations of the sampling procedure as well as the limitations in the application of ECOS, as stated by the developers (Price, 2000), it was also crucial to test the reliability of the extracted theoretical results experimentally. Before arguing on the limitations introduced by the pore properties of the substrate this research considers more vital to investigate the kinetic deviations that occur irrespectively of the site properties.

It has long been appreciated that in the phase equilibria of complex salt systems, kinetic factors often override thermodynamic considerations (Ostwald, 1896). It was also early observed that when crystallizing salts from seawater, certain thermodynamically expected stable salts never crystallized (Van't Hoff, 1905). The importance of the hygroscopic behaviour of atmospheric species in world climate and ecology induced research in this area (Seinfeld and Pandis, 1998, and references therein). A lot- of attention has been given to the identification of the parameters that govern kinetics. Apart from the thermodynamic explanations that have been attempted a number of experimental techniques have also been developed in order to obtain kinetic information on the hygroscopic behaviour of salts and gases (Dougle *et al.*, 1998; Tank and Munkelwitz, 1993). However these techniques either offer limited information on morphological changes or have slow data acquisition for imaging such fast processes.

In conservation studies there are very few examples of ***in-situ*** salt phase transition investigations. Pique *et al.* (1992), investigating the implications of salt phase equilibria on wall paintings found kinetic deviations of calcium nitrate deliquescence and crystallisation using thermogravimetry and differential thermal analysis. Steiger (2000) also investigated the equilibrium conditions for mirabilite hydration as well as the system Na-K-Mg-NO_3-SO_4-H_2O by means of X-ray diffraction (RHXRD) where he depicted in detail the kinetic deviations from the thermodynamic equilibrium.

Environmental scanning electron microscopy (ESEM) is a recently developed technique, which enables microscopic monitoring of salt deliquescence and crystallisation under controlled conditions. In addition the chemical composition of the salt crystal can be identified simultaneously with the help of an EDX microanalyser. The samples do not need any preparation thus coating does not obscure the crystal morphology.

The literature on the use of this technique in salt equilibrium research is still very limited but it has already demonstrated spectacular results. The DRH of some individual species was not always in agreement with the predicted value. More precisely Ebert *et al* (2002) detected water film formation on sodium chloride crystals before the predicted DRH and droplet formation in a considerably higher RH (78.3%). In the same study the temperature dependence of DRH has been proven very reliable in ESEM, meaning that the sample and the cold stage are in thermal equilibrium. Doehne and Lombardo (2004) have also experimented on the reproducibility of ESEM results concerning salt phase transition kinetics and found that the only limitation that influences the results significantly is the size of the salt crystals, i.e. the smaller the crystal the faster the rate of dissolution.

ESEM has been warmly welcomed by conservation scientists and it has found numerous applications in weathering studies from varnish cracking (Messier and Vitale, 1993) to pigments discoloration (Grout and Burnstock, 2000). For the time being there are few publications concerning the use of ESEM on salt weathering. Doehne (1994), investigating the generation of high superaturation in salt weathering managed to monitor the presence of liquid water in the hydration stage of sodium sulphate. In this case, the process, despite involving three phases, remained simple. Veniale *et al.* (2003) also recorded with ESEM that the growth of thaumasite crystals took place in conditions far from the equilibrium. There have not been any papers published so far on salt mixtures behaviour, which might prove a bit more challenging. The possibilities in the application of this technique in salt weathering research are unexplored.

ECOS calculates a theoretical sequence of relative humidity values for a given temperature that correspond to phase equilibria of the predicted salt species. In terms of conservation this can be translated as a range of relative humidity, above or below which the present salt system is "deactivated". Although deliquescence might correspond to the predicted equilibrium conditions it is well known that sufficient supersaturation for crystallisation to occur demands lower relative humidity values. Moreover despite the complexity of mixtures found on monuments usually there are only a few major ions that quantitatively dominate the thermodynamic potential of the solution. In theory a large variety of salts can crystallise from such a mixture but kinetically only a few salts will be able to (Mullin, 1993).

Whereas it is rather early to consider whether ECOS can be applied to predict sustainable conditions, i.e. a range of ambient relative humidity, which would guarantee "stability", further research is definitely needed to expand the present methodology to a number of other parameters, which strongly influence the hygroscopic processes, such as substrate properties. Also, a greater number of case studies would be really useful for critical comparison.

For the moment ESEM can satisfy adequately the necessity to evaluate the extent of this project's intended correlation between the thermodynamic predictions of ECOS and the observed trends of the actual evolution of the present salt systems. In the same prospect, this project will also contribute to a potentially clearer definition of the "judicious" use of ECOS.

The present investigation included single salts as well as salt mixtures that have been found on the wall paintings of Delos. Since the technique is not yet directed by an established methodology the experimental set-up has been customised after trial and error. To achieve and monitor the desirable process it was essential to balance a large number of parameters[10]. The methodology is outlined below although more particularities that influenced the results will be mentioned along with the *discussion*:

- Each cycle has been determined by complete deliquescence (drop formation-no visible crystals) and complete efflorescence of all species (no visible water). For technical reasons (imaging), it was undesirable to include full 0-100% RH cycles.
- Relative humidity has been controlled by changes in vapour pressure with steps of 0.1 Torr. Around the expected DRH three minute intervals have been applied between the steps in order to permit the samples to stabilise. The temperature was maintained at 5° C. Higher temperatures would require higher vapour pressures for deliquescence, which are prohibiting for imaging.
-. The crystallisation substrate was the standard cold stage of the apparatus. The cold stage was maintained at 10mm distance from the detection window to achieve best imaging under this set up. This distance directed a specific window diameter for the lowest magnification. It was thus essential in order to monitor the process to maintain a standard size of crystals and droplets. Therefore single salts were inserted in ESEM in the form of solid crystals ground to 200-300 microns in diameter. They were left to stabilise at considerably lower relative humidity than the expected equilibrium for 5 minutes. In the case of mixtures well-defined hemispheric droplets of 200-300μm in diameter were applied on the surface using a crystal pipette. Similarly the droplets have been left to stabilise at a considerably higher relative humidity than the equilibrium. The cold stage surface can be considered flat (180°) relatively to the size of the crystals and the solution droplets used in the experiment.
- The salts mixtures were analysed by EDAX. In order to use spot analysis for the identification of the involved elements without disturbing the process the wavelength of the X-ray had to stay constantly at 5nm.
- The hygroscopic behaviour of the salt mixtures has been predicted by ECOS.
- The cycles were monitored and recorded by the computer interface of the apparatus and by a video recorder.
- Each experimental cycle has been repeated once.

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[10] More on the use of ESEM can be found in Danilatos (1988) and Cameron (1994).

10.2 Results - Process description

The following results comprise a very detailed description of the process for each single salt and mixture separately, without any attempt to correlate it to the predicted equilbria, which will follow in the discussion part. The events are marked by the recorded pressure in Torr units while the respective value of relative humidity is found in the parenthesis. The corresponding values of relative humidity have been supplied by the manufacturer and depend on the initial standard calibration. Images of the processes as well as the calculated theoretical equilibria of the mixtures (ECOS) can be found in appendix VIII.

NaCl crystals became deliquescent at 4.7 torr (RH 71.7%) and without any further raise of pressure they developed a water film around them after a few seconds. The film remained stable and the crystal did not change shape. At 4.8 torr (73.4%) a droplet was formed spontaneously. It continued growing and became stable after gaining considerable size. No crystals were visible at that stage inside the droplet. We can assume that at this stage dissolution was completed. By decreasing the pressure the water droplet did not decrease in size and crystallisation occurred instantly at 3.5 Torr (RH 53.4%).

KCl crystals developed a water film on their surface at 5.2 Torr (80%), which remained stable for 3 minutes without advancing to further deliquescence. A water droplet was formed around the crystal immediately after the pressure was raised to 5.3 Torr (81.7%). The droplet continued growing without further raise of pressure in a steady rate. After the droplet size stabilised the pressure was slowly decreased to 5.0 Torr without any change on the droplet size. At 4.8 Torr (73.4%) the first crystals formed on the edge of the droplet and stabilised without any further crystallisation. The crystals grew steadily by decreasing the pressure and at 4.4 Torr there was no visible water on the crystals.

$CaCl_2$ is very soluble salt and at 5C remained in solution even at very low pressure. By maintaining the pressure down to 0.1 torr the temperature was slowly raised and crystallisation occurred after slow withdraw of the water at 25C. By increasing again the pressure at the above stable temperature the crystal became unstable at a range between 3.4 – 3.7 torr (around 15%) and then became completely dissolved at 4.5 torr (around 19%).

$MgCl_2$ is also a very soluble salt, which constitutes one of the main species of sea water. Again the temperature had to be raised up to 25C at 0.1 torr pressure to achieve crystallisation. The crystals were covered by a water film at 6.6 torr (28%) and the crystal started to dissolve (changing shape) at 7.1 torr (30%) without the formation of a droplet. A clear droplet was not formed until 7.6 torr (32%). The crystal effloresced again from the solution at 6.6 torr (28%).

$MgSO_4$ developed a water film at 5.9 torr (90%) and started slowly to dissolve. It did not grow a water droplet even at 6.2 torr (95%) and the crystal was still visible after 15 minutes. The crystal was left to dissolve completely for considerable time before decreasing again the pressure. Crystallisation occurred at 4.9 torr (75%) without complete evaporation of the water. The crystal continued to grow slowly and the solution was visible around it until 4.1 torr (63.4%). There were no signs of dehydration down to 1.3 torr (20%).

Na_2SO_4 became unstable at 5.9 torr (90%) by very fast periodical occurrences of water film around the crystal. A water droplet was finally formed and stabilised at 6.2 torr (95%) without however complete dissolution. The crystal was slowly dissolved at 6.3 torr (96.7%) after 6 minutes. By decreasing the pressure the solution became unstable again at 5.9torr (90%). After a crystal was formed from the solution small water droplets started growing and disappearing very fast on its surface until it was finally stabilised without any change in pressure. At 2.8 torr (43.4%) the crystal dehydrated by breaking up into smaller aggregate like crystals. The dehydration completed without any further decrease of pressure. There was no other change down to 1.8 torr (27.5 %). By increasing the pressure again a water droplet was formed instantaneously around the dehydrated aggregate at 4.3 torr (66.2%) and after a period of tense instability (droplet size) a large hydrated crystal formed at 4.5 torr (68.7%). The crystal increased its size by about a third in diameter between 4.1–4.5 torr.

CaSO4 although sparingly soluble developed a water film around it at 6.3 torr (95%). By increasing the pressure up to 6.4 torr (98%) the water film increased in size without though forming a clear droplet. It was not possible to increase more the pressure since another 0.1 torr step corresponds to 100%. Nevertheless the crystals were slowly dissolved after around 20 minutes. By decreasing the pressure in slow steps of 0.1 torr there were no signs of crystallisation until 4.9 torr (75%) when it occurred very fast and all the water was evaporated in less than one minute. Signs of dehydration occurred at 2.6 torr (40%) in the form of unstable water bubbles on the surface of the crystal without any change however in its shape or size.

$Ca(NO_3)_2$ was very unstable at 5C° and consequently temperature had to be raised to 20C in order to visualise clearly the equilibrium conditions. It developed a stable water film 8.2 torr (46.5%), which continued to grow steadily by increasing the pressure until it formed a droplet at 8.6 torr (48.5%). Whereas the crystals were previously stable at 20C° recrystallisation did not occur even at 25C° and very low pressure of 1 torr.

$NaNO_3$ crystals formed a water film at 4.8 torr that remained stable without further dissolution. They developed a droplet and began to dissolve fast at 5.0 torr (76.7%RH). The pressure was increased to 5.5 torr (85%RH) until the droplet stabilized its size and then it was decreased again in slow steps. The crystals effloresced from the solution steadily at 4.3 torr (66.3%RH). All the water was evaporated without further decrease in pressure.

Salt mixtures were introduced in ESEM in the form of solution. The solution for each mixture was prepared using the necessary amount (weight) of each salt to produce an equimolar composition and then adding water until all the salts were dissolved. ECOS predictions for the investigated mixtures can be found in appendix VIII.

$NaCl$ – Na_2SO_4 mixture was stable at 5C and 5.2 torr (80%). Both species crystallised simultaneously from the solution at 3.8 torr (58.4%). The mixture crystallized as amorphous brine, containing all the species as well as in a crystalline form where the two salts could be identified distinctively. At 3.3 torr (50%) the brine became momentarily unstable but clear signs of dehydration were observed at 2.4 torr (36.6%). Increasing the pressure the brine became unstable again at 4.5 torr (68.4%) by developing water bubbles, which evaporated immediately. At 4.7 torr (71.7%) a clear water droplet developed throughout the brine and grew very slowly. After 15 minutes the crystals were still visible with very few changes. Dissolution advanced faster by increasing pressure to 4.9 torr

(75%). The large droplet that was formed obscured visibility so it was impossible to determine if $NaSO_4$ was also dissolved. Spot chemical analysis on the droplet showed only Na and Cl. Instead of increasing the pressure the droplet was left to stabilize for a considerable and time and then the pressure was again decreased to crystallization relative humidity which revealed that $NaSO_4$ had not change shape or position. The droplet's size kept increasing by raising the pressure up to 5.9 torr (90%).

NaCl – $CaCl_2.6H_20$ mixture was inserted in the chamber at 5C and 5.2 torr pressure (80%). The first cubic crystals, identified as NaCl, formed at 3.1 torr (47%) where it remained stable for at least 20 minutes. The rest of the solution surrounding the crystals and containing both Ca and Na withdrew steadily by respective decrease of pressure. Water was still visible around the crystal at 1 torr. Maintaining the pressure low the temperature was increased slowly and finally total crystallization was achieved at 25C. $CaCl_2$ crystallised around NaCl in an amorphous shape. Temperature was increased again and $CaCl_2$ was dissolved at 5C^{o}. Keeping the temperature steady the pressure was increased back and NaCl was dissolved at 3,9 torr (60%). In order to test the experiment's temperature dependence pressure was raised to 4.2 torr where it was kept stable and temperature was decreased steadily. Crystallisation occurred instantly for both species at 25C^{o}.

NaCl – $CaNO_3.4H_2O$ mixture was initially stabilised at 5C and 4.9 torr (75%). A large NaCl crystal formed first at the centre of the droplet at 3.6 torr (55%). The crystal continued to grow until 3.1 torr (47.5%RH) when smaller $NaNO_3$ crystals began to crystallise from the edge of the droplet. They continued to grow steadily until 2.6 torr (40%). By decreasing the pressure further the remaining water containing Ca and Cl withdrew fast without crystallisation. At 1.0 torr (15%) there was still water surrounding the crystals. The remaining solution did not crystallise after increasing the temperature up to 30C^{o}. The temperature was decreased again to 5C^{o} and the pressure began to increase slowly. The solution took up water steadily and at 2.9 torr (45%) all the crystals began to dissolve. The pressure was maintained steady for 10 minutes at 3.3 torr (50%) and 3.6 torr (55%) were most of the crystals were still visible. Total dissolution was achieved at 3.9 torr (60%) where the droplet gained size fast and remained stable at 10 minutes.

NaCl – $MgSO_4$ mixture was inserted at 5C° and 5.5 torr (85%). The first crystal formation occurred on the edge of the droplet at 3.7 torr (56.7%) and it was identified as NaCl. Faster growth of the crystals began at 3.5 torr (53.4%) and stabilised at 3.3 torr (50%). Smaller crystals that contained Mg and S crystallised instantly at 2.9 torr (45%). The remaining solution which contained Mg and S as well some Na and Cl was crystallised spontaneously to an amorphous mass surrounding the NaCl crystals at 2.6 torr(40%). At 1.0 torr (15%) the $MgSO_4$ mass dehydrated progressively, changing colour and cracking to dendrites. Increasing back the pressure, liquid water was initially formed on $MgSO_4$ at 4.3 torr (66.2%) which can be interpreted as a sigh of hydration. The resulting solution expanded fast to cover NaCl crystal as well. At 4.6 torr a water droplet was spontaneously developed around the brine which kept dissolving progressively until 5.2 torr (80%).

NaCl – $CaSO_4$ mixture could not be inserted in the chamber in the liquid state because of the low solubility of gypsum. The difference in size between the droplet and the crystal would cause difficulties for imaging. Thus equal volumes of both salts were mixed and then placed dry on the cold stage. The mixture was introduced to the chamber at 5C and 3.9 torr. Increasing the pressure in slow steps NaCl developed a water film at 4.7 torr (71.7 %) and a droplet at 4.8 torr (73.4%) following the observed behaviour for single salt. The droplet attracted the surrounding gypsum crystals, which formed a cell around the NaCl crystal. The NaCl crystal was still visible after 10 minutes. By increasing the pressure NaCl was dissolved spontaneously at 5.4 torr (83.4%). Gypsum dissolved progressively at corresponding increase of pressure. Decreasing the pressure the water withdrew slowly and NaCl was spontaneously recrystallised at 3.6 torr (55%). Halite and gypsum crystals were now composing a unique amorphous mass. At 2.6 torr (40%) $CaSO_4$ dehydrated without any particular change in size. Rising the pressure back to 2.9 (45%) the brine became very unstable. Water bubbles were formed and evaporated spontaneously on the surface of the crystals mass. This explosive behaviour stabilized by shifting the pressure over the observed hydration value.

NaCl-KCl-$MgCl_2$ mixture was inserted in the chamber as liquid droplets at 5C° and 4.9 torr (75% RH). The first crystals formed at 3.8 torr (58.4%) from the edge of the droplet and they were identified as NaCl. The crystals grew to equilibrium and the remaining solution contained K^+-Mg^+-Cl^-. At a second stage at 2.6 torr (40%) the existing crystals changed shape and grew considerably. The resulting brine contained crystals identified as Na-Cl, K-Cl as well as K-Mg-Cl while the solution contained only Mg^+ and Cl^-. The remaining solution did not crystallize at 5C°. The water was progressively evaporated and total crystallization was achieved at 25C°. The aggregate crystals were identified as $MgCl_2$. By returning to 5C° the aggregate $MgCl_2$ were completely dissolved. The droplets containing the Mg-Cl solution were stable around the larger crystals without dissolving them at further raise of the pressure. At 2.3 torr (35%) a water droplet developed around the remaining crystals and dissolved them progressively.

Seawater sampled from Delos was inserted in the chamber at 5C° and 5.9 torr (90%). The first crystals effloresced from the droplet at 3.8 torr (58.4%) and they were identified as NaCl. $CaSO_4$ amorphous crystals also formed on the cubic halite crystals. At this stage crystallization was not complete. There was still water around the crystals containing Mg, S and Cl. At 3.3 torr (50%) the surrounding solution became unstable and partially crystallised to $MgSO_4$. After the pressure was decreased down to 1.9 were there was still visible liquid water. Increasing the pressure liquid water grew progressively around the brine. At 3.3 torr the surface of NaCl began to change, indicating water uptake. MgSO4 was completely dissolved at 3.9 torr. Spot analysis revealed that the solution contained some Na as well. The water film around NaCl kept growing steadily until 4.6 torr (70%) where it completely dissolved very fast. $CaSO_4$ crystals were still visible up to 5.9 torr (90%) when the slowly dissolved.

10.3 Discussion – Kinetic deviations

Single salts

Halite (NaCl) and sylvite (KCl) are both moderately soluble chloride salts. Their thermodynamic behaviour at 5C° consists of two phases, one as solid crystals and one as solutions. They are both found frequently on masonry materials. Halite was the most common salt sampled from the wall paintings of Delos both outdoors and indoors. K^+ ions were constantly present in the wet analysis but KCl was identified as a single salt in very few cases.

Both these chlorides became deliquescent at a lower RH than expected and they both developed a stable water film before becoming completely dissolved. NaCl developed a water film at 71.7%RH and dissolved at 73.4%, very closely to the value predicted by ECOS (74.4%) for 5C° temperature. KCl also developed early a water film (80%) but dissolved at a much lower value (81.7%) than the expected (86.4%). In both cases the crystals were completely dissolved at the RH of droplet formation although NaCl dissolved faster than KCl.

Both salts crystallised at a much lower value than the ERH as expected. NaCl crystallised spontaneously at 53.4% while KCl crystallised progressively from 73.4% to 67.5%. The delayed crystallisation of NaCl probably shows that a very high supersaturation is needed for crystal growth. On the contrary KCl that initially crystallised closer to the ERH followed progressive steps until total crystallisation, where solids and solution were in equilibrium.

Bischofite ($MgCl_2.6H_2O$) and antarcticite ($CaCl_2.6H_2O$) represent two very hygroscopic chloride salts. They do not frequently effloresce on masonry materials since they should remain in solution under average environmental conditions. Their presence increases significantly the time of wetness, accelerating the deposition of aerosols and affecting the phase equilibria of other less soluble salts. Bischofite consists a main crystal phase of seawater and antarcticite usually crystallises from seawater in colder climates.

Contrary to the results of ECOS none of these salts crystallised at 5C°. Bischofite dissolved at 25C° close to the predicted RH (31.8%) although it developed a water film at 28%, where it also crystallised. Antarcticite dissolved at 25C° and 19% RH, much lower than the predicted 26% and it was crystallised only at 0%RH. None of them dehydrated at 25C°.

In this case it was revealed that these very soluble salts remain in solution even at very low relative humidity. The predicted values supply this information, they leave nonetheless the freedom to assume that even very soluble salts should crystallise under extreme conditions of low relative humidity whereas according to the ESEM investigation this is not very likely. Bischofite that was always accompanying halite in the samples from Delos might be responsible for the wet appearance of the wall paintings even under at very high atmospheric temperature and direct solar radiation.

Less soluble salts do not represent a significant hazard for porous materials since their phase transitions occur at very high relative humidity. Hydrated salts though like epsomite and mirabilite can exist in more phases transferring the transitions equilbria at lower, more frequently occurring values of RH. Both these salts are commonly found on masonry materials and they are considered very aggressive. Epsomite has been identified by SEM in Delos wall paintings at room MD and mirabilite at room HG. Both salts dissolved very slowly at slightly lower values than the predicted. Although these values are still very high, ESEM investigation shifted the equilibrium towards more easily achieved conditions. As expected they both crystallised at much lower values.

Epsomite should dehydrate at three distinct steps, from heptahydrite (94%) to hexahydrite (88%), tetrahydrite (47%) and anhydrite (19%), decreasing progressively in volume. Instead ESEM revealed a progressive crystallisation from 75% to 63.4% during which solid and solution was constantly in equilibrium. However ESEM cannot give information for the crystal's identity. It was whatsoever obvious that Mg-SO_4-H_2O system presents a much shorter range of phase transitions than the thermodynamically expected.

Mirabilite dehydrated to thernadite as expected but at a lower value than the predicted. Hydration though occurred very close to the equilibrium. During hydration liquid water in the form of a bubble was instantaneously present revealing the dissolution of thernadite and the re-crystallisation of mirabilite from a very supersaturated solution. This observation, initially documented by Doehne (1994), explains the aggressiveness of Na_2SO_4 at conditions that do not favour the dissolution of mirabilite.

The observations on ESEM followed closely the predicted phase transitions of mirabilite. On the contrary the thermodynamic predictions of epsomite were not kinetically favoured. The absence of crystallographic analysis does not permit the identification of hydrated forms. Nevertheless morphological observations can reveal valuable information for the phase transition habits between hydrates. Mirabilite dehydrated intensively by cracking down to aggregates of considerably smaller size. The dehydration was followed by very dramatic change of the brightness levels on the crystal. The hydration of thernadite was marked by the presence of liquid water as well as the increase in volume. Alternatively, epsomite did not crystallise spontaneously from the solution but followed small steps that might be translated as a progressive formation of other hydrates as well.

Gypsum is one of the most common salts of masonry materials. It derives on masonry as the result of the dissolution of $CaCO_3$ from H_2SO_4, formed primarily by atmospheric SO_2. As such it is mostly found in urban and industrial environments. It can also be found in coastal sites since it constitutes one of the main species of seawater. Gypsum is sparingly soluble and as a single salt it does not represent a great hazard for porous materials. ECOS described very accurately the hygroscopic behaviour of gypsum despite the fact that it developed a water film earlier than the ERH (99%). The solution crystallised as expected lower than the ERH. It also dehydrated at a lower value than the predicted without dramatic change in shape or size.

Nitrocalcite ($Ca_2(NO_3)_2.4H_2O$) also results from the interaction between $CaCO_3$ and atmospheric NO_2 in urban and industrial environments. It was also identified in Delos during May 2003 although it derived from biologic sources rather than anthropogenic. Contrary to ECOS calculations nitrocalcite did not crystallise at 5C°. It remained very unstable during changes in temperature which revealed its strong temperature dependence. At 20C it followed closely ECOS predictions for dissolution but it became unstable again during crystallisation.

Nitratine ($NaNO_3$) is a moderately soluble salt that does not form hydrates. Its behaviour was accurately described by ECOS. As most other salts it developed a water film earlier (73.4%) than the ERH (77.6%) and dissolved after forming a droplet (76.7%). It crystallised as expected lower than the ERH at 66.2%.

Overall ECOS gave a fairly accurate description of the equilibrium conditions of single salts. Very soluble salts presented a strong dependence on temperature, which was not predicted by ECOS and hydrated salts did not followed all the dehydration and hydration steps. As expected the CRH was significantly lower than the predicted ERH.

Salt mixtures

$NaCl-Na_2SO_4$ is a commonly found mixture in buildings materials. $Na-Cl-SO_4-H_2O$ system constitutes the main composition of chloride depleted marine aerosols and as such it contaminates directly buildings found in industrialised and urban coastal regions. The interest of this system lies in the presence of a common cation in the potential species and in the influence of NaCl on the hydration and dehydration of Na_2SO_4. The presence of NaCl delayed considerably $Na_2SO_4.H_2O$ formation. Both salts crystallised simultaneously at 58.4% RH while theoretically Na_2SO_4 crystallisation should start at 96% and be completed at 75%, while at the observed value it should be already dehydrated.

Previous results revealed that under the same conditions Na_2SO_4 alone crystallises at 80%. On the contrary NaCl crystallisation although delayed against the theoretical prediction (75%) was slightly accelerated by the presence of Na_2SO_4 since, as a single salt, it crystallised at 53.4%. Dissolution started at the recorded RH for single NaCl but it was suppressed probably because the NaCl initial solution dissolved some of the Na_2SO_4 as well. Total dissolution of NaCl was finally achieved at the theoretical value. It was not however obvious whether Na_2SO_4 was completely dissolved at a lower RH than the observed, although ECOS successfully predicted the start of dissolution at a lower RH corresponding to the complete dissolution of NaCl.

Dehydration of mirabilite to thernadite occurred at a surprisingly low RH (36%) while the predicted one was at around 64% and the one observed for single Na_2SO_4 at 43.4%. No assumptions can be made at this stage for the influence of NaCl in the delayed dehydration of mirabilite. On the contrary we can assume that hydration which took place between 68.4%-71.6% RH was more violent than the one recorded for single Na_2SO_4 because NaCl was also dissolved in the liquid water which was present during hydration, delaying the formation of mirabilite and resulting in aggressive instability.

Overall ESEM revealed a wider range of phase transitions for this system than the predicted one. ECOS produced a very clear picture of the events during the increase of relative humidity but failed to describe some kinetic anomalies during crystallisation and dehydration. Another feature that could not be described by ECOS was the aggressiveness of the hydration process, which might have serious implications for salt weathering.

ECOS predicted that the presence of $CaCl_2$ would accelerate the dissolution of NaCl. In this case the event was observed but earlier than predicted. Crystallisation of NaCl was delayed and spontaneous as for single NaCl but occurred at a lower RH as predicted by ECOS. Again a shift towards lower values was observed. Very soluble salts as $CaCl_2$ stay in solution for a wider range of RH than calculated by ECOS and this effect can be still observed for salt mixtures that contain these salts. Nevertheless the most interesting observation in this case is the influence of temperature that seems to have a dramatic effect on very soluble salts. ECOS although it described the general events presents here a limitation.

Similarly $CaNO_3$ delayed the formation of NaCl as predicted by ECOS but it did not crystallise at all at 5C. $NaNO_3$ also crystallised from the solution as ECOS informs us but considerably later than expected. It was not consumed though to nitrocalcite and halite but remained stable even in very low RH. Both $NaNO_3$ and NaCl were progressively dissolved from 45% to 60% as very accurately calculated by ECOS.

Again ECOS successfully calculates the presence of a salt that did not participate in the initial solution as well as the quantitative behaviour of the system towards dissolution. Both nitratine and halite were forced, by the presence of a very soluble salt, to dissolve at a lower RH than their equilibrium. Halite dissolved before nitratine as expected but it crystallised first contrary to ECOS results. The crystallisation sequence in this case was not accurate and occurred at much lower values. Halite crystallised at a very close value to the one it crystallised as a single salt. Natritine crystallised at a much lower value. It can be assumed that nitrocalcite had a stronger influence on nitratine than on halite. Still this case reveals the weakness of ECOS in predicting the crystallisation behaviour. The inability of nitrocalcite to crystallise at $5C^o$ agrees with its behaviour as a single salt but again it conflicts ECOS calculations that favoured the consumption of nitratine to nitrocalcite at around 40% RH.

$NaCl$-$MgSO_4$ is a mixture that was identified at Delos in room MD. The interest is similar to the mirabilite-halite mixture in the sense that halite is more soluble than epsomite, which in turn dehydrates at a higher relative humidity than halite's ERH. Contrary to the previous mixture the halite-epsomite system does not share a common cation. Alternatively, according to ECOS calculations, these species should exchange ions resulting to the initial crystallisation of mirabilite.

Despite ECOS prediction the formation of mirabilite was not kinetically favoured. The solution crystallised initially as halite at a higher RH than the observed as a single salt. The crystallisation of halite at 56.7% was not the higher so far observed. When mixed with mirabilite that is less soluble than epsomite, halite crystallised at a higher RH, while when mixed with more soluble salts it crystallised at a lower RH. We can assume that the crystallisation of halite is influenced by the solubility of the other component. More specifically the more soluble the one component the later crystallisation occurs for the other. This kinetic observation is in accordance with the thermodynamic calculations.

According to ECOS epsomite should not crystallise at all from the solution. Instead hexahydrite should crystallise initially. Nevertheless mirabilite that should crystallise at the expense of epsomite did not but unfortunately there was no way to investigate the identity of the Mg-SO_4 crystal that formed first. Contrary to mirabilite, hexahydrite did not crystallise simultaneously with halite. Probably the presence of common ions has a kinetic influence on crystallization from mixtures. Hexahydrite crystallised later than halite opposing the predictions of ECOS at a value where it should theoritacally exist as starkeyite (tetrahydrite). The $MgSO_4$ crystals grew progressively, along with the decrease of RH, while they were constantly in equilibrium with the solution following the behaviour of single salt.

Dehydration occurred at a very low RH (15%). At this value ECOS predicted the transition from starkeyite (tetrahydrite) to kieserite but since this would be kinetically unfavourable we can assume that the dehydration event was more likely the transition from hexahydrite to starkeyite or an accelerated crystallisation of kieserite bypassing the intermediate step. Sidesteps to kinetically more favourable forms have been usually observed in relevant studies but the influence of other salts has not been investigated

(Mullin, 1993). It would be tempting to relate the differences that were observed during the dehydration of $MgSO_4$ as a single salt and as a component of a mixture to the presence of halite but the present set up does not supply the necessary crystallographic information. Nevertheless qualitatively ESEM revealed a kinetic preference to more simple processes than those thermodynamically expected.

Hydration was again suppressed by the presence of halite as in the case of $NaCl$-Na_2SO_4 mixture. Liquid water was initially observed on $MgSO_4$. The solution that should normally crystallise to a hydrate dissolved some of the halite. Both salts were spontaneously dissolved at 70% close to the observed ERH of halite. Nevertheless the droplet kept growing until 80%, close to the upper limit predicted by ECOS and much earlier than the observed dissolution of single $MgSO_4$. It was obvious that the hydration of $MgSO_4$ accelerated the dissolution of NaCl, which in turn accelerated the dissolution of the hydrated form of $MgSO_4$. ECOS again followed very closely the behaviour of this mixture during the raise of RH.

The case of $CaSO_4$-NaCl mixture is very common in urban coastal areas and has been extensively discussed in literature. It is well known that the presence of NaCl increases the solubility of $CaSO_4$, which as a single salt is sparingly soluble. ECOS results verify the above statement as well.

The observation on ESEM however revealed a completely different and very interesting behaviour. The presence of gypsum delayed considerably the dissolution of halite, which occurred spontaneously at 83.4%. The implication of this observation for salt weathering is that this mixture appears less aggressive than expected (smaller range of phase transitions). We could argue that the presence of liquid water that surrounded the crystal at its observed ERH definitely dissolved some of the gypsum as well. This far ECOS calculation is accurate. However that has not been predicted by ECOS is that the presence of dissolved gypsum in the solution suppressed the complete dissolution of halite, which now needed more water uptake to reach the equilibrium. After this stage it was obvious that gypsum began slowly to dissolve in the halite solution though as expected complete dissolution acquired much higher RH.

Halite crystallised again from the solution at the CRH that has been registered for single salt. The observed relationship between the solubility of the second component and the CRH of halite was not verified for $CaSO_4$-NaCl mixture. The reason was that gypsum was remotely dissolved and the solution was mainly comprised by halite. The concentration of each component plays a very significant role in its behaviour. ECOS in this case supplies valuable information since in real conditions the salt mixtures are not ideal as in this experiment.

Although the discussed mixture presented moderate behaviour during dissolution and recrystallisation the resulting brine became explosively unstable during the hydration of the anhydrite. The water droplets that appeared all over the brine close to the predicted value of hydration probably dissolved some halite suppressing the crystallisation of gypsum and creating violent instability. This observation gives us the liberty to assume that the aggressiveness of this mixture is more likely related to lower values of RH capable of causing the formation of the anhydrite than to the decrease of gypsum's DRH.

One could also argue that a much larger ratio of halite/gypsum would be necessary to shift the ERH of gypsum at RH values frequently encountered at moderate climates. In this case the participation of gypsum in weathering would be questionable. Despite the increased intensity of gypsum's crystallisation, its low concentration would diminish its effects. Furthermore the observed delay of halite's dissolution supports the argument that the mixture is harmless at the upper limit of its equilibrium. Alternatively the values observed for the dehydration and hydration of gypsum can be very easily achieved especially in conditions of direct solar radiation and air movement that cause intense evaporation. The explosive state of the brine that caused spontaneous and persisting dissolution and re-crystallisation cycles appears definitely more violent.

Carnallite ($KCl.MgCl_2.6H_2O$) is a very soluble binary salt that crystallises from sea water. Since the concentration of K and Mg is very low in seawater a mixture of equal quantities of halite, sylvite and bischofite was used to monitor the interesting interaction of these species. The interest of this mixture lies in the wide range of solubility of these three single salts and the predicted formation of a binary salt. The sulphates, which also crystallise from seawater, were not included because gypsum is supposed to crystallise very early without interacting with the other salts and epsomite's capability to hydrate would cause very complex behaviour, difficult to follow. Although the concentration of Na and Cl in seawater is determinedly higher it was anticipated that the above mixture would reveal the interactions that take place on the surface of halite and whether these interactions are responsible for the remote thermodynamic behaviour of seawater from pure halite solution.

According to ECOS sylvite and halite should crystallise in their normal sequence but shifted towards lower values due to the presence of bischofite. Bischofite in turn shouldn't crystallise at all while along with sylvite should be consumed as carnallite. The observations on ESEM provide us with an alternative prospect. Halite initially crystallised from the mixture at a higher value than the one observed for single salt. This behaviour agrees with previous observations where less soluble salts, when present in the mixture accelerate the crystallisation of halite, while more soluble salts delay it. In this case though both a more soluble and a less soluble salt were present. We can assume that since sylvite was still in solution during halite's formation its influence prevailed. Sylvite's crystallisation was considerably delayed, initially due to the presence of halite and then due to bischofite. We could assume that if bischofite was absent, sylvite would crystallise together or immediately after halite.

Contrary to what was predicted sylvite was not consumed to carnallite and as a result the remaining solution contained only Mg and Cl. The absence of carnallite agrees with experimental observations (van't Hoff, 1905). In accordance with the result for single salt the Mg-Cl solution did not crystallise at all at 5C. As in the case of pure Mg-Cl solution crystallisation occurred only at a much higher temperature and at conditions rarely encountered in reality. This observation has serious implications for the behaviour of seawater. Since carnallite's formation was not kinetically favoured the remaining ions form a very soluble salt that remains in solution even at very low RH. In the same way Mg-Cl took up water vapour very fast covering the rest of the salts, which started dissolving progressively at a much lower RH than expected. The argument that a film of chlorides constantly covers seawater brines (Cheng *et al.*, 1988) is reinforced by these results. This effect might be responsible for the damp appearance of objects contaminated with sea salt even under direct solar radiation. We can assume that stronger presence of halite would shift the observed behaviour towards higher values of relative humidity more frequently encountered in real conditions. But can we attribute seawater aggressiveness solely to this kinetic deviation?

Sea salt is mainly comprised by Na and Cl and its interaction with water vapour is supposed to follow closely the behaviour of halite. It has been found in laboratory experiments that sea salt constitutes a more aggressive agent of weathering than pure halite (Rivas *et al.*, 2003). Although the complex composition of sea salt has been held responsible there is no experimental evidence to support it. The quantitative predominance of NaCl directs that at least thermodynamically seawater shouldn't present any different behaviour than that of pure NaCl solution.

Seawater is a very complicated mixture composed of over 70 elements. Its primary constituents only can form a great number of single, binary and hydrated salts. ECOS calculations reduce their numbers to 10. More specifically ECOS predicts the formation of gypsum (82.5%), halite (73%), hexahydrite (69.4%), gorgeyite (64.5%), sylvite (58.6%), carnallite (51.4%), anhydrite (49.5%), starkeyite (46.2%), bishofite (31%) and kieserite (17.9%). This wide range of phase equilibria could be interpreted as very hazardous for a porous material, considering that there isn't a pragmatically plausible range of relative humidity to "deactivate" this mixture. On the one hand we should argue that halite dominates quantitatively and thus a very small range should be avoided but on the other hand the significant measure for damage is crystallisation pressure and not volume. A more realistic approach should consider which of these transitions are kinetically plausible. Nonetheless ECOS provides at least the information that seawater contains species in adequate concentrations to interact with each other and result to species with very different hygroscopic behaviour. More simply that seawater should not be considered as a halite solution.

ESEM investigation in this case can go further identifying the kinetic details that dominate the behaviour of seawater and could not be predicted by thermodynamics, as well as their rate. Several single salts that crystallise from seawater as well as mixtures of them have already been investigated revealing very interesting remote behaviours. We can mention the very slow rate of dissolution of gypsum, its influence on the dissolution of halite, the explosive behaviour of hydrates and its effect on halite, the inability of some very soluble salts to crystallise and the absence of some thermodynamically expected species. Linking these single observations to seawater would result in an image even more dramatic and complicated than ECOS predicts. Nevertheless seawater did not present such complicated behaviour. Halite crystallised earlier than what has been observed as a single salt and a much slower rate. This behaviour was expected since the solution contained less soluble salts as gypsum. It is not quite clear why this happens but we can assume that some gypsum had already crystallised, seeding the solution with nuclei, which serve as crystallisation sites for halite. Gypsum was identified on the surface of the large cubic halite crystals as small amorphous aggregate. Epsomite crystallised slightly later than in the halite-epsomite mixture, probably delayed due to the presence of Mg-Cl. There were no signs of sylvite or carnallite formation. The remaining Mg-Cl solution did not crystallise at all. On the contrary it took up water vapour at a very fast rate dissolving, as was identified by spot analysis on the solution, some halite as well. The dissolution of halite started earlier than expected. A water film was initially developed around the brine. Apart from the faster water uptake of Mg-Cl we can assume that Mg-S hydration enhanced the dissolution as it did in the halite-epsomite mixture. Gypsum remained insoluble even after the droplet stopped gaining size.

ECOS calculation revealed that sulphate is not all consumed in gypsum. The remaining sulphate should crystallise as hexahydrite. There was definitely crystallisation of an Mg-S salt but it was not possible to identify which. Its formation was accurately predicted after the formation of halite. It was not quite clear whether its presence accelerated the dissolution of halite but undoubtedly it participated in the progressive phase transitions of the brine affecting the overall equilibrium.

Removing gypsum from the initial composition doesn't change the thermodynamic potential of the rest of the species. As was witnessed gypsum doesn't play a significant part in the equilibrium of the mixture. It was quite clear that once crystallised gypsum stays in its solid form despite the presence of other very hygroscopic salts.

The decisive factor however in sea salt's different behaviour and probably its aggressiveness seems to be the presence of $MgCl_2$. Carnallite that would normally bind

Mg and Cl did not crystallise as in the case of halite-sylvite-bischofite mixture permitting the remaining Mg-Cl to stay in solution. It was anticipated that the strong presence of halite would decrease the solubility of bischofite, as verified by ECOS, but surprisingly bischofite did not crystallise even at conditions rarely encountered in reality. It has thus been demonstrated that sea salt brine maintains a water film. The presence of bischofite also enhanced the water uptake during increase of RH and as a result dissolution occurred earlier than expected.

Although seawater follows a more modest behaviour than predicted by ECOS it was quite obvious that it was activated over a wider range than pure halite. This investigation was limited in respect of realistic environmental conditions. Further research including fluctuating temperature as well would reveal more interesting observations since some of the species are strongly influenced by it. It was not of course possible to identify why sea salt is more aggressive than pure halite but we must undoubtedly relate it to its thermodynamic properties. On the other hand one could argue that more realistically when seawater contaminates a porous material, the salts are progressively withdrawn from the system, as the remaining solution recedes, and consequently they do not interact. Nevertheless this argument could be used alternatively, as sea spray is constantly deposited on the surface of the material providing fresh solution that might interact in more complicated ways with the isolated species. Another area of study which will reveal more about the ionic interactions of seawater in response to the observed phenomena by ESEM is the multi-salt modelisation of crystallisation pressures, which will be more closely related to the generation of damage.

Summary - Implications

Overall the dramatic kinetic deviation was clearly depicted by the ESEM investigation. The critical supersaturation needed for crystallisation was in all cases reached at surprisingly low relative humidity. As it was stated by ECOS developers the thermodynamic model predicts "an upper limit of critical humidities". Thus initially we can argue that there is a wider range of relative humidity where phase transitions will occur. On the other hand separating CRH from DRH can be interpreted, in terms of preservation, as a more limited chance of damage since when relative humidity fluctuates around one of the two phase transitions will not occur. For example if halite was the only salt present in Delos where most of the time relative humidity fluctuates around its ERH (75%) we should not expect any damage.

In most cases a water film was developed on the surface of the crystals before the formation of the droplet. Usually it took place well before the predicted DRH. Although we cannot regard the formation of film as the critical relative humidity in some cases it enhanced or lead eventually to dissolution. With only an observation value we can say that the more soluble salts were more influenced by the film formation than the less soluble ones. It was also evident that this initial deliquescence was induced by surface asperities. It is rather reasonable to assume that the crystal morphology plays an important role in deliquescence. In this respect different crystal habits of the same salt might present different behaviour. For example we can assume that the halite whiskers found it the upper area of MD will dissolve faster than the dense halite crusts of room HG.

Single salts equilibrium conditions can be easily followed since the phase change can be visually interpreted. The case of hydrated salts introduces the limitation of EDAX to identify specific salt phases. In some cases dehydration and hydration could be identified as brightness changes, cracking, presence of liquid water or generally instability. Other methods like RHXRD (Steiger, 2000) provide more solid evidence of phase transition without the advantage of imaging. In other cases the absence of visual signs did not permit any assumptions. Generally hydrates presented more complicated behaviour. It was obvious that hydration was suppressed or did not occurr at all while dehydration took place at lower values than the predicted. It was also obvious that in the case of multi hydrated salts some phases were bypassed.

When single salts maintained a rather predicted behaviour salt mixtures presented significant deviations. The weakness of the analytical identification of ESEM was even more dramatic in the case of salt mixtures. Elementary analysis alone identified the ions that composed each phase but only assumptions could be made for the identity of the salt. Visual evidence like crystal morphology did not provide much help since in most cases the final product was amorphous and only NaCl presented a tendency to maintain its cubic form. Nevertheless more systematic elemental analysis throughout the process offers an excellent tool to track qualitatively which ions participate in the crystallisation and which compose the remaining solution. The beam's size that depends on the gas pressure was very significant for clear imaging but spot analysis was plausible on a rather large surface. Mapping, which is also provided by the analytical interface, can serve only in stable phases of the process because it demands several minutes to complete. Summarising the results it can be stated that more soluble salts induced the deliquescence of less soluble ones, which in turn suppressed the crystallisation of the first. The presence of hydrates in the mixture was determining. The hydration process was explosive in the presence of other salts. It was quite obvious that the presence of liquid water during hydration influenced adjacent species which in turn did not permit the completion of the process resulting to a very aggressive instability. Also the exchange of ions did not always occur while some expected phases never crystallised. These deviations resulted in either more or less aggressive conditions although their behaviour in terms of preservation was not always evident.

In the context of determining the critical limits for phase changes, ESEM can provide very useful information on the appropriate use of ECOS but more experimental work is needed in order to reach more solid conclusions. Future research should involve a wider variety of species, the influence of temperature, more realistic environmental cycles as well as the influence of the crystallisation site. The combination with other techniques, especially crystallographic, will make ESEM a very powerful tool in equilibrium thermodynamics research shortening the gap between theory and application. The next step in phase transitions *in-situ* investigations should definitely focus on the critical conditions for supersaturation inside the pore space and the calculation of the resulting pressures (Putnis and Mauthe, 2001; Steiger, 2005).

CHAPTER 11. Salt spray weathering simulation

11.1 Introduction

This project fails so far to embody the particularities of wall paintings. The sequential drilling gave some indications on salts accumulation in the external layer, which can not however be attributed to the hydraulic discontinuity between the layers, since similar trends have also been observed in non layered materials (Warke and Smith, 2000). The explanations attempted so far on the generation of distinct weathering patterns affecting primarily the paint layer (flaking) were based on the thermodynamic properties of the salt mixtures found at the particular areas and over the recorded environmental cycle.

The ongoing work on moisture and salts movement in layered porous materials has clearly demonstrated the accumulation of moisture between layers of different pore structure (Pel, 1995). This kinetic effect is taken for granted as a weathering hazard for wall paintings whereas it does not describe the damage mechanism. In order to investigate the weathering morphology that usually appears on wall paintings and thus define the parameters that caused it, a more descriptive experiment is needed.

Among the usual weathering patterns, like pitting, flaking, sand disintegration and scaling that appear in mortars and stones, the most important for wall paintings are those which affect directly the external layer. Its importance is of course attributed to the fact that it carries or encapsulates the painting and the finishing details. The mechanical impoverishment of the bearer layers endangers of course the preservation of the paintings but usually, if the external layer maintains an adequate resistance, it can be conserved or even restored. On the contrary the pulverisation or flaking of the external layer puts irreversible restrictions in the application of most first aid, maintenance or restoration treatments, aiming to consolidate or desalinate the structure.

The external layer is also susceptible to superficial treatments, like fixation and gauzes attachment that paradoxically aim to protect them against the weakening of the bearer layers. The various conservation techniques that have been applied over the years, successful or not, copy the techniques applied on stones, undermining the multilayer nature of wall paintings and similar structures. It would be unfair to impute this to a deliberate choice of the conservator or lack of expertise, when research, which predominantly sets the guidelines, considers visibly common weathering patterns of stones and renderings as a result of similar weathering mechanisms. Provided that no generalisations can be made, one should at least consider the "white wash" layer as a highly vulnerable and individually weathered element of a structure. Research has got to focus on the particularities of wall paintings as ICOMOS recently declared[11] (ICOMOS, 2003).

The external layer is usually composed of a lime wash without aggregates. The pigments are mixed with it before it dries, in the case of frescoes, or applied on it by another medium after it dries. In either case, it is usually applied by brush and it hardens, after interaction with atmospheric CO_2, to a fine thin $CaCO_3$ film of a few tens of microns, which does not need further polishing. Normally it has a very low porosity, though the application, drying and hardening conditions influence strongly the generation of microcracks.

Apart from the aesthetic function of wall paintings or finished renderings, external lime wash layers are used as protective agents as well. Their low porosity prevents the penetration of rain and accumulated particles. Nevertheless the application of lime washes is easy and inexpensive, in other words lime washes are expendable. It is still today a tradition in the Cyclades and other parts of the Mediterranean to lime wash the buildings every spring. Apart from the symbolism, it is apparent that this tradition has a practical purpose. The decay rate in the Cyclades, induced by salt spray and rapid evaporation, due to intense winds and direct solar radiation, is amazingly fast. It is striking to notice that lime washes that have been applied in the spring, are already exfoliating in September, and it is surprising that there are still preserved external wall painting layers in unsheltered areas of Delos. Considering additionally that white wash flaking is also present in the sheltered areas, which receive less sea spray and suffer less rapid evaporation effects, it is evident that the investigation of this hazard is far more complex than understood so far.

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[11] Article 5: "....Any intervention in the monument must take into account the specific characteristics of wall paintings and the terms of their preservation...."

The decay mechanism of wall paintings and white washes in particular is still poorly investigated. The basic salt weathering principles can be applied in any porous material but the nature of wall paintings itself demands a more holistic approach. A simple observation of weathered wall paintings immediately signifies some particular patterns of damage. Their particularity lies exclusively in the sequential layer loss or detachment of material. As mentioned above, this pattern has been attributed to the accumulation of moisture between layers without any particular consideration. Similar stone weathering patterns like flaking do not provide any particular insight in the understanding of wall paintings salt weathering since it has been demonstrated that it can be reproduced independently of the orientation of the bedding planes (Rivas *et al.*, 2000). In other words preexisting fissuring parallel to the exposed surface that would constitute a cause of hydraulic discontinuity or better of accumulation of moisture between the bedding planes, doesn't seem to play any significant part in the generation of flaking.

In this area of study, accelerated weathering tests, as a means of reproducing specific weathering patterns, have proven valuable tools in the investigation and understanding of particularly complex processes (Rodriguez-Navarro *et al.*, 1999; Rivas *et al.* 2003). Several organisations have elaborated numerous standards on salt weathering testing. The most common salt weathering tests are those applying full or partial immersion of the samples in a specific solution and drying, such as RILEM V1-V2 (1978). These standards however address processes where water and salts are supplied by ground capillary penetration and cannot explain salt weathering associated with sea spray deposition above the evaporation zone (Rivas *et al.*, 2000). The generalisation of the weathering process neglects significant kinetic deviations deriving from various parameters such as the solution supply or the substrate's nature. By modifying the basic guidelines of the standardised procedures or implying new elements we can successfully address the particularities of any special case like specific salt mixtures (Robinson and Williams, 2000) or specific environmental conditions (Goudie and Parker, 1998).

In order to address more specifically salt weathering in coastal areas a series of more specialised tests have been developed, applying salt spraying and environmental cycles (BS 14147; ASTM B117; DIN 50021). Nevertheless, most of these standardised procedures are useful for comparing natural or treated stones resistances to salt spray but fail to reproduce some typical damage patterns of natural and building stones in coastal sites like honeycomb. A suitable explanation is that the long spraying periods of these standards resemble immersion conditions. A more recently published standard, based on a design by Auger (1989), implying more frequent and brief spraying under constant temperature reproduced more accurately the coastal environment. The key factor for this, as was clearly shown in a comparative study between this technique and RILEM V1 (1978), is the equilibrium between wetting, mobilisation of salts and drying (Cardell *et al.*, 2003). The frequent spraying and the short drying cycles allow the samples to absorb the solution gradually causing subflorescence near the surface (Rivas *et al.*, 2000; Birginie, 2000). This kinetic effect could be very useful in the investigation of wall paintings weathering, provided that it is governed by different layers permeability. Furthermore the application of this test using different salt spray composition showed that sea water produced intense scaling on granite samples, while sodium chloride alone failed to produce any visibly significant damage apart from superficial efflorescence and some weight loss which was translated as internal sand disintegration (Rivas *et al.,* 2003). This important observation, apart from dictating the use of sea salt against pure sodium chloride in similar tests, as the authors concluded, poses some far more serious implications since the thermodynamic behaviour of sea water and pure sodium chloride is not that different.

As we already discussed in chapter 9, the presence of other salts modifies the solubility of sodium chloride, but as was predicted by ECOS and confirmed by ESEM the amount of other ions apart from sodium chloride in sea water ($14\%w_{salt}$) is thermodynamically insignificant to cause this variant behaviour. This demonstrates again the key role of kinetic factors as well as the need for a combined approach. We can only speculate that the various species contained in sea water accumulate fragmentally in depth resulting in more destructive combinations at certain areas. More specifically we can focus on gypsum, which should crystallise first and thus near the surface and can be very destructive in combination with specific ratios to halite. On the other hand we also speculate that the hydraulic discontinuity between the layers might also influence the fractionation of the species.

Especially in the case of marine aerosols and wall paintings we have to add the fact that salts and moisture penetrate the material from the external layer inwards. We can safely make the assumption that a salt solution tends to evaporate when proceeding from a layer of fine pores to a layer of larger pores just as it does when moving from a small capillary to a larger one or from the pore throat to the pore chamber (Benavente *et al*, 2003). Since the movement of the solution is governed by the specific permeability of the material and thus by the porosity and the pore radii, which in turn dictates the position of crystallisation, the above assumption is very significant for the generation of damage between layers. On the other hand during drying, sea water probably leaves behind trapped islands of various mixtures that can generate higher supersaturations than expected. Nonetheless in order to distinguish this mechanism from common scaling (flaking), it would be necessary to test simultaneously both lime washed and not lime washed mortars of the same composition and porosity.

Trying to investigate salt weathering by applying a test that normally addresses homogenous material to layered ones draws instantly a basic argument: comparability. Obviously there are no counter arguments since there no other similar attempts have been reported to date. Nevertheless we should argue that the purpose of this experiment is not the comparison between the resistance of different layered materials but the identification of the parameters that influence the reproduction of a specific weathering pattern. Modifying standard procedures for the same purpose is common in this area of study; unfortunately though in this particular case there are no standards to modify. Standards evaluating the resistance of paint and varnish films to salt spray such as ISO 7253 and BS 3900F12 offer some useful guidelines on the evaluation of damage but the rest of the process addresses a totally different weathering mechanism (corrosion). Thus, the experimental design for this purpose should be composed by parts of some basic standards and modifications from the literature and original parts defined through trial and error. The application of the lime wash layer presents some limitations in terms of reproducibility. Nonetheless the thickness and the pore structure of the film can be evaluated microscopically by cross sections.

Another limitation for which accelerated weathering tests are usually criticised is scaling (Viles, 2001). However the application to conservation studies presents some serious advantages against geomorphology and materials science. Time and dimensions of weathering patterns of the tested samples are much closer to heritage structures decay than to geomorphologic features. Additionally the damage caused on the samples represents a significant risk in the scale of wall paintings. Similarly whereas in materials science the results have got to be interpreted in order to serve for the evolution of new materials or modern structures, in heritage studies the presence of the damage itself dictates the unfavourable parameters that caused it. A limitation however is that heritage materials are already weathered. The implications of this limitation have not been investigated thoroughly.

11.2 Methodology

Experimental design

- Chamber design: the chamber is composed of a single spraying nozzle placed in one of the perpendicular sides of the rectangular cabinet. The nozzle is connected externally to the solution and the compressed air containers by plastic tubes. The flow is controlled by electric solenoids connected to an electronic timer producing approximately 2 *l/h*. An electric lamp is used as heat conductor connected to a thermostat, probed inside the chamber, for temperature control. A ventilator creates a circular air draft towards the abductor exit. The ventilator produced a 10m/h current which corresponds to intense turbulence. The electric parts of the lamp and the ventilator are insulated from the salt spray (specifications app. X.D).
- Environmental cycle: The environmental cycle has been composed by 1 minute of spraying and 29 minutes of drying while the temperature was maintained constant at 40°C. This cycle, as proposed by Auger (1989) and standardised by AFREM (1996), represents approximately one week of intense weathering under the southern European climate (sic). We must argue that this cycle has been chosen for reasons listed above and we do not adopt this assumption since we are not interested in scaling the results in real time. The experiment should go on for 15 days of continuous simulation (760 cycles). This time is considered adequate to extract readable results presuming that mortars are more susceptible than granites that have been tested under the same conditions.
- Salt solution: Artificial sea water, representing pure marine aerosol, has been chosen for reasons listed above. The composition of the solution can be found in App.X.B.

- Samples: two types of mortars have been tested. Both types originate from the same matrix composed of 3:1 sharp sand and lime (app.X.B). The samples named *type A* are plain and the samples named *type B* have been lime washed. The sides of the samples have been insulated by liquid latex (app.X.B) in order to ensure contamination and evaporation from the exposed surface only.
- Holder: the Perspex holder has been placed perpendicularly facing the spraying nozzle at a small angle of 15-20°. The samples were placed in boxes of equivalent dimensions (fig. IX.2).
- Samples examination techniques:

i) *Visual evaluation*: evolution of the exposed surface decay in a stereomicroscope. Unfortunately there is no standardised terminology to describe microscopic observations on wall paintings weathering as in stones (Fitzner *et al.*, 2000). The observations focused on the lime wash layer cracking, flaking and loss and differences in the type, the generation and evolution rate of patterns between the two types of mortars.

ii) *Salts depth distribution*: Microprobe-EDX mapping on cross sections perpendicular to the exposed surface. This investigation focused on the different penetration rate of salts during the test between the two types of samples and the identification of any fractionations.

iii) *Weathering rate*: weight loss measurements. This investigation has only been used as a comparative measure between the two types of samples and has not been scaled to real conditions.

iv) *Weathering pattern*: apart from the visual evolution of decay forms, particular interest focused on the microscopic evolution of the layers interface and pore system in cross sections.

v) *Salts morphology*: SEM-EDX surface and cross sections imaging and analysis. This investigation aimed to identify particular forms like whiskers that might influence the process.

Calibrations and adjustments

The construction of the chamber and the experimental set-up proved to be more than challenging. The first adjustment that had to be ensured was the regular operation of the spraying device. The nozzle represents an interchange where the gas and the liquid mix to produce, with the help of a rotating thread, a fine spray. According to the constructor's technical papers (Spaying systems Co, 1997) the flow of the gas through the nozzle builds an opposite pressure on the liquid's pipe that drives the liquid to the nozzle. Thus the liquid does not have to be pressurised. Through trial and error we discovered that this could be applied only in continuous spraying conditions. The gas pressure builds initially an opposing load to the air that is already contained in the liquid's pipe, inhibiting the suction of the liquid. By forcing the liquid through the pipe we achieve equilibrium but when the gas pressure stops the liquid retreats permitting an opposing gas pressure again. Furthermore the consumption of gas in this case is much higher and as a result we would have to change the gas tank almost everyday.

Thus we had to exert an opposing pressure to the liquid as well. Air pressure in the liquid tank required elaborate equipment and time-consuming set up that we could not afford. Alternatively we managed to balance the pressure equilibrium by placing the liquid tank higher than the nozzle. In order to avoid dripping during the stop of the gas pressure we had to control the flow of the liquid as well. This was achieved by synchronising the flow of the liquid and the gas through the solenoids using an electronic switch. The only problem that occurred with this set up was that while the pressure of the gas could be controlled and maintained constant from the valve, the pressure of the liquid was progressively lowered due to its consumption. The pressure of the liquid depended on the height and the surface area. Although the area of the tank was wide enough we had to maintain the height of the liquid to a specific range in order avoid deviations of the spraying volume and thus the tank was filled regularly with solution.

By maintaining the pressure of the liquid constant we could control the volume of the spray by adjusting the gas pressure from the valve. It was essential to achieve initially homogenous spraying for all the samples. The nozzle's diaphragm was specifically chosen to produce plain round spray. It was adjusted to a wide radius which reached the cross section of the chamber (40X40cm) at approximately 50cm. Obviously the sample holders had to be placed above this distance to achieve homogenous spraying. Nevertheless by placing the samples too close the effect of spraying due to the high volume of spray was lost and by placing it too far we would risk insufficient deposition. It was finally decided by trial and error that the suitable conditions were 70cm distance from the nozzle at 2bars(30psi) gas pressure. The diagram of the tank is depicted in fig.

11.1. The even distribution of the aerosol and the homogeneity of deposition have been tested by SEM-EDAX mapping of the surface of reference samples (App. IX.A,B). In order to achieve better imaging we also tested the deposition on non porous adhesive surfaces (App. IX.C). The reference samples have been placed in random positions on the samples holder.

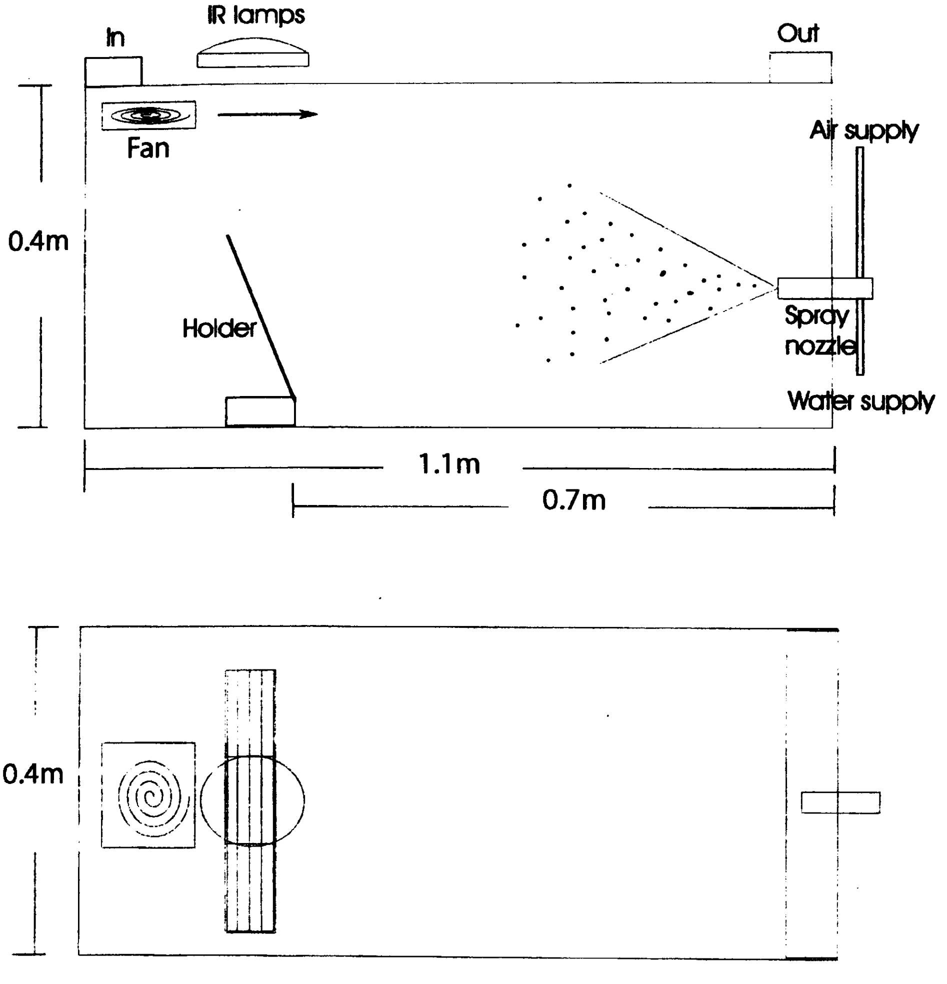

Figure 11. 1 Chamber diagrams

Evidently the time of spraying was also an important parameter controlling the amount of spray deposited on the samples. This parameter has a two fold effect, the amount of water absorbed by the sample that controls the penetration depth and the drying process, and the amount of salt that indicates the number of cycles needed for damage to occur. It has been calculated by weight measurements that according to the above set-up each sample receives approximately 0.01gr of salt during 1 minute of spraying. On the other hand the time of drying must be sufficient for crystallisation. Weight measurements on samples sprayed with deionised water showed that under the conditions mentioned in the methodology the samples reached their initial weight in the first 10 minutes. Also after spraying with salt solution they reached constant weigh after 10 min as well. Thus the permeability of each sample type will determine the amount of salt that will crystallise inside the pores.

The rest of the aerosol has got be driven off the chamber since secondary deposition due to gravitational settling or other mechanisms can not be controlled. This was achieved by building a pressure gradient at the two ends of the chamber by electric fans. The air current however had an effect on the spray cone and thus it was activated only during drying. The fan has been wired on the electronic switch at the opposite period of the spray.

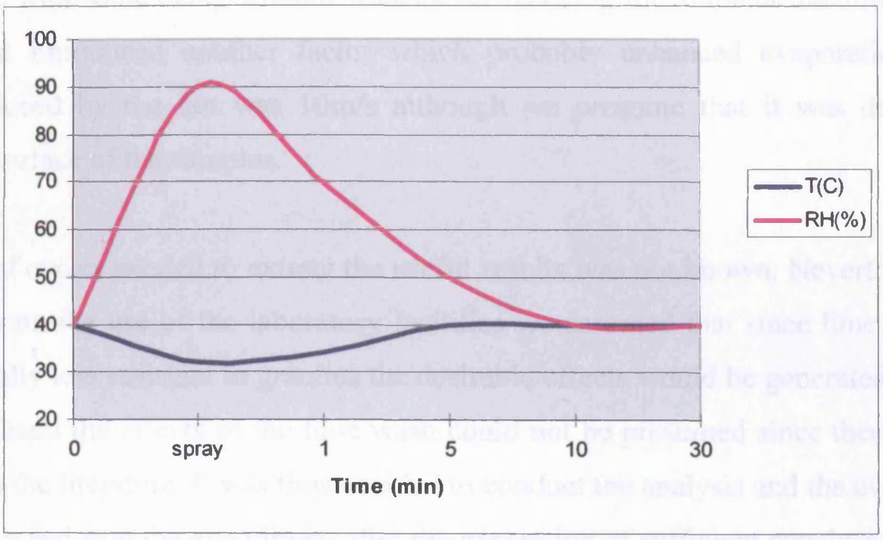

Chart 1 Temperature and relative humidity cycle of the simulation

It was also essential to provide and maintain the desirable temperature for drying. The first obstacle was that the standard heating generators used in laboratory testing are not resistant to salt spray. Alternative solutions are available in built-in chambers, which were prohibitive for the budget of this project. It was thus decided to use heat sources externally. Two 250W infrared lamps have been placed directly over the samples and by controlling their distance it was possible to build the desired temperature of 40°C. Nevertheless since the samples were positioned perpendicularly there was an unacceptable temperature gradient in height. Furthermore the temperature was decreased during spraying and it was difficult to reach the desirable value in the time limits of the cycle. Both these problems were confronted by the generation of the air current mentioned above. Although there was no initial intention to use fans it was evident that the generation of the air movement helped the stability of the cycle and the even distribution of temperature. After only a few cycles the conditions were surprisingly stable. Nevertheless although the temperature cycle remained constant after several days of testing a thermostat probe was placed in the middle of the samples holders as a precaution measure against excessive temperature. The final cycle of temperature and relative humidity is presented in chart 11.1. Additionally in order to test the response of the samples to the ambient temperature 3 penetration probes have been placed inside random samples. Unfortunately the measuring device (app.X.B) did not have logging application and thus only a few measurements have been taken. The measurements showed that at approximately 2mm from the exposed surface the temperature follows the ambient cycle with some delay without whatsoever reaching the ambient maximum. The air movement introduced another factor which probably enhanced evaporation. The velocity produced by the fan was 10m/s although we presume that it was decreased reaching the surface of the samples.

The number of cycles needed to extract the useful results was not known. Nevertheless in order to program the use of the laboratory facilities we assumed that since lime mortars are mechanically less resistant to granites the desirable effects would be generated earlier. On the other hand the effects of the lime wash could not be presumed since there are no equivalents in the literature. It was thus decided to conduct the analysis and the evaluation simultaneously and stop the experiment after the generation of sufficient conclusions.

The samples have been prepared as for the deposition experiment (chap.7). The problems introduced by mortars construction for testing and the differences from stone samples have already been mentioned. Nevertheless it is worth mentioning that the porosity of the samples is generated during drying and thus the pore properties are controlled from the ratio of aggregates and lime as well as drying conditions. The pore structure of the mortar samples is generated by the heterogeneity of their composition. Alternatively the lime wash that was applied on the samples does not develop a pore system but the absence of the aggregate matrix produces microcracks due to shrinkage during drying (fig. 11.6). As can be seen in thin sections of reference samples the mortar has an evenly distributed pore system composed by large pores of 10-20μm interconnected by small capillaries of 1-5 μm in diameter (fig. 11.5). We can also see that the lime-wash comprises an even nonporous layer that developed perpendicular cracks of 1-5 μm in diameter (fig. 11.4). The pore space is tinted blue, while the brown areas correspond to the lime and the white areas to the sand aggregates. The non layered samples present large pores on the surface while the lime washed samples result in small capillaries (not visible to the eye) that correspond to the cracks (fig. 11.2-3). The lime wash also decreases the pore space near the surface of the mortar since when applied it penetrates the mortar before drying. Thus there is no clear interface between the mortar and the lime wash. The interface could be interpreted as a horizontal area of sharp pore space decrease where the perpendicular capillaries of the lime wash meet the larger pores of the mortar. All the samples were insulated around the edges by liquid latex (app.X.B).

The solution has been prepared by adding 300*g* of artificial sea salt to 10*lt* of deionised water (2.9%). The composition of the salt mixture as described by the suppliers is very close to the average composition of sea salt (app.X.B). The properties of the solution are thus very similar to those of seawater.

Fig. 2 Type A sample

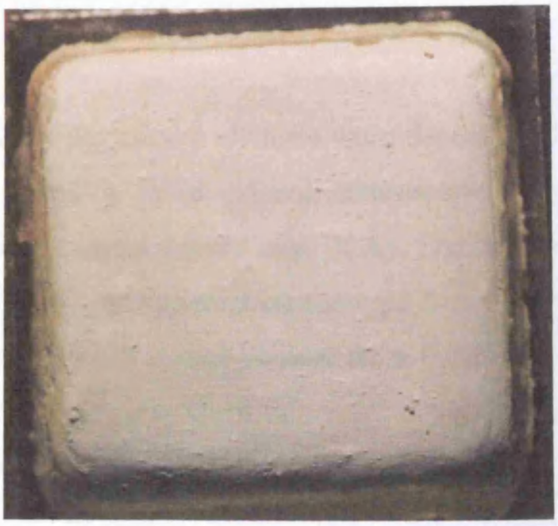

Figure 3 Type B sample (lime washed)

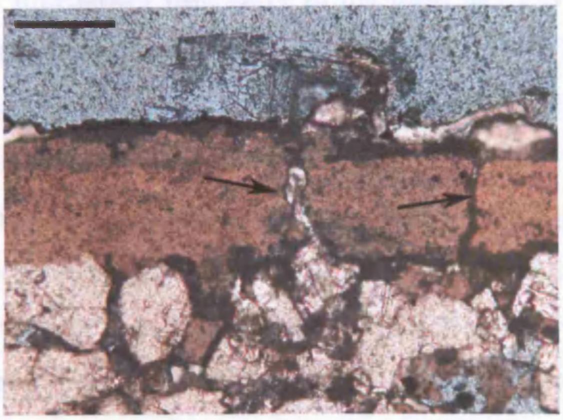

Fig. 4 Perpendicular cracks on lime wash layer (sc.20μm)

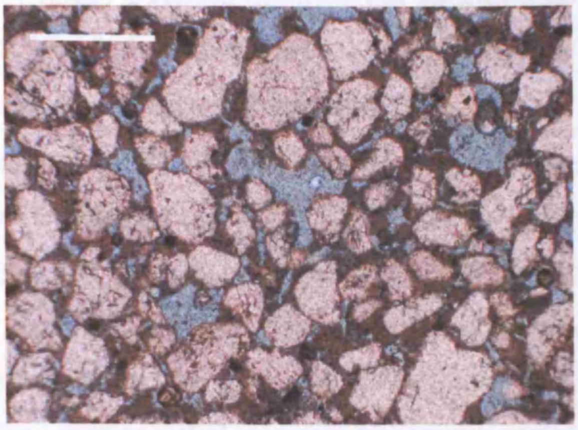

Fig. 5 Cross section of mortar sample (sc.30μm)

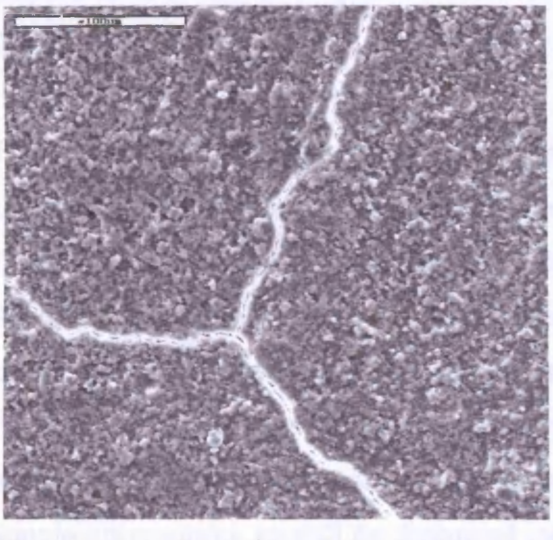

Fig. 6 Crack on the surface of lime washed sample (sc.100μm)

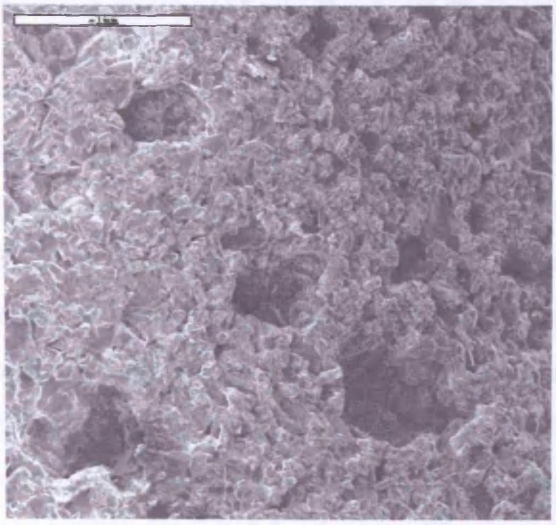

Fig. 7 Surface pores of type A sample (sc.1mm)

11.3 Results

Visual observations (app. IXD)

All the samples were observed daily and visually significant changes were documented using a Nikon AF (60mm/f28) macro lens and a Wild optical stereoscope (low magnification microscope) with attached digital camera (specs app. X.A). During the second day of simulation (≈100 cycles) a salt crust was apparent on the type B samples. Despite the absence of a visual crust on samples type A it was evident from the 2nd day that both types samples surfaces were wet during spraying. Until this point there was no visible evidence of a water film on the surface of both type samples at the end of drying.

Surprisingly fast, early in the third day (<150 cycles) a visible deformation appeared on the surface of two type A samples (fig. IX.18). The deformation had the form of a round swelling without whatsoever alter the superficial pore structure. Microscopic observation in the stereoscope revealed that the surface large pores were not filled with salts whereas the rest of the surface area had a disintegrated appearance (fig. IX.20). The swelling continued growing throughout the seventh day (≈336 cycles), reaching a height of ≈3mm without though any evidence of cracking or flaking. Over the same period the type B samples didn't present any visible change apart from the build up of a surface salt crust. On the sixth day microscopic observation of the crust revealed microscopic cracks on the surface of the lime wash layer and flakes incorporated in the body of the crust (fig. IX.24-27).

From the 4th day small sand and lime aggregates from type A samples were observed on the base of the sample holders. The swelling of type A samples collapsed on the 8th day, followed by a small detachment of around 2mm in diameter (fig. IX.20,23). The detachment revealed that the swelling incorporated an >1mm thick surface crust while the space underneath was void. The new surface that was exposed was already covered by a dense salt crust. However after washing off the salts, the mortar flake that was detached turned out to be a salt crust containing pulverised material of the mortar surface. This simple observation, as will be discussed later on, is very essential for the identification of the weathering mechanism. No other significant change was observed on type A samples until the end of the experiment apart from visible aggregate size detachments on the holder's base and the progressive built up of a superficial salt crust after the 10th day.

Surprisingly it was not until the 10th day (500 cycles) when the first deformations, in the form of cracks on the lime wash layer of type B samples, initially around the edges and later in the centre of the sample, were macroscopically visible (fig. IX.28,29). Two days later (576 cycles) the first large lime wash flake was clearly detached (fig. IX.30). During the next days the growing crust obstructed visual observations and the evolution of cracks and flakes could be followed only microscopically. Nevertheless on the 18th day (864 cycles) a swelling similar to the one of type A samples was observed on sample B. It continued growing for the next days without whatsoever disrupting the surface until the end of the experiment (≈1000 cycles).

The samples of cluster I, used for the weigh investigation, were washed off with deionised water after the completion of the experiment in order to measure the net weight loss, revealing some very interesting visual observations that were obscured by the salt crusts. Firstly the deposited salt crust cemented the detached debris and flakes which were released after wash-off. Samples type A had lost most of their original surface while the swellings collapsed in pulverized debris (fig. IX.37-39). Samples type B released primarily lime wash flakes while it was obvious that the layer had been extensively detached (fig. IX.33-36, 40).

It must be stated that the weathering intensity was not similar for all the samples, at least visibly. Since there was not any obvious relationship between the weathering intensity and the positioning of the samples the variability can only be attributed to the properties of each sample. Nevertheless it was clearly observed that all the samples presented similar weathering effects according to their type at an earlier or later stage of the experiment.

Similarly we must underline the strong localisation of damage on samples B. Flaking started from the edges and particularly at the corners. These patterns though similar to those that appeared in the centre of the samples have a localised nature that might have been influenced by the presence of the latex insulating film and as such they did not mark the starting point of weathering. Nevertheless the time of the damage appearance, strikingly though different in each sample type, is not as significant as the damage pattern, which constitutes the initial research interest.

Day	Cycles	Type A	Type B (lime washed)
2	96		Formation of crust
3	144	Surface swelling	
4	192	Growth of swelling/ Sand disintegration-debris release	
6	288		Microscopic lime wash flakes
8	384	Swelling collapsed/ Detachment	
10	480		Cracks on lime wash layer
12	576		Large lime wash flakes
18	864		Swelling

Table 1 Outline of visible observations

Weight measurements (appIX.E)

The samples of cluster A were weighed every 24 hours (48 cycles) at the end of the cycle's drying period, using a microbalance (App. X). According to the cycle the samples had up to this point been left for more than 20 minutes in a sufficiently dry environment (40°C/30%r.h.). The samples had been initially weighed after being left to dry at 40°C for 24 hours. The initial weight is marked in table 11.2 as N and the final weight gain as G. After the completion of the experiment the samples have been washed several times with deionised water in order to extract the salt species and then left to dry in 40°C for 24 hours in order to measure the net weight loss (marked as W in table 11.2). Table IX.E1 shows the weight change of the samples during the experiment.

The results of daily weighing, summarised on Chart 11.2 as the difference from the initial weight, clearly demonstrate that the samples kept gaining weight throughout the experiment. Measuring weight loss in a weathering experiment serves primarily as an indirect evaluation tool of the mechanical resistance of the material (Theoulakis, 1993). In this context "weight loss" cannot adequately evaluate the effects of the present experimental set up. The needs of conservation research introduce alternative uses of the traditional experimental techniques and in this case weighing can provide a very clear view of the progressive salt input by aerosols. This process although accelerated is described distinctively by periodic weighing which linked to the timing and the intensity of the observed weathering effects can reveal qualitative relations between salt input and damage. Undoubtedly this experiment, designed to cause little to moderate damage, is more efficient in predicting qualitative rather than quantitative conclusions.

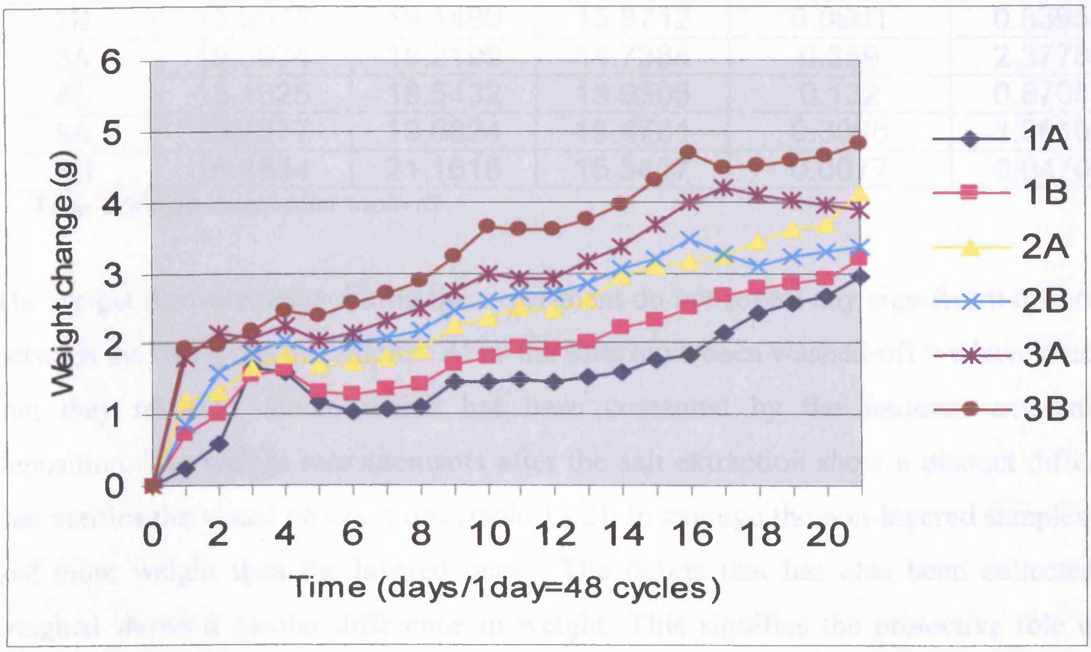

Chart 2 Weight change during the simulation

One could argue ovr whether the daily weight gain was the difference between the salt input and the detached material or just the salt input without reaching any significant conclusion without quantitative microdetachment measurements. It is quite clear through the daily observations that the cluster I samples didn't lose any material during the experiment. Evidently according to visual observations the weight increased steadily even after the start of the weathering effects. The fitted line plot however on chart IX.1 shows a significant change in the weight gain rate that has been frequently observed in similar salt spray tests (Rivas *et al*, 2000). The decrease of the weight gain rate is located between the 3rd and 4th day just when the first weathering effects were observed. The weight of sample 1A increases slightly on the 3dr day while it decreases dramatically from the 4th to the 7th day. Microscopic examination of cross sections revealed intense weathering right under the surface of the samples at exactly this period. On the other hand it was evident that in many cases parts of the external salts crusts were falling off during the experiment (fig.

IX.31). The reason for the salt crusts detachment was probably the perpendicular growth of whisker crystals underneath them (fig. IX.32). We can thus attribute the weight change to crust loss as well.

Sample	N	G	W	Weight loss	%
1A	14.5444	17.5063	13.8881	0.6563	4.51239
2B	15.9573	19.1486	15.8712	0.0861	0.53956
3A	15.0974	19.2198	14.7384	0.359	2.37789
4B	15.1625	18.5432	15.0305	0.132	0.87057
5A	15.7877	19.6824	15.4781	0.3096	1.96102
6B	16.3534	21.1618	16.3457	0.0077	0.04709

Table 2 Weight change after wash-off

The weight measurements during the experiment do not reveal any significant differences between the two types of samples. After the salts have been washed-off we have observed that they released debris, which has been cemented by the frequent external salt deposition. The weight measurements after the salt extraction show a distinct difference that verifies the visual observations (table 11.2). In average the non-layered samples have lost more weight than the layered ones. The debris that has also been collected and weighed shows a similar difference in weight. This signifies the protective role of the lime wash layer, which restricts the penetration of the salt. From one hand there must be salt content threshold that the lime washed samples did not reach during the experiment and from the other the presence of the lime wash layer must have decelerated the drying process of the underlying porous layer.

Another interesting feature is the periodicity that can be observed in the weight change chart. Considering that the main weight change corresponds to salt input we speculate that this periodicity might be attributed to periodic changes in spray velocity corresponding to pressure fluctuations due to the decrease of the solution height and refill in the tank. There is no obvious correlation between the final weight gain and the net weight loss (table11.2). Sample 6B which gained significantly more weight than the others -also evident by its thick salt crust suffered minimal damage and net weight loss, while sample 1A lost a significant weight although it gained less weight than the other samples.

Optical microscopy - Thin sections (App. IX.F)

Visual observations of the damage patterns that appeared on the surface of the samples, although very dramatic and useful to link the experimental results to the actual weathering patterns of wall paintings, do not supply sufficient insight on the particularities of the weathering mechanism. The visual effects of the process that already identified two distinct mechanisms, flaking for the lime washed mortars and sand disintegration for the plain ones, refer to the end result in the sense of material loss and not to the cause itself.

In order to investigate the evolution of the process inside the pores thin sections were taken out of two samples (one of each type) periodically. The period was set to 4 days, independently of the visual effects, for practical reasons. Since this method is destructive the samples were removed from the experiment and a shorter period would require a larger number of samples difficult to handle within the time and space limitations of the experimental set up. The samples have been immersed immediately after drying in resin dyed blue. The thin sections preparation was undertaken by the rock cutting laboratory of the Geology Department, UCL. In all the stages of preparation, which proved to be more than challenging, acetone has been used instead of water in order to maintain the salts. It was thus necessary to prepare the sections by hand, which increased the time and the cost of preparation permitting a limited number of samples.

Two thin sections of samples that have not been subjected to the experiment served as reference. In both samples we observe a good distribution of large pores interconnected by small capillaries. The dark brown areas represent the SiO_2 sand, the light brown areas which surround the sand aggregate is the lime ($CaCO_3$) and the blue areas represent the pores, which are filled with the dyed resin (fig. 11.4-5).

The thin lime wash layer is clearly seen in samples B as a light brown area. The lime wash penetrates initially in the large pores of the mortar, smoothening the surface on which it then forms a distinct non porous layer. Small perpendicular capillaries formed during drying in the layer connect the internal large pores of the mortar to the exposed surface. These capillaries are probably sections of microcracks formed during drying as can be seen on a fresh sample (fig 11.6).

There is no clear interface between the two layers but more likely a boundary zone where large pores meet the lime wash layer capillaries. We can assume that since there is no gap there must be hydraulic continuity between the two layers. According to Hall and Hoff (2002) the initial deceleration of moisture transport should be progressively replaced by a steady rate of supply. Nevertheless the small time of spraying probably did not permit the moisture supply to reach a steady rate resulting to the observed superficial efflorescence. Drying on the other hand was relatively rapid and intense. According to Petrovic *et al.* (2004) the porous bulk of the sample should dry faster driving the solution to accumulate at the interface where it will evaporate slowly.

The first thin sections were extracted during the 2nd day. Before then no change had been observed in either type of the samples apart from the formation of a crust on the surface of samples type B. The pore structure seems undisturbed in both samples. The salts have been crystallised in the small capillaries while the larger pores stayed empty. Salt spray deposits on the surface forming small islands, which appear as crust in the naked eye. The perpendicular capillaries of the lime wash layer are already filled with salts while supplying slowly the adjusting larger pores. In some cases the pore walls near the surface are covered by a thin salt efflorescence (fig.IX.41-44).

Thin sections of samples extracted on the 6th day revealed that while the solution could be easily transported through the large pores of sample A to a significant depth, the small capillaries of the lime wash layer delayed the solution in sample B causing the salts to crystallise still on the surface forming the observed crust (fig.IX46). The debris liberation and the deformation of the surface that had already been observed in samples type A is clearly demonstrated by the thin sections. As we observe in fig. IX.45 the pore structure has collapsed under the surface leaving a superficial cemented debris layer. The larger pores are still empty while the salts have already advanced through smaller capillaries to the undisturbed deeper areas. Clearly the samples type B are well preserved. Although we had already observed microscopic flakes incorporated at the salt crust there are no similar indications still in the thin sections.

The action of salts is clearer however on the lime washed samples extracted on the 10th day of simulation. We observe in fig. IX.46,47 that the salts crystallised at the interface have started creating a small but clear gap at the interface. Simultaneously the perpendicular cracks have widened causing minor flaking. In some cases small flakes are embodied in the salt crust and in other cases the loss of the flakes is only indicated by gaps in the continuity of the layer (fig. IX.48-59).

On the other hand the large swelling of the exposed samples is dramatically demonstrated in the thin sections. As can be seen a large internal area has collapsed. Probably the decay that was previously observed continues in the deeper areas and the external detachment creates the observed swelling pattern. Although this detachment looks like a flake, as was previously described, it comprised a cemented layer of pulverised debris. Obviously the calcareous matrix (brown fragments) has lost its continuity (fig. IX. 60,61). This external layer of damage shows that the larger pores are also filled with salts attaching it to the external crust. The swelling is probably a result of the salts dissolution cycles, which deform its appearance. Otherwise we should except that the mortar can suffer deformation over the non linear elasticity range. Weathering continues as sand disintegration of the deeper parts, also observed by debris liberation during the simulation.

Although on the 14th day of simulation the visual effects on the external layer are limited to random flaking the thin sections demonstrate clearly that the two layers have become detached. The clear gap between the layers is filled with salts while near the edge of the sample the lime wash has collapsed to a large flake (fig. IX.62-67). The outcome of this has been visually observed only after the 18th day of simulation as swelling. As can be seen in the underlying surface is in good condition. Although the experiment had to conclude we presume that the exposed porous layer will be susceptible to similar weathering as the non lime-washed samples.

Microprobe elemental mapping (App. IX.G)

The thin sections, after the microscopic evaluation, have been subjected to elementary analysis mapping in the Microprobe SEM-WDS. Time limitations directed the analysis of a small number of elements. Since it was essential to map Ca and Si as the background, we decided to monitor only the two major anions of the solution, chloride and sulphate (sulphur). We were not expecting any major fractionation of sodium, while it would be difficult to trace magnesium and potassium due to their low concentration.

The thin sections have been covered by a fine carbon coating and the glass has been covered by conductive tape to avoid secondary emission of Si. Each sample has been left for over one day in the microprobe since the area of the section to be mapped was quite large (1x2.5 cm). Despite that the final image acquisition provided a matrix of 4μm large pixels. The dimensions of the pixels might have jeopardised the accuracy of the analysis. Nevertheless apart from single elements the map indicates clearly pixels with disputed results either as combination of two or three elements. The investigated elements required acquisition voltage of around 15kV which restricts considerably the analysis and imaging efficiency of the apparatus.

The results of the mapping are not quantitative and thus we do not have precise data of the salts depth distribution. Nevertheless the maps clearly demonstrate the distribution habits and the evolution of the pore structure during the simulation. Although we cannot quantify the salt content the density of the coloured areas indirectly indicates the concentration in depth. We can also see the accumulation of salts in specific areas related to weathering (deformations). Whereas other evaluation techniques like wet analysis of drill cores supply specific and comparable results they lack the background data of the substrate, provided by the cross sections. Since the purpose of this experiment is the investigation of weathering habits generated between the finishing layer of the wall paintings and the underlying mortar it is evident that the applied technique is preferable.

The samples extracted after one day of exposure present a significant difference which we did not observe microscopically. The salt solution has penetrated and crystallised considerably deeper in the non layered samples (fig. IX.68-71). There is a superficial area of around 1mm which presents very high concentration but clearly we can trace salts at almost half the depth of the sample (around 5mm). On the other hand the layered samples present much smaller concentrations without any particular accumulation zone (fig. IX.72-74). It is interesting to observe in samples A that sulphur did not follow chloride in depth presenting a stronger accumulation near the surface (fig. IX.71). Due to the large size of the pixels we cannot monitor clear differences between larger and smaller pores. Although the large pores seem filled with salts we should trust the microscopic observations, which permitted more detailed imaging, indicating salt accumulation around the pore walls.

The concentration definitely increased in samples B extracted on the 6th day but still remained much smaller than the concentration of samples A extracted on the second day (fig. IX.79-82). The distribution is even throughout the sample. The only indication of a concentration gradient is that the lime wash layer is not clearly marked as Ca but as Ca-Cl. The same is true for Ca-S but with a stronger accumulation near the lime wash layer (fig. IX.82). The porosity looks undisturbed while the large pores are still empty. The collapse of the porosity near the surface of samples A, observed microscopically, clearly indicates a large salts accumulation around the fissures (fig. IX.75-78). The superficial flake also presents a collapse of the calcareous matrix and a strong concentration of salts. It is interesting to notice that the parallel to the surface fissure corresponds to very high concentration at the undisturbed area of the sample. At the sides of the sample where the surface has collapsed we notice an uneven distribution indicating that the solution was free to move deeper. Sulfur follows in general the distribution of chloride but the strong correlation to Ca indicates the presence or the generation of gypsum. A second sample type A which did not present any deformation was extracted the same day as a comparative measure. The elemental map clearly shows the initial concentration of salts at a depth of around 2mm (fig. IX.83,84). We can also observe the superficial crust that started to form much later on samples A as well as a zone of strong Ca-S presence.

The sample B extracted on the 10th day shows that the concentration of salts has reached the levels of samples B extracted the second day and a corresponding clear accumulation near the surface. Nevertheless none of the lime washed samples presented equivalent decay forms. As testified by the thin sections and the elemental map the pore matrix is still undisturbed (fig. IX.85). We can assume that the lime wash layer apart from delaying the penetration of salts and hence the generation of a critical concentration gradient, restricts as well the occurrence of damage even when this critical concentration has been achieved. We speculate that the presence of the lime wash has a beneficial effect not only during supply by during drying as well. Probably the deceleration of the evaporation rate restricts the generation of critical supersaturations irrespectively of the pores size or the relatively fast decrease of the ambient relative humidity.

The sample A extracted on the 10th day presented a very large swelling. Microscopic observation has already revealed the presence of a wide gap under a flake around 1mm thick. Elemental mapping verified the strong salt accumulation at the disruption zone under the flake (fig. IX.86,87). We also observe that the cemented flake is primarily composed by chloride.

The accumulation of salt at the interface between the lime wash layer and the mortar has already been verified by microscopy at the sample B extracted the 14th day. The maps though offered an interesting false image which shows clearly the decay pattern and the salt distribution (fig. IX.88-91). The large gaps at the bulk of the samples probably originate from mishandling of the samples rather then weathering as indicated by the absence of salts. The rest of the porosity and the calcareous matrix look undisturbed.

Crystal Morphology – SEM (App. IX.H)

The salt spray on reference carbon surfaces revealed various salt species and forms. Cubic-like halite crystals dominated the species as expected, accompanied by other crystals in lower concentrations and primarily gypsum rods (fig. IX.92-94). Gypsum crystallised either around the halite crystals or effloresced on them.

Both types samples extracted at the end of the experiment for microscopic surface observations had already suffered significant deformations. Samples A presented swelling and surface loss by sand disintegration and sample B white wash flaking. As can be seen despite swelling sample A maintains its surface structure (fig. IX.95). The large pores (0.2-0.5mm) are not filled with salts. Halite and gypsum crystals can be seen in smaller capillaries. Gypsum presents two forms, rod-like (acicular) efflorescence near halite crystals, assumingly effloresced by fresh spray and tabular crystals, probably a result of sulphation (fig. IX.96,97).

Samples B developed microscopic cracks on the lime wash layer during drying and setting as already seen earlier. In figures IX.98,99 we witness halite crystals efflorescing from the cracks. The particular crystals are quite large and obviously they refuse to obtain the shape of the fissure, growing against it. These samples developed early a saline crust. As we can see in fig. IX.100 the crust tends to maintain the cubic form. Interestingly we discovered whisker like crystals right under the crust (fig. IX.101,102). The whiskers grew perpendicularly against the crust which was occasionally disrupted and detached (fig. IX.103).

A flake detached from sample B has also been investigated microscopically (fig. IX.104). On the external side we can see the usual saline crust composed primarily by halite (fig. IX.105). On the same picture we also witness a cross section of the layer and its very low porosity. The internal side, representing the interface with the mortar revealed strong accumulation of gypsum. The hexagonal form and in some case the affinity of the crystals on the calcareous layer indicates strongly that these crystals are generated by sulphation of the original material (fig. IX.106). Especially in fig. IX.107 we do not witness gypsum crystals but more likely a sulphur rich area of the calcareous material disrupting and adopting the crystalline shape of gypsum.

11.4 Discussion

It was evident that each evaluation technique alone offered limited indications which could not be interpreted clearly where the correlation between them permits us to form a solid discussion. The overall holistic approach proved to be more fruitful for the needs of the particular investigation than the standardised rigid procedures. Similar approaches can offer the necessary freedom to pose questions addressing the particularities of conservation research.

Although the investigation focused on the deterioration of lime washed mortars the comparative approach designed for this case, applying simultaneously the weathering simulation on layered and unlayered samples proved to be essential for the understanding of the phenomenon and the interpretation of the results. The first and most striking difference was the decay rate. The thin sections proved that this difference was only superficial. Since there is not an objective measure of damage we can not calculate the decay rate of each type and thus the significance of this difference. But obviously at the end of the simulation the layered samples preserved the integrity of the calcareous matrix which had partially collapsed in the non lime washed samples at only the 1/10 of the simulation time. Thus we can safely conclude that lime wash acts protectively for the underlying mortar and probably for other porous materials of similar characteristics.

The test simulated the natural conditions of salt supply in the coastal environment. The sprayed droplets deposited directly on the exposed surface. Although the spraying time was very short, compared to other tests applying even 6 hours of spray, and it was followed by rapid drying, the salts penetrated the samples of both types. The supply rate though was evidently different for each type. The lime wash layer delayed considerably the supply due to its low permeability. This was evident in the cross sections as well as the surface of the lime washed samples which developed rapidly a visible crust. Probably this crust delayed further the penetration of salts since they restricted the deposition of the aerosol directly on the surface. Although we cannot safely correlate the salt concentration to damage we have to accept that the decay rate between the two types of mortars corresponded to the supply rate. The first strong indications of damage on samples A appeared at a stage where samples B have been barely contaminated. We must argue that in non accelerated conditions there might be others parameters like particles aerodynamic detachment or rain wash-off which would delay the salts penetration on lime washed samples further. On the contrary the exposed mortars absorbed more easily the salts and developed a crust much later. It is not random that all A type samples presented weathering at a distinct depth. Probably there is also a relation between crystallisation site, supply and drying rate. The same principle exists for the lime washed samples enhanced by the hydraulic discontinuity between the layers.

Although at a later stage the salt supply of the lime washed samples increased considerably reaching the penetration patterns of the non layered samples, damage was still localised at the interface. Thus although we do not have specific concentration measurements we can propose that there isn't a critical concentration gradient controlling the occurrence of damage. It has already been proposed that a criterion for damage is the supersaturation rate controlled either by environmental factors (fast evaporation) or pore size distribution. Here we present a specific case where the supersaturation rate is decelerated by the presence of a hydraulic buffer. The lime washed mortars dry out slowly restricting the generation of excess supersaturations and consequently of damage. Alternatively significant pressures are built at the interface which at the particular case is found near the surface. It was not quite clear why damage did not occur earlier since the small capillaries at the interface were already filled with salts. It was evident though that as long as the underlying porosity was open the solution crystallised at the walls of the larger pores without the generation of damage. Damage in the form of parallel cracks to the surface occurred much later. Probably the blocked porosity restricted the penetration of solution while the fast relative humidity cycles affected only the species accumulated near the surface. Moreover the intense radiation might have influenced more severely the species near the surface. Still we cannot explain why the superficial calcareous matrix did not fail in a more random pattern. The only explanation is that after the perpendicular capillaries collapsed resulting to wider cracks on the surface the fissures at the interface served as the only possible site of high supersaturations. It was evident that the cracks evolved progressively. Probably the widening of the cracks was a combined result of supersaturation site and the existence of a tension capacitor (i.e. an area of non-uniform distribution of tensions) which absorbed the generated pressure. The accumulation of moisture near the interface during drying did not permit the generation of critical supersaturations in earlier stages of the simulation. This would mean that damage in this case occurs as a concentration threshold phenomenon but it is not triggered by it.

The salt distribution presented progressive increase towards the surface in both sample types. The penetration increased in time and thus we speculate that during spraying the increase in relative humidity caused deliquescence on the already accumulated salts which advanced further inside the sample. On the other hand there were some indications of salts fractionation. In both cases we observed a distinct accumulation of sulphate in the damage zones as well as a distinct correlation to calcium. Unfortunately these indications were not clear in the absence of quantitative analytical data. If this is true it raises significant thermodynamic considerations. It has been shown that gypsum along with halite is more destructive than each salt alone. If damage is located at sites presenting particular accumulation of specific salt mixtures it would mean that the behaviour of multi salt solutions is more significant for the generation of damage than other parameters. Moreover since the initial solution resembled the composition of sea water this observation would raise serious arguments for the susceptibility of coastal structures.

Additionally we could argue on the neoformation of gypsum by calcite dissolution, accelerated by the presence of halite. In order to answer these significant questions we need to develop more elaborate analytical techniques which would permit in tempo monitoring of the salt distribution.

The decay rate has been evaluated only by phenomenological indications. Thin sections revealed that the lime washed samples were less susceptible to salt spray. Surface observations also testified the fast decay rate of the exposed samples although the salt crust restricted observations on the lime washed samples. Weight loss measurements did not offer great insight into the decay rate. Under an experimental design permitting a larger number of samples it would be possible to extract them from the simulation and measure their weight after washing off the salts. Nevertheless this technique used in this case only at the end of the simulation revealed a good agreement between the visual observations and the final weight loss. We must notice that these observations address the particular mortars tested. Probably the pore distribution of these mortars is responsible for the high susceptibility of the exposed samples. Maybe mortars with different characteristics would not present so extreme difference in the decay rate between lime washed and exposed samples and even contradicting results. Nevertheless the main query of this investigation has been addressed since both mortar types came from the same matrix. Another important issue is that some samples of each type presented different weathering rates. The results address the samples that formed earlier the anticipated patterns. Several causes might have induced this discrepancy like mistreatment during the construction of the samples, mishandling or differential deposition. Small environmental differences inside the chamber observed during set up must be excluded since there was no localisation of the phenomenon.

The crystal morphology does not seem to play a particular role. The whisker like halite crystals grew externally as frequently observed *in situ*. There were no indications of whisker growth between the layers as proposed by Arnold (1996). Nevertheless it was testified that the whisker like halite crystals grew perpendicularly to the surface and probably under conditions of low moisture supply. We can accept that at later stages, when the lime wash flakes would have become detached whisker like crystals could develop against them as they did for the salt crust. It is worth mentioning that the superficial whiskers left at room temperature at the end of the simulation developed a twisted habit exactly similar to those found on the wall paintings in Delos (fig.IV.27-29).

Overall the simulation produced successfully the anticipated weathering pattern of wall paintings external layer and distinguished it from other mechanisms that affect the porous support. It was also evident that detachment and flaking is a result of the action of soluble salts and in the particular case a mixture of salts representing the composition of sea water. Significant damage has been produced in the time scale of the simulation. On the other hand the environmental cycle, although it did not imply excessive conditions, cannot be corresponded to real time and thus the rate of weathering cannot be defined. Nevertheless the dimensions of damage do not have to be scaled since the resulting patterns are corresponding to real ones and unacceptable for heritage wall paintings. The detachment of flakes must follow the similar principles as sand disintegration leaving behind solution islands in smaller pores (Scherer, 2004), but for wall paintings this mechanism is localised at the interface, resulting to flakes (or detachment) rather than pulverized debris.

The detachment of the lime wash layer was not always visible to the naked eye. This raises a serious problem for conservation since visual documentation would not indicate this very significant damage. Either way desalination or mechanical cleaning would cause significant damage to this particular sample. On the other hand it is evident that consolidation is not plausible since the gap between the layers is filled with salts. The detached layer is extremely fragile and although at this stage the flakes have a considerable size restoration seems rather idle. Probably at further stages of salt accumulation the flakes might not resist further deformations and consequently crack down to smaller fragments. Considering the monumental size of wall paintings the application of microtechniques used for easel paintings and smaller objects would require an impractical amount of time and expenses. Environmental control seems the only solution in this case.

CHAPTER 12. Sustainability against salt weathering in the coastal environment: General discussion, conclusions, limitations and further research

Introduction

The "sustainable environment" is not a modern concept. The principles of sustainability follow simple evolutionary rules that aim in the preservation of life. Organised social structures experimented on sustainability issues that evolved from household economy to globalisation. The contemporary needs of developed societies elevated the concept of sustainability to a major challenge. Ecological sustainability triggered the widest ever social discussion but the think tank is undoubtedly composed by experts and the arguments derive by intense research activity.

Heritage conservation participates in this wider social agenda. Urban conservation and sustainable development have been related since the 60's, concerning both historic sites (Rodwell, 2003) and museums (Ashley-Smith, 2002), while heritage sustainability in the coastal zone has only recently received some attention (Howard and Pinder, 2003). Although the planning of a sustainable environment for the built heritage comprises a multi-disciplinary agreement, it is fundamental that the basic arguments arise from weathering research. The modern objective of conservation science has moved from the intervention on the material to the intervention on the material's environment, hence the development of a sustainable environment in agreement with the principles of heritage deontology and the needs of heritage management. All the same the arising question is not if a certain structure is sustainable in the context of a certain natural or artificial environment but if sustainability is actually definable in the context of very complicated physicochemical processes?

This project, following the challenge, aimed at the production of solid arguments that would contribute in a wider discussion on the sustainability of wall paintings against salt weathering in the coastal environment. The archaeological site of Delos that served for the application of the proposed methodology is a prominent example of mismanagement. The fruitless discussions, controversial decisions and obscure planning of the authorities clearly indicate the lack of argumentation followed by insecurity, anxiety and pessimism. Accordingly, UNESCO that has adopted the site remains sceptically silent. On the other hand it was obvious so far that the complexity of this weathering mechanism in relation to heritage structures particularities introduces major difficulties in the clear definition of the optimal conditions for preservation. In the following discussion we will try to summarise the limitations of this investigation, outline the conclusions and set new tasks for future research.

Site assessment

The aim of site assessment is to investigate in every possible detail the interaction of the material and its environment in order to determine the parameters that cause damage. Consequently by manipulating these parameters we can create sustainable conditions with minimum interventions. Normally in order to identify the interactions between the material and the surrounding environment that trigger the weathering mechanism we must describe accurately both. Nevertheless sensible time and cost limitations demand applicable methodologies restricted to the absolutely essential data. The description of the environment in Delos for the purpose of this project introduced several limitations both in terms of quality and quantity. Principally, we decided that it was necessary to include both climatic and aerosols measurements.

As far as it concerns the description of the climate, we faced a major dilemma as for the amount of data needed in order to correlate it to the thermodynamic resultants. Since phase transitions can occur within seconds, averages are not sufficient for these purposes. It was essential to monitor at least the diurnal cycles. On the other hand such detailed data is difficult to handle for a long period of at least one annual cycle. Furthermore since the particular period was not representative of the average climate of Delos to what extent was our data sufficient to describe processes that might have lasted for decades?

This problem was significantly decreased by the comparative character of the investigations. Although we had to approach the interpretation of the results with approximations the conditions were met in most cases. Still the description of the climate was based in a sampling procedure. The accuracy of the description was not satisfactory for wind speed measurements as proven by the deposition investigation. On the other hand we described clearly the dependence of temperature and relative humidity on wind direction over the coastal zone.

Some presumptions that were attempted in order to correlate indoors and outdoors deviations to visual observations of weathering proved to be absolutely coincidental. The complexity of the salt mixtures behaviour could not have been predicted in the absence of chemical analysis and thermodynamic modelling. Thus arguments based solely on climatic data are groundless. Undoubtedly more work is also needed in order to form satisfactory methodologies to correlate climatic data to thermodynamic investigations.

The environment has also been described in terms of atmospheric chemistry and deposition. The simple technique that has been used was successful and in accordance with the major variables. Qualitatively we described the deposition parameters in the coastal environment of Delos and we identified sea spray as the major contaminant. Although we also had indications for other atmospheric species it was not possible to identify their particulars of contamination. Quantitatively it was obvious that the existing shelters in Delos buffer significantly the deposition of marine aerosols although we did not have the chance to correlate deposition to wind speed precisely. The morphology of the landscape and the building itself effects deposition significantly. Thus costal location alone is not a sufficient argument for sea spray contamination. The results can be generalised since the distance of the collectors from the sea justifies the deposition of bulk marine aerosol that can be transported in large distances and not splash or spume drops.

The salt content of the investigated wall paintings has been described according to a simple variables system. These variables proved to be essential for the interpretation of the results since the number of samples was restricted by ethical rules. It was clear from the beginning that we cannot follow statistically acceptable sampling methodologies. More holistic approaches are generally demanded in heritage studies and despite the unavoidable approximations we managed to distinguish the significant elements required to describe the salt content and contamination as well as their fluctuations in time. The variables system comprises actually an equation that can be resolved for any hypothetical data. Hence, apart from enhancing the interpretation, we minimise the risk of a self fulfilling prophecy deriving from a rigid strategy biased by the question itself.

The results were quite surprising. We could not have predicted the complexity of the salt content by the deposition investigation or by crystallographic data of the effloresced species. The need for thermodynamic modelling was obvious. Nonetheless, although any attempts to correlate damage to salt content would have been fruitless in the absence of thermodynamic calculations, in most cases the "grey areas" indicated salts interaction.

The high content of sulphates indicated the presence of a secondary source of salts. The variable of height revealed that sulphates originated from the conservation mortars of the floor mosaics and they were transported to the masonry through ground moisture capillary rise. Coincidentally only the sheltered areas mosaics have been treated. This biased element could not have been predicted. The result of sulphate contamination was primarily the production of gypsum. It was not though quite clear if gypsum was a product of the authentic material's chemical dissolution or if there was a secondary source of calcium. Supplementary samples revealed the presence of calcium in the ground while microscopic investigations provided evidences of sulphation. The deposition investigation was not sufficient to describe all the contamination particulars. More detailed investigations of contamination are necessary since they might play a serious role in the prevention of damage by either eliminating the source or blocking the pathway. The number of samples in height is very significant. Visible indications like efflorescence and damage patterns can help indicate the optimal number of sampling sites but more likely the results of the first campaign will determine the needs of accurate representation. In this respect the strategy must be flexible enough to accept changes.

The variable of sheltering, although biased, introduced some important facts. The absence of direct solar radiation permitted the build up of higher relative humidity and ground moisture infiltration. As a consequence the ground species could be mixed with the deposited aerosols creating complicated mixtures. Sheltering from rain was also an important variable since the efflorescence of the exposed surfaces was washed off during the rainy season decreasing significantly the concentrations. The conclusion that shelters buffer sea spray deposition significantly was verified by the salt content investigation as well.

The variable of depth distribution was also essential. In most cases the concentrations were higher in the surface samples. The comparison between the different sites of sampling and the evolution of the distributions in time in relation of course to phenomenological observations served to analyse the salts mobility, efflorescence and contamination. Correlations between the ions distributions revealed interesting relations that proved to be very useful in the interpretation of the ECOS resultants. Nevertheless the technique of microdrilling introduces a major limitation when applied in wall paintings. The depth is very small and since there is a need to distinguish the first layer the superficial sample is even smaller. As a consequence the concentrations are close to the analytical error and when calculated as percentages of the sample's weight they tend to fluctuate considerably. In some cases though extremely high concentrations can be interpreted as superficial efflorescence. Furthermore it is not possible to extract undisturbed cores and thus we have to depend on dexterity and good luck. The technique has not been tested in controlled laboratory conditions. Tests in samples imitating wall paintings and having known salt distributions will contribute in the interpretation of the in situ application.

Another limitation of the depth variable is the extension of the salt system in the masonry. Sampling was limited to the mortar. In some cases we had to speculate which species might have moved further in the building materials, the conditions for damage at the interface between the mortar and the stone and the conditions of hydraulic discontinuity. The sampling technique is not plausible in stones. Electrical drills that supply the force to penetrate stone might be dangerous for the wall paintings. The development of new techniques apart from serving more adequately the investigations will also provide the chance to non experts to participate increasing the number of relevant case studies.

Stoichiometric results offer limited correlations to the observed weathering patterns. The predictions followed the thermodynamic approach only in the cases of clear dominance of a specific salt like the lower zones but then again the interpretation was problematic. In most cases, even when a single salt dominated persistently, several species coexisted. The salt fractionation is not thus as absolute as frequently described (Arnold, 1996). In many cases the salts interactions that influenced the distribution have been verified by ECOS.

Summarising the site assessment we must repeat the major conventions that we had to accept. The first convention is the samples replication. Replicates can be extracted from continuous processes like the industrial production control. In our case each sample is unique and thus the evolution of the salt system in time is assessed by different samples taken from a seemingly homogenous area. The other convention also relates to the time aspect of the investigation. We had to accept that weathering is still active and thus the salts samples are descriptive of damage. The samples were never extracted from large lacunae where the traces of the damage mechanism might have vanished along with the material.

Pathology

The state of preservation of the investigated wall paintings has been documented in detail by the local authorities and completed for the needs of this research by the author. The state of preservation has not been considered for the choice of the investigated sites. Nevertheless it was obvious that the mortars were better preserved in the exposed areas and this fact comprised a major issue for the conditions of damage under the shelters and the potential creation of a sustainable microenvironment.

More careful investigation revealed that the wall paintings in the exposed area receiving the highest deposition of sea spray might have suffered serious damage although seemingly in good condition. There were indications of complete loss of the lime wash layer and extensive detachment from the masonry. The weathering simulation revealed that sea spray in relation to fast drying cause significant damage to the lime wash layer independently of the bulk mortar while ECOS resultants suggested that the conditions are not met for further damage on the particular site.

The sheltered areas presented multiple weathering patterns. The localisation of the patterns and crusts helped relate the salt mixtures to damage and predict the rate. Interestingly both sites presented the same zone of lime wash flaking at relevant heights with corresponding salt compositions, distribution, crystalline habit and annual cycle. On the other hand it was problematic to interpret the sand disintegration of the lower parts although some speculations were attempted concerning the interaction of gypsum with other species which could not be confirmed by ECOS due to software limitations.

Samples from Delos and from the laboratory simulation both provided visual indications of sulphation. The mechanism was not clarified although in both cases localised near the surface. If sea spray alone can cause the effects of urban gases, even in a much smaller scale, we should reconsider the preventive measures against weathering in the coastal zone. Undoubtedly we need more proofs to correspond the observed in situ pathology to the simulated one.

The present investigation reinforced the belief that the coastal environment is particularly aggressive but it also revealed aspects that had been neglected so far. The aerodynamic deposition of sea salts on vertical surfaces is the primary occasion but not the cause. In the Mediterranean region the intense solar radiation enhances the generation of damage of exposed surfaces. Sea water is multi salt solution. We had indications for localisation of damage and the resulting pattern (lime wash flaking) due to species fragmentation. The accumulated mixtures were more destructive than halite since they present phase transitions on a broader range of environmental conditions. On the other hand sea water thermodynamic modelling does not reveal the cause of this difference since it presents similar behaviour with halite. Likewise kinetic deviations as depicted by ESEM revealed that gypsum is not active and thus we speculated that the presence of the very soluble salts is responsible for the aggressiveness of sea spray. Still we did not consider the implications of salts fragmentation as the solution propagates through the pores system. Hence the composition of a contaminant mixture of salts is not adequate to explain the conditions of damage. In the case of wall paintings fragmentation of salts and localisation of damage is induced by the hydraulic properties of the interface between the layers.

The salt spray weathering simulation provided useful information on the pathology of wall paintings in the coastal environment. The simulation accompanied the *in situ* investigation clarifying details that were obscured by the particularities of an open system or lost along with the authentic material. Lime wash renderings actually act as sacrificial layers for the preservation of the mortars or the stones. This layer which carries the pigments is independently weathered. The salt accumulates at the interface causing the detachment of flakes. Although the layer is detached it does not necessarily crack or exfoliate, cemented by the salt crust which develops due to decelerated absorption. The restoration is obviously problematic. More likely the solution should focus on the prevention of further damage. Under these conditions sheltering against driving rain is absolutely essential. On the other hand the uncovered porous support presented sand disintegration at a much faster rate. As a consequence the weakening of the support will eventually lead to the loss of the painting as well.

The acceleration of the simulation cannot be scaled in real time. The dimensions however proved to be significant and intolerable for heritage wall paintings. The sustainability of wall paintings demands specific planning, individual of the masonry materials. The pathology of wall paintings presents very complicated problems that cannot be dealt with the common conservation practices like desalination and consolidation. Preventive conservation requires expert practices that might be considered unnecessary for stones and bricks. The arguments for preventive measures are more dramatic in the case of wall paintings.

Preventive conservation

Sustainability principles for the natural environment underline the small efficiency of remedial action. Prevention is in general considered better than remedy but in some disciplines, like social security fund management and forestry, preventive planning is the backbone of sustainable development. The objective of preventive conservation is in principal the deactivation of the weathering mechanism. In most cases it would be easy to neutralise an object from the weathering agents by restricting exhibition and sacrificing its educational value. As far as it concerns immovable archaeological finds the easiest technique which supposedly ensures preservation is reburial.

Nonetheless museums and sites cannot afford to withdraw the artefacts from the public. Denial of exhibition cancels the social role of heritage. Conservation scientists are thus called to define sustainability in a much more complicated context. Salt weathering is not yet described entirely, thus any decisions for preventive management cannot be supported efficiently. In this respect the modelisation of salt mixtures behaviour comprises a determining step towards the definition of a sustainable environment.

Still the encountered limitations restrict considerably the extraction of secure conclusions. Primarily even if we manage to compose a phase transitions periodic model we cannot ensure that these transitions will cause damage and hence preventive measures might be exaggerating. We had to accept that damage is ongoing at the investigated sites in order to correlate our results to the observed weathering patterns. The domain of crystallisation pressure modelling for salt mixtures and pore properties will definitely enhance our ability to describe the optimal conditions for preservation. On the other hand the comparative approach followed in this project succeeded its goal to distinguish the supposed weathering particulars of each case and the major parameters that influenced them. More field applications are certainly needed in order to form proper methodologies of site assessment. Otherwise salt mixtures modelling will be consumed in verbalism.

The aerodynamic deposition of marine aerosols proved to be a major factor for the loss of the lime wash layers. The effect is more intense on the windward side which receives more spray. Since deposition occurs directly on vertical surfaces other solutions like vertical blocks might be more efficient than shelters. The cycladers protect their vegetable gardens from sea spray by thick and tall vegetation, resistant to salts. The latter is a perfect example for the collaborative nature of the elements composing a wider sustainability agenda involving traditions, crafts, materials, ecosystems and monuments. Still deposition alone is requisite but not capable of damage. The environmental conditions in Delos favour the loss of lime wash during the summer months under direct solar radiation while enclosed shelters offer the conditions for ground capillary rise during the rainy season.

The exposure variable was biased by the existence of conservation cements but it was obvious that the resulting damage is a synergetic effect of the artificial microclimate and contaminants as described by ECOS. Undoubtedly each case is unique and the optimal conditions for preservation against salt damage must be investigated in detail by sampling and analysis procedures. Still is there only one potential of damage for each case?

The spatial variables supported that multiple potentials can coexist even on the same wall. Hence the optimal conditions of preservation for a particular zone of damage might be conflicting for the preservation of another at the immediate proximity. Furthermore can we ensure that the same model is valid for the other walls even if they present similar weathering patterns? Is it worth taking more samples? According to the finds of this project sampling can be limited by a variables system. The definition of the significant variables and the number of the composing elements cannot be modelled since each case presents different requirements. The use of ECOS is not a panacea against salt weathering but a useful tool for very specific questions.

The time variable was necessary to model the periodicity of phase transitions. The results exceeded our expectations. Despite the difficulty of open systems where the composition of the salt mixtures changes in time due to continuing contamination by various pathways and sources as well as removal, we managed to correlate the climatic variables to our results and the observed phenomena. Still, were the number of campaigns, the time span and the particular period enough to describe weathering reliably? The answer came from the last supplementary campaign that we decided to include for representability reasons. A random event that caused the enrichment in nitrates changed the behaviour of the previously found species and disturbed the model. The ratio between the species also deviated from the model, definitely a consequence of salts interactions. Supposing that we would not have this information it would be rather hazardous to apply preventive measures based on the previous model. Furthermore we should not be surprised with damage acceleration in Delos due to coexistence of nitrocalcite and gypsum. Here we must also mention the major disability of ECOS to include gypsum in the model and that more work is required by the developers to confront this problem.

The possibility to create an artificial sustainable environment in Delos, the implications and the limitations has been discussed in detail previously (chap. 9). Sheltering comprises a basic requirement for the application of environmental control. On the other hand the particular site is an excellent example of the difficulties that might be faced. The density of the site prohibits the creation of additional protective structures while the vastness of the already excavated area would require an unrealistic budget. Other solutions like the blocking of contamination also derive from the applied approach and they are case specific. The conclusions were not obvious by the deposition investigation since the thermodynamic approach revealed relations that could not have been predicted. Still since the monuments are already contaminated we must prevent the hazard. Desalination is not plausible on brittle materials and it is not satisfactory controlled. Solar radiation proved to be a major factor of the weathering process. We might thus consider sheltering solutions primarily against direct radiation, lighter and more plausible than the heavy concrete structures that have already been used.

On the other hand kinetics cannot be predicted by thermodynamic calculations. The investigation of salts interactions by ESEM had a limited application in the results of Delos since it was difficult to reproduce the complicated mixtures found *in situ.* Nonetheless the observations on ideal mixtures were indicative of some very important limitations of the site assessment. Primarily we identified as a general rule that crystallisation takes place at a much lower relative humidity, it depends strongly on salts interactions and the behaviour of mixtures is salt specific. In many cases the predictions of ECOS as far as it concerns the upper limit of phase transitions were verified. Also in most cases ECOS predicted accurately the tendencies between specific species and a relative dependence on their solubility. We also identified the influence of crystal morphology on deliquescence conditions. Accuracy was a major problem of the used technique. ESEM requires more work in the calibration of relative humidity. Despite that the applications on salts and environmental conditions are unlimited. The next step should focus on the monitoring of phase transitions inside capillaries. In general kinetics is an area that must receive more attention in the future.

Sustainable development within the coastal zone faces the maintenance of a delicate balance between the marine and the continental environments. Salt weathering comprises a characteristic natural process of this balance. Heritage sustainability on this constantly changing boundary seems from a pessimistic point of view a lost battle. Nonetheless since the preservation of the coastal cultural heritage comprises an important directive of the social agenda, conservation science is obliged to continue the discussion for sustainable sites and monuments. Weathering research must provide the arguments.

Although we still do not have the appropriate means to define precisely a sustainable environment against salt weathering the first determining steps point towards an optimistic direction. Evidently no generalisations can be made for the moment. Literature has clarified various kinetic details responsible for the observed deviations from the theoretical models. In order to apply these advances in our understating of the weathering process to preventive conservation we need to correlate these details in a unified model, plausible to heritage restrictions and flexible to heritage diversity. According to the "Charter of Venice" any other attempt would be fruitless, since conservation practice must stop where doubt begins (article 9).

Summary

The deposition of marine aerosol constitutes an effective mechanism of salt enrichment for vertical porous surfaces. The contamination degree is relative to the exposure degree and the orientation. Thus sheltering decreases contamination by reducing the circulation of air. The variable of orientation plays a significant part since sea spray deposits on the windward side of structure and is relative to wind speed. Nonetheless the contamination degree can be influenced dramatically by land and built obstacles that disturb the flow of the aerosol.

The higher availability of salt aerosol over the coastal environment does not represent a precondition for damage. The atmospheric concentration of marine aerosol is not measure of salt weathering if the conditions for deposition are not met. Moreover the contamination degree does not indicate the intensity of damage. In the particular case that has been investigated the surface facing the prevailing wind direction and receiving accordingly the highest amounts of salt deposits presented complete loss of the external lime wash layer. This observation however proved to be coincidental.

According to ECOS calculations the environmental conditions do not favour damage in this particular area. We have however identified other parameters such as direct solar radiation and air movement which by inducing evaporation influence the intensity, the site and the pattern of damage. Moreover we identified fragmented distribution of sea salt leading to distinct concentrations at the site of damage. The above findings were reinforced by a laboratory simulation of the weathering environment. We also had indications of sulphation of the authentic material at the site of maximum sulphate concentrations.

Furthermore secondary sources of salts and alternative contamination mechanisms alter the composition of the mixtures and consequently their behaviour. In some cases these salts originated from interventions that aimed in the preservation of the monuments. We can thus conclude that the environmental conditions that trigger the damage mechanism are more important than the salt loads. In this sense sheltering alone is not a sufficient measure for preservation since it does not provide the means to deactivate salt damage.

Thermodynamic modelling despite the profound limitations proved to be an essential tool for the investigation of the damage mechanism. Apart from the strict use of the salts interaction approach as means to define the optimal conditions for preservation, it also provided a wide range of information considering the contamination processes and the ions distribution in the material, alternative sources of salts, the activity of previous damage mechanisms and the applicability of environmental control. Future models including crystallisation pressure calculations will provide more solid evidences to predict an optimum range of phase transitions but we should also consider their applicability in preventive conservation since we have identified multiple and sometimes conflicting ranges in different locations of the same areas. We should thus anticipate more holistic approaches for environmental control expanding further than simply relative humidity and temperature optimum ranges.

On the other hand we investigated the kinetics of salt mixtures phase transitions and found that in several cases the results were inconsistent with the theoretical predictions. The most important observations affect the lower limit which in every case is considerably lower than predicted, the solubility of less soluble salts which is not considerably influenced by the presence of other salts and the crystallisation of very soluble salts which occurs only in extreme and rare in the natural environment conditions.

Another kinetic factor that influences specifically wall paintings is the pore distribution of the material. We tested the hypothesis of enforced crystallisation between layers of considerably different pore properties and found that the external layer that carries the primary information of renderings and paintings is particularly susceptible to salt spray and intense radiation. Damage was located at the interface resulting in the distinct loss of the external layer in large flakes, a weathering pattern frequently encountered in real conditions. We identified two possible explanations: the entrapment of solution islands across the interface during evaporation which maintain higher supersaturations and the creation of a concentration gradient due to fragmented distribution of sea salt species. In both cases the hydraulic discontinuity created by the external low porosity layer is responsible for the localisation of damage.

For the moment we are not able to define precisely the optimal conditions for preservation against salt weathering. Sustainability of wall paintings in the coastal environment should be approached by several aspects such as blocking of aerosol transport and deposition by shelters and vertical obstacles, case by case identification of the major parameters that contribute to the creation of the weathering environment, material properties and especially layers distribution and preservation status.

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APPENDICES

APPENDIX I: Maps and pictures of Delos and the investigated monuments

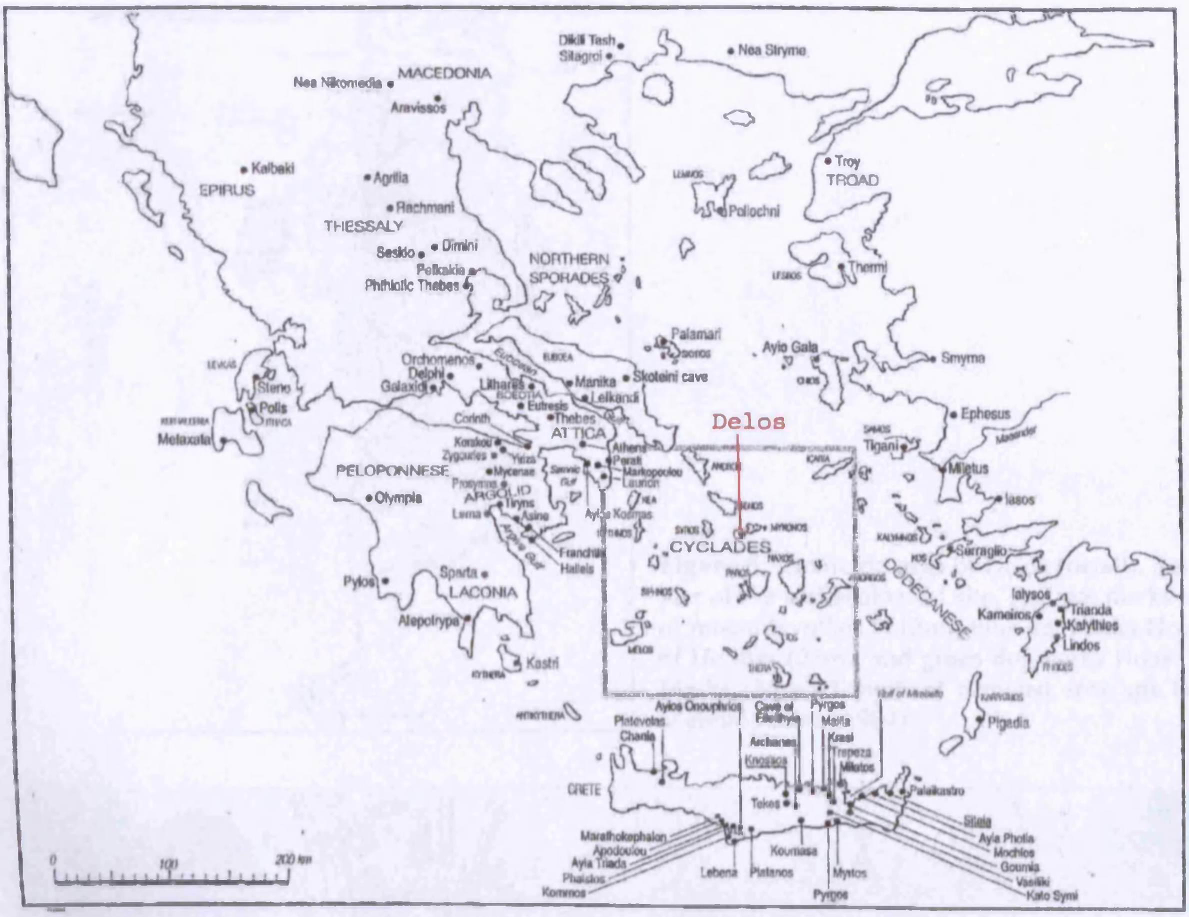


Figure 1. Map of Greece depicting sites of archaeological interest. The rectangle marks the Cyclades complex and Delos is marked in red

Figure 2. Satellite image of the Aegean Sea

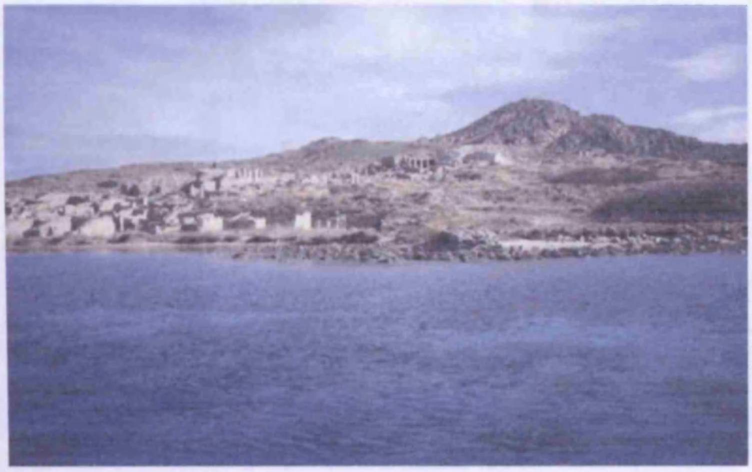


Figure 3. Delos Island. View from the west

Figure 4. Map of Delos (scale 1000m). Red line indicates borders of figure 5 (Zafeiropoulou, 1984)

Figure 5. Isometric map of Delos (detail). South part of the archaeological site. Red dot marks top of mount Kynthos (112m), blue dot marks House of Hermes (25m), and green dot marks House of Masks (35m). Length of depicted area apx.1km (Zafeiropoulou, 1984)

Figure 6. View of the central archaeological site from mount Kynthos (towards NW)

Figure 7. The vast archaeological site expands throughout the island.

Figure 8 (left). Aerial photo of Delos (from NE)

Figure 9 (right). The theatre quarter. Most of the walls are preserved to the original height and bear renderings. The density of the site limits the sheltering solutions

Figure 10. The House of Hermes (NE view). The concrete shelter served in the reconstruction of the 2nd floor

Figure 11. The House of Masks is partly sheltered by concrete slabs (SE view).

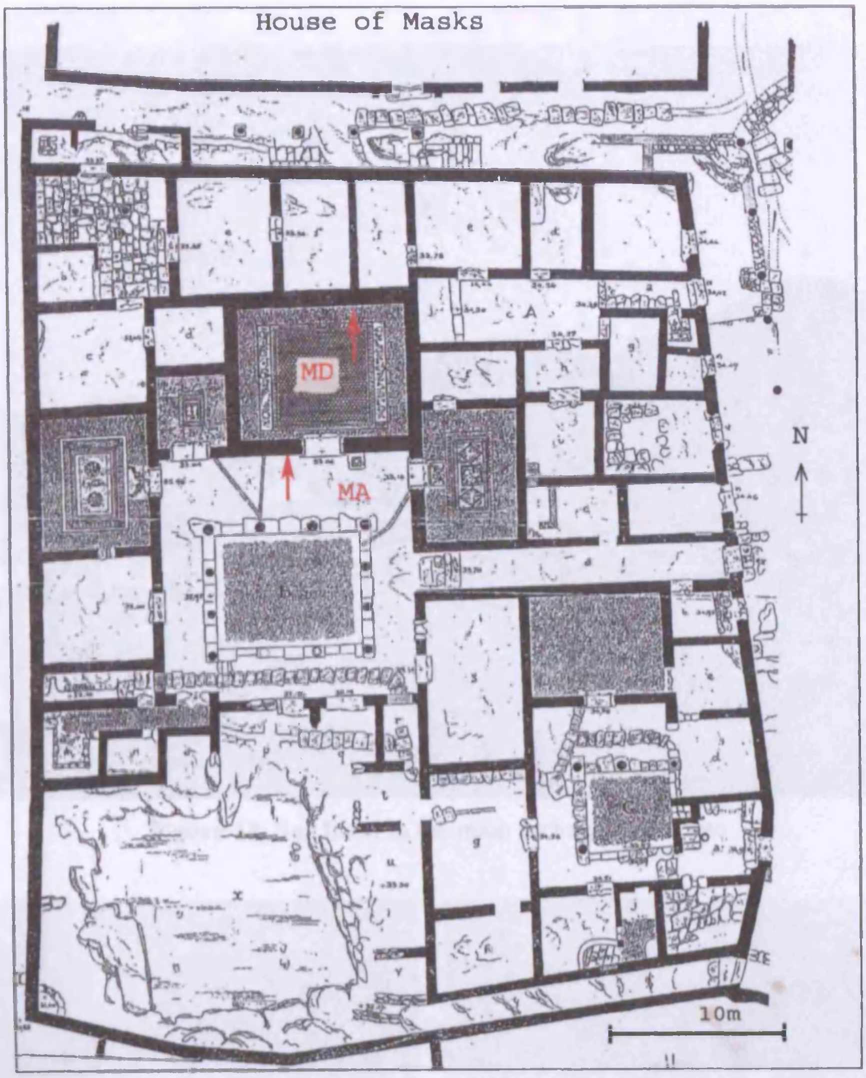


Figure 12. House of Masks ground plan. Red arrows mark sampling locations

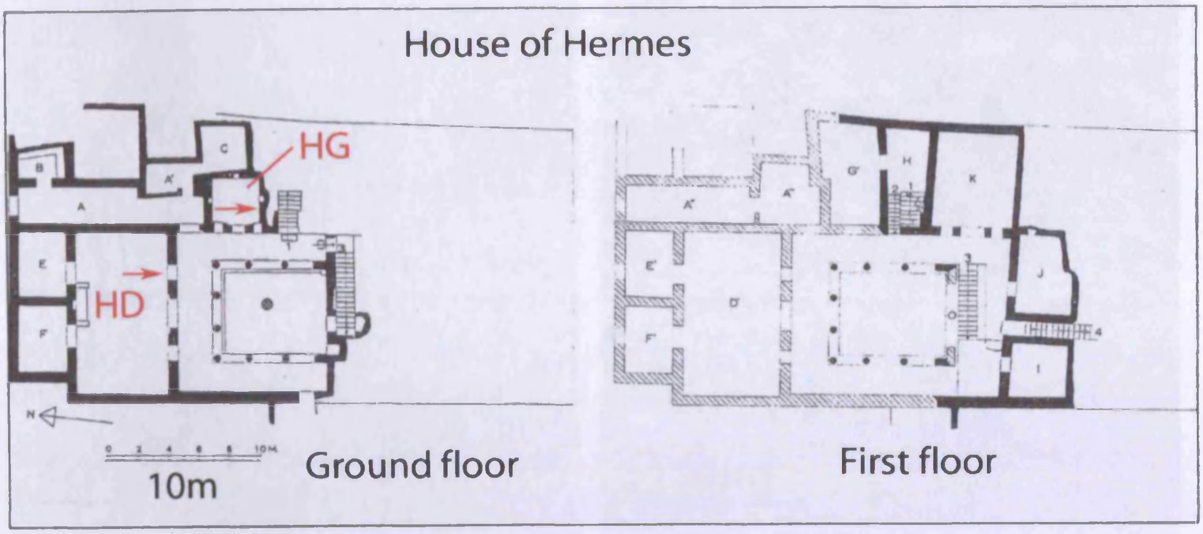


Figure 13. House of Hermes ground plan. Red arrows mark sampling locations

Figure 14. Sea flood in the main archaeological site

Figure 15 Salt crust and lime wash flaking in MD

Figure 15 Dense crust in HG

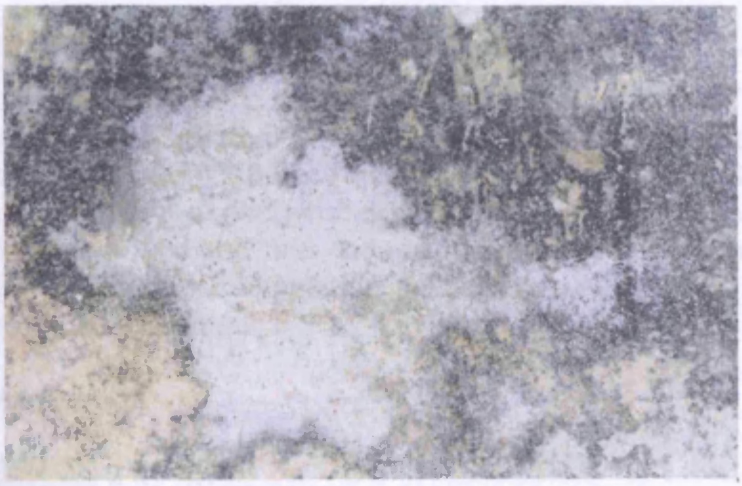


Figure 16 Powdery salt efflorescence in MD (veil)

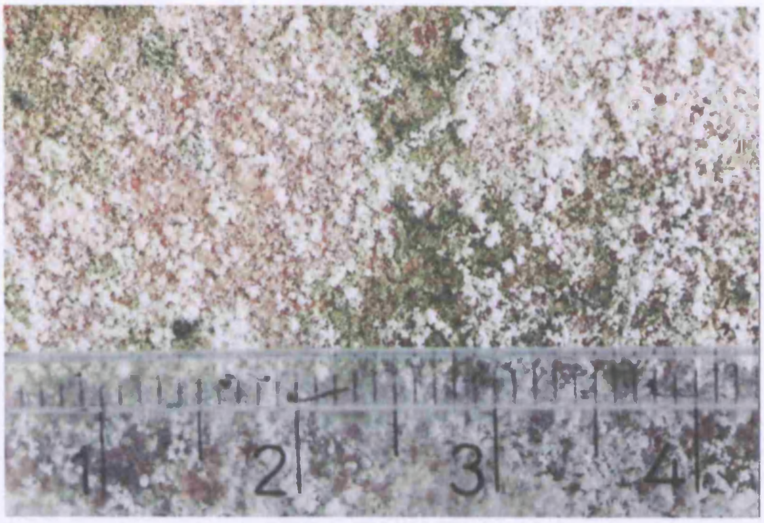


Figure 16 Whisker like efflorescence in HG

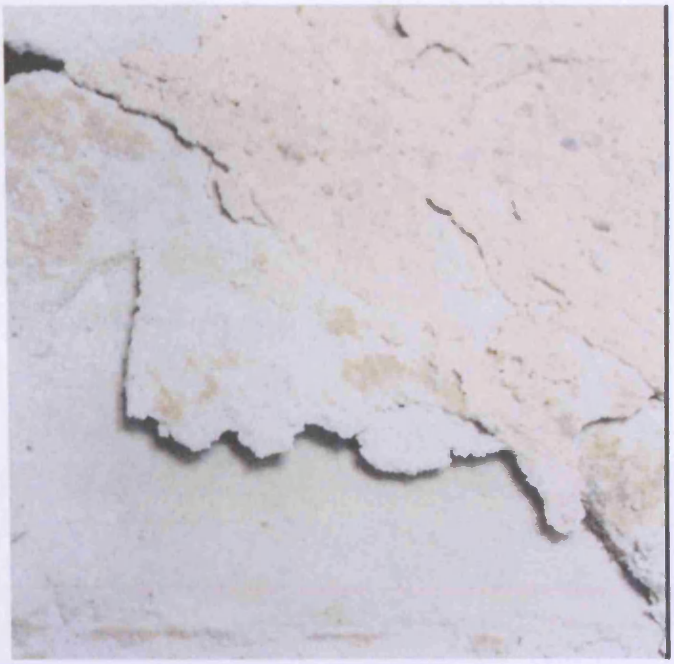


Figure 17 Multiple layers detachments

APPENDIX II: Graphic documentation

The graphics have been acquired by the directorate of conservation, Hellenic ministry of culture and modified for the purposes of this project. They depict parts of the walls with preserved renderings. The documentation has been completed in progress and thus it contains information acquired in several campaigns. It is not representative of a certain period but more likely the result of various observations. Furthermore several people have been involved and thus the result subjects to their conception. Apart from the sampling locations the documentation includes as well walls of the same rooms that have not been sampled as reference.

Legend

🟩 Salt efflorescence
⬜ Conservation mortars
🟪 Detachments
🟨 Flaking
🟧 Lime wash loss
🟥 Mortar loss
🟦 Microorganisms (algae)
▩ Pulverised material
• MD2 Sampling location

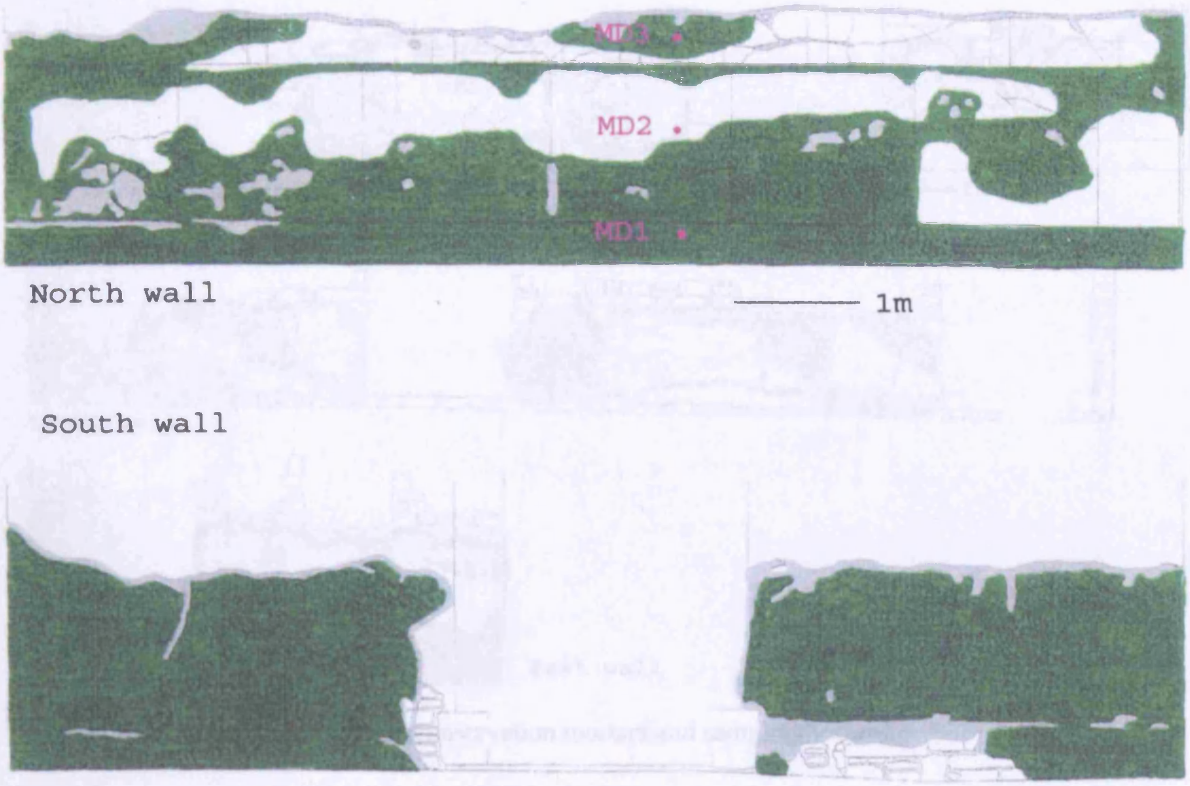


Figure 1. Room MD. Salt efflorescence and sampling locations

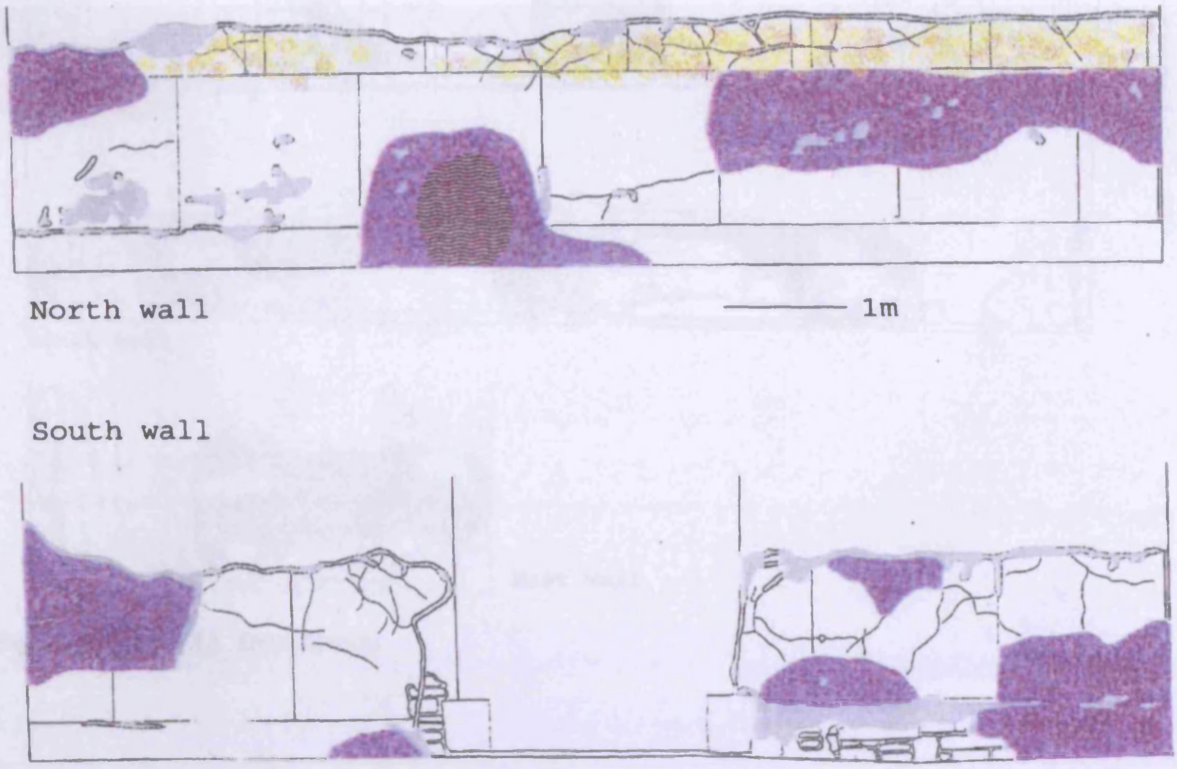


Figure 2. Room MD. Detachments and flaking

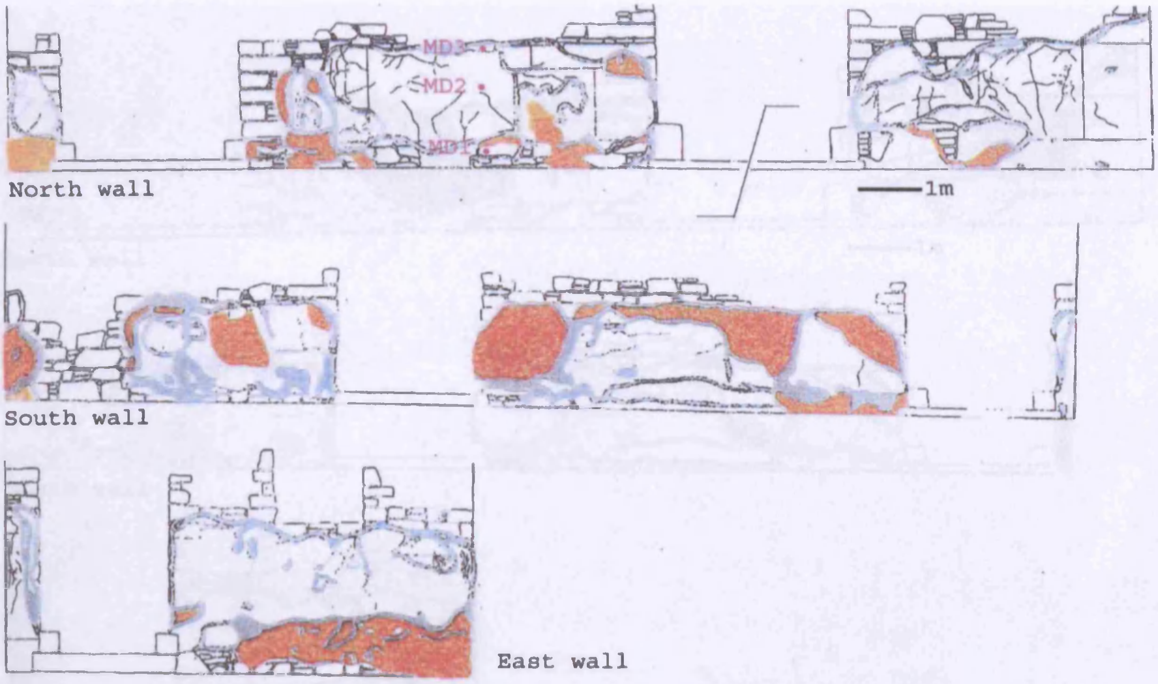


Figure 3. Room MA. Material loss, conservation mortars and sampling locations

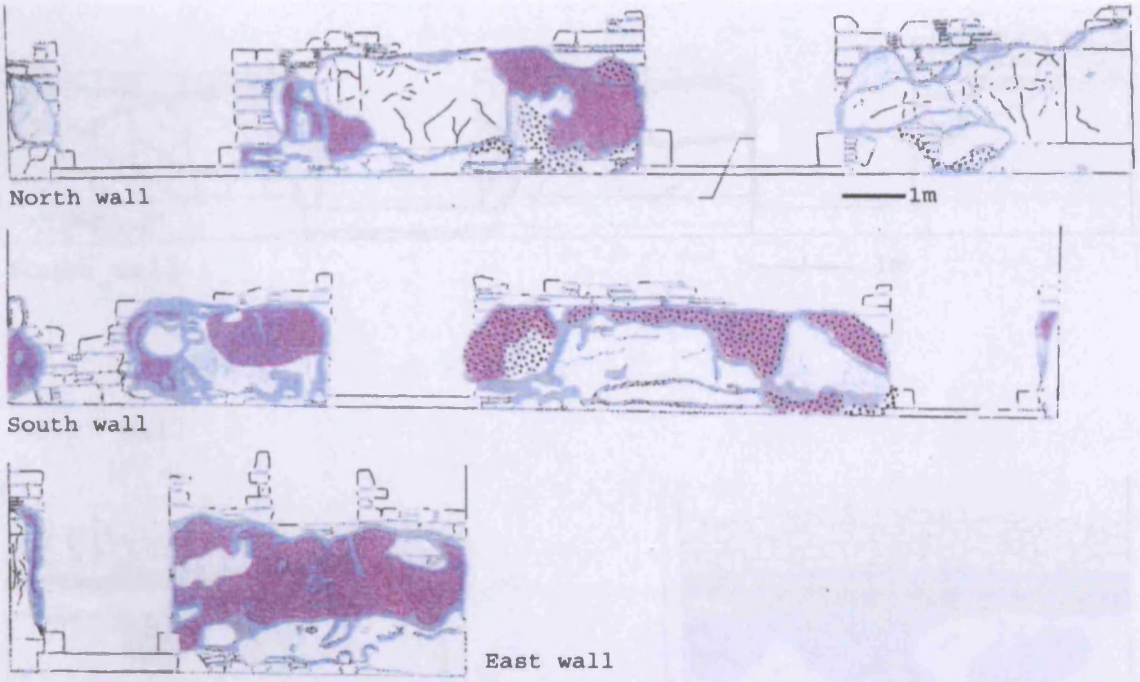


Figure 4. Room MA. Detachments

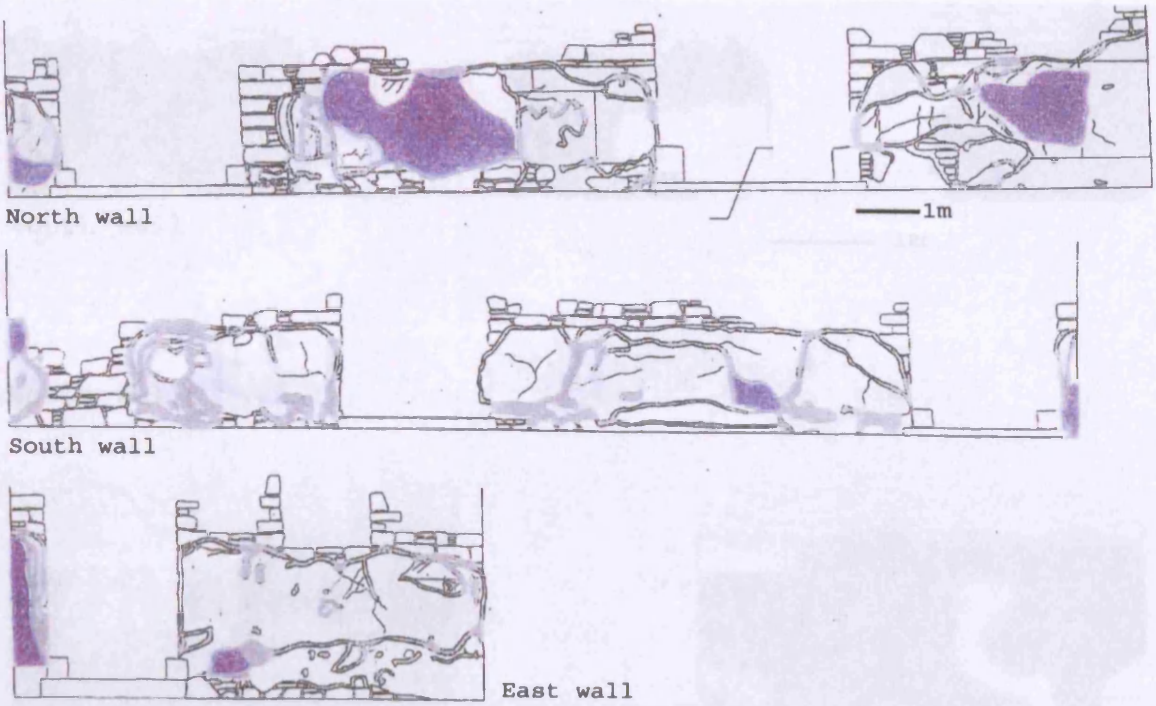


Figure 5. Room MA. Detachment (supplementary)

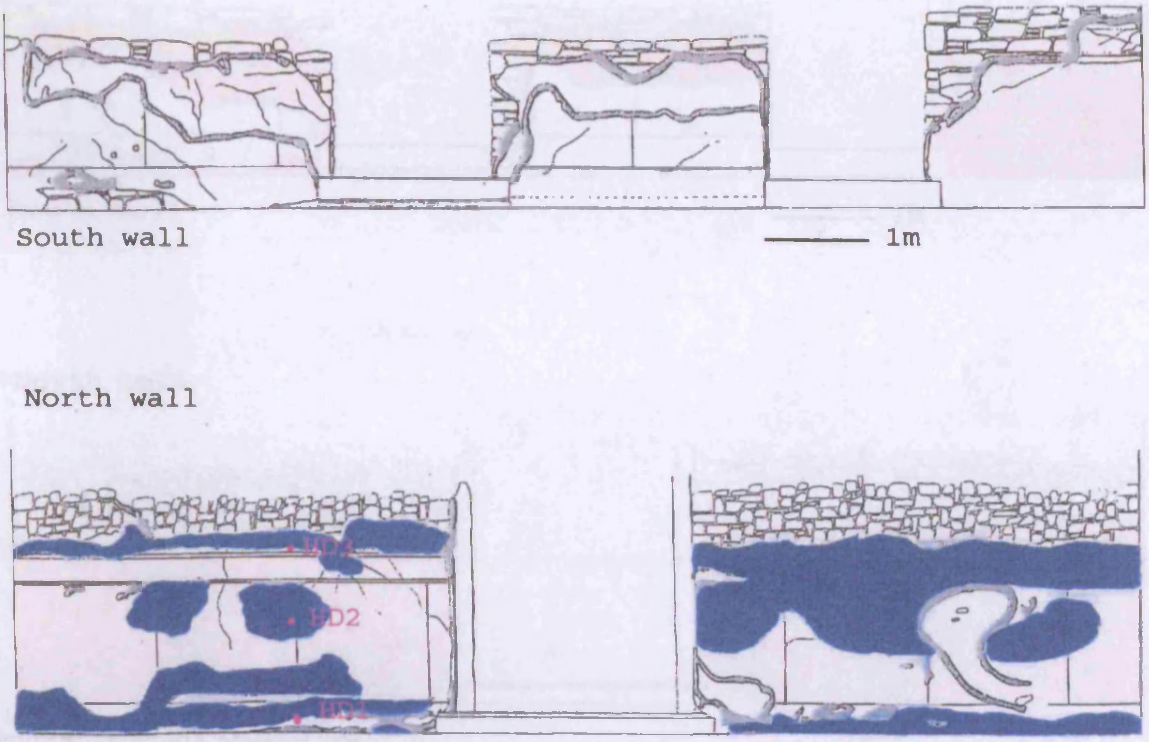


Figure 6. Room HD. Biological remains, conservation mortars and sampling locations

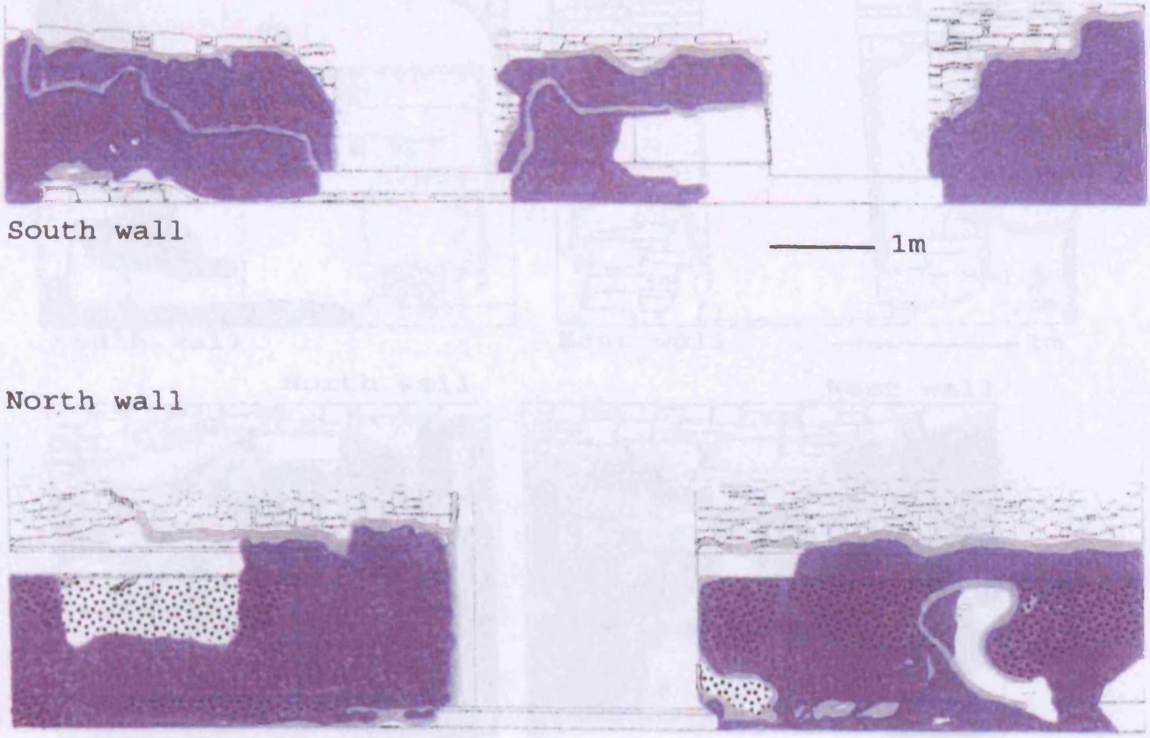


Figure 7. Room HD. Detachments and pulverized material

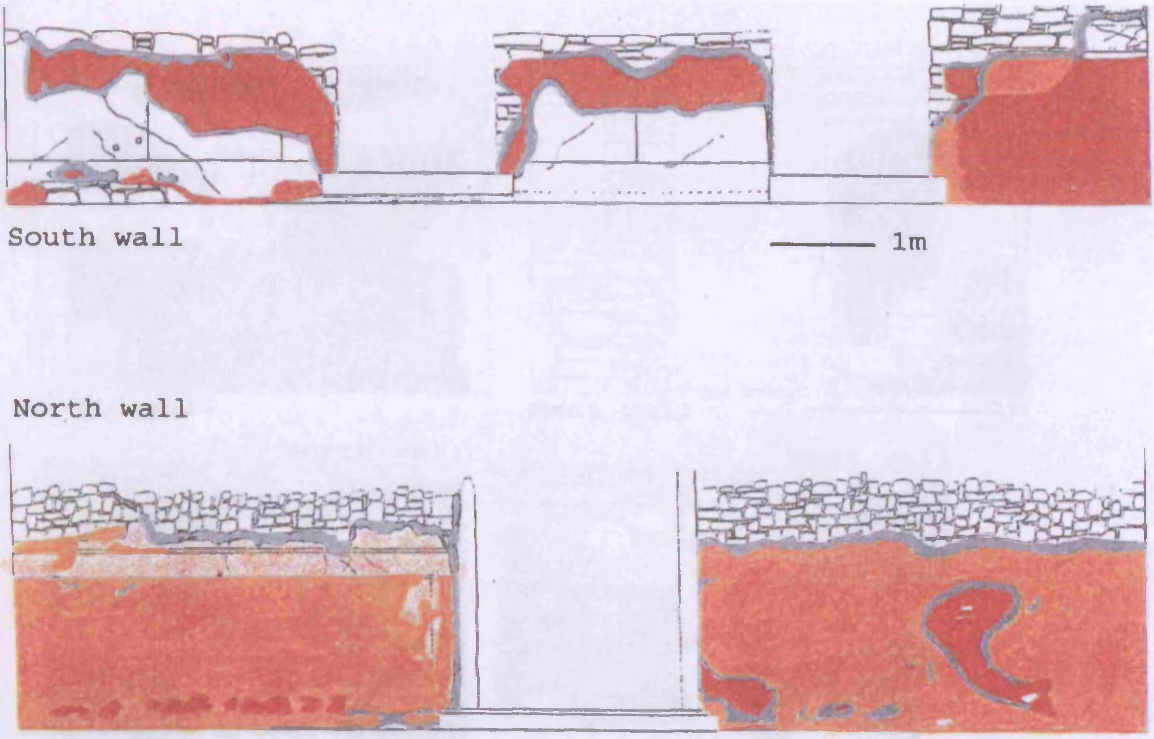


Figure 8. Room HD. Material loss

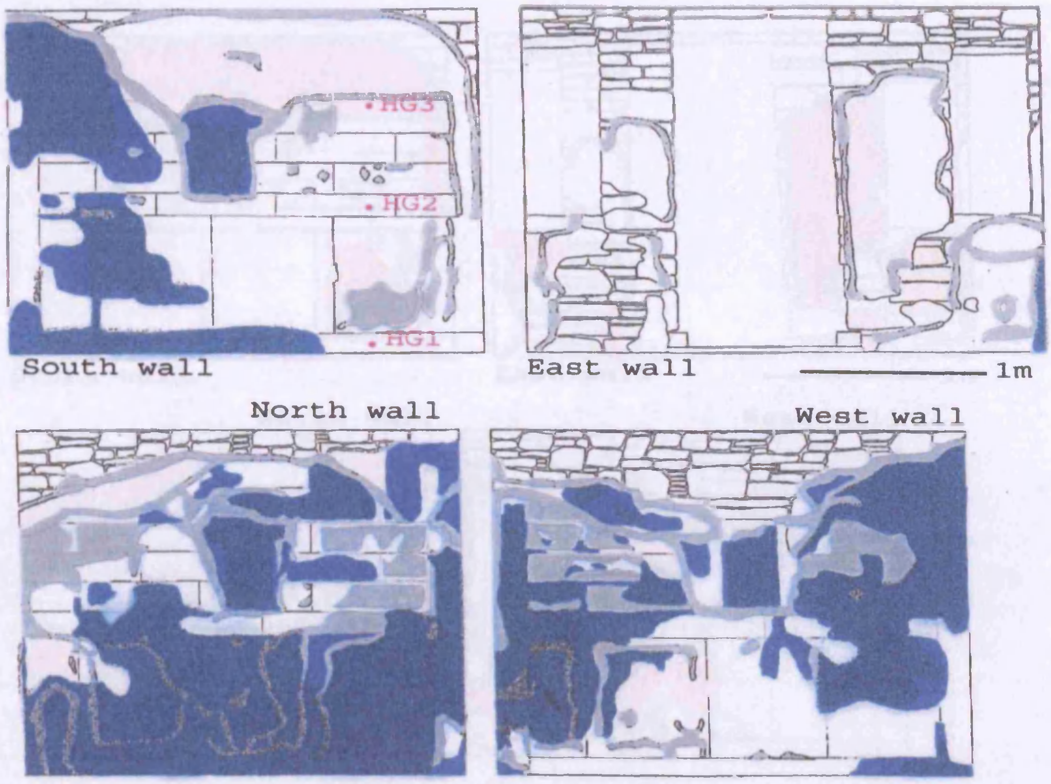


Figure 9. Room HG Algae, conservation mortars and sampling locations

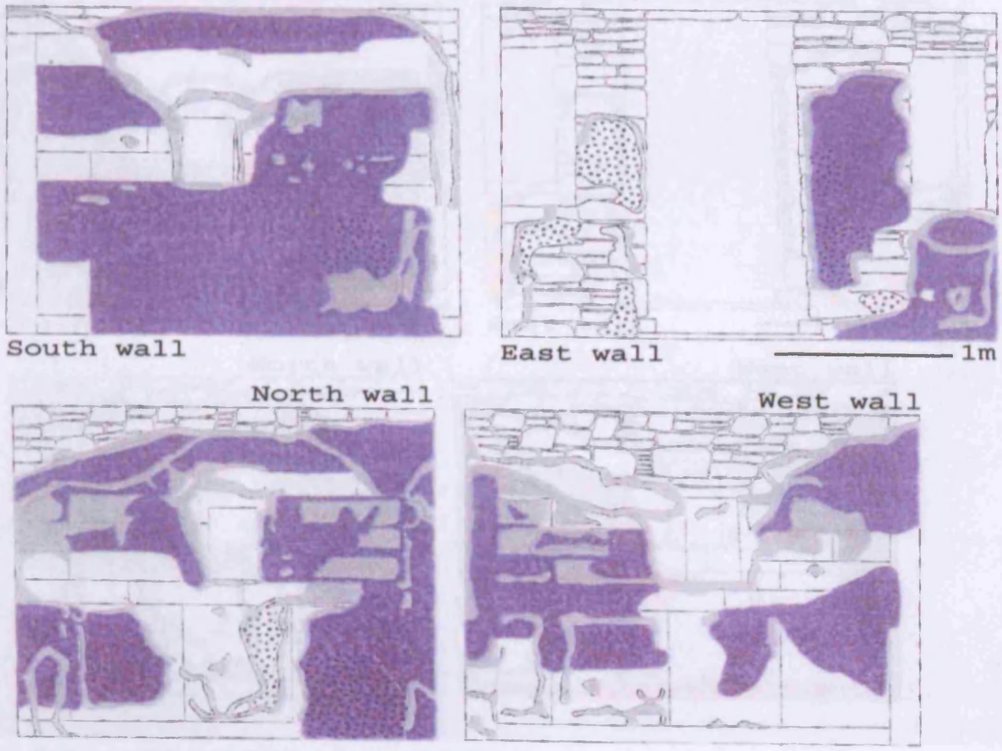


Figure 10. Room HG. Detachments

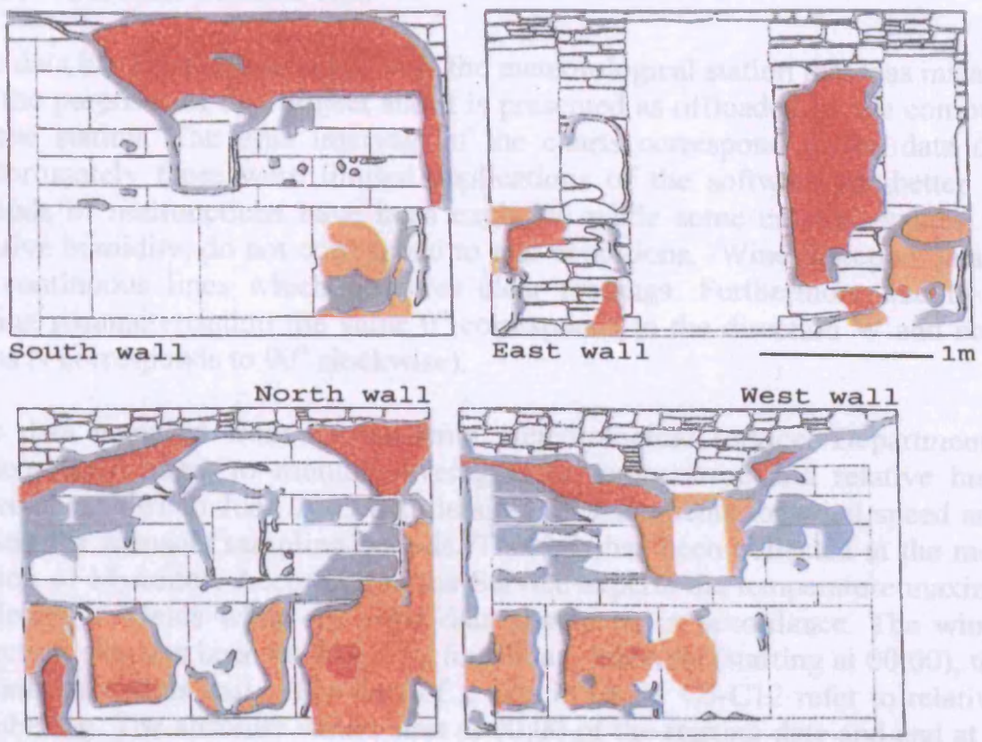


Figure 7. Room HG. Material loss

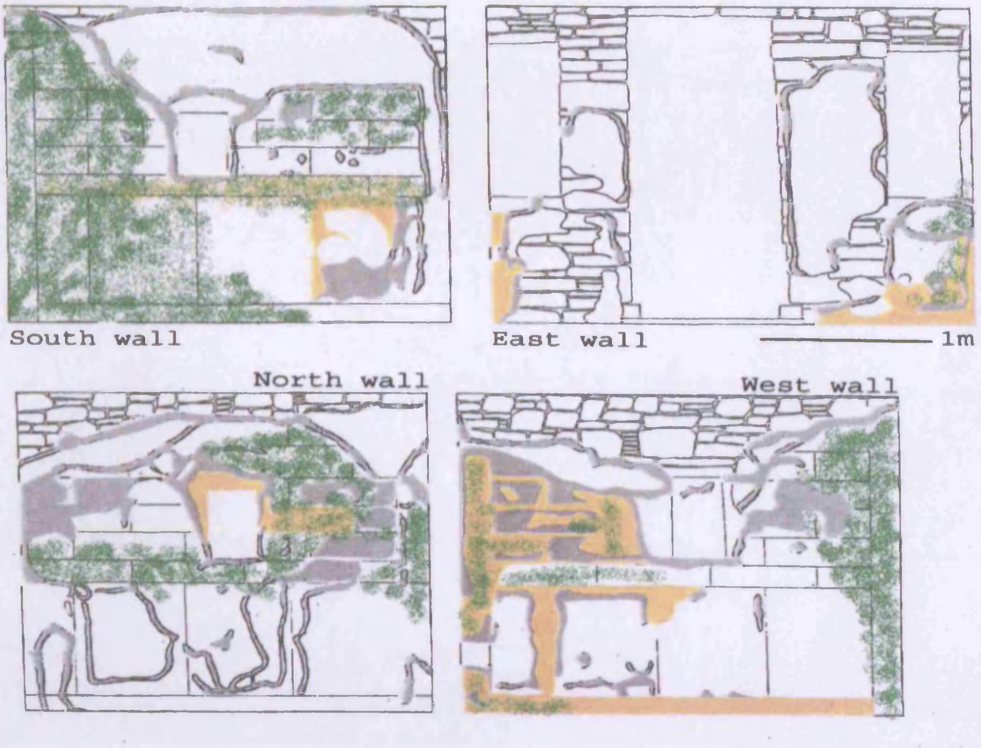


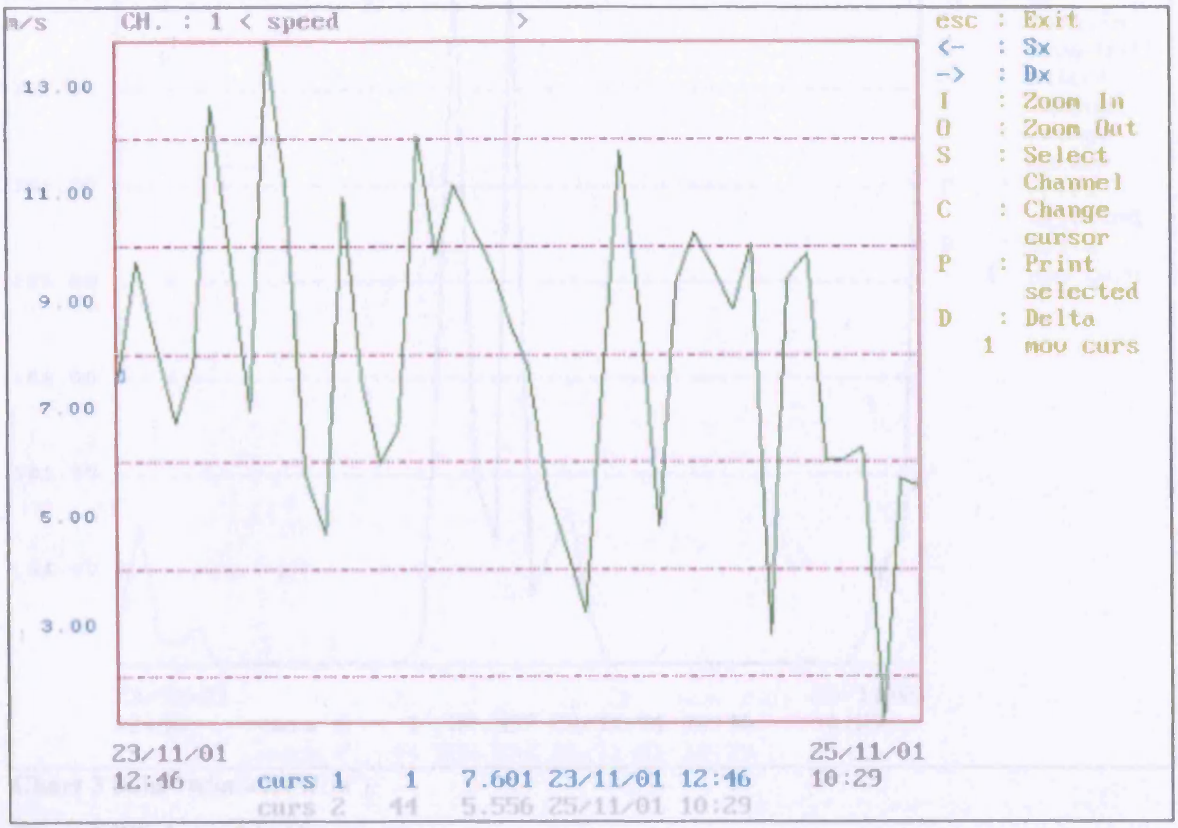
Figure 8. Room HG. Salt efflorescence and flaking

APPENDIX III: Climatic data

The data has been downloaded from the meteorological station that was installed in Delos for the purposes of this project and it is presented as offloaded by the computer software of the station. The time intervals of the charts correspond to the data downloading. Unfortunately there were limited applications of the software for better presentation. Periods of malfunctions have been excluded while some extreme values, primarily of relative humidity, do not correspond to real conditions. Wind direction data is presented by continuous lines which obscures clear readings. Furthermore due to mishandling during parameterisation the value 0^o corresponds to the direction W and not N as usual (thus N corresponds to 90^o clockwise).

The data acquired from the Hellenic meteorological service, Department of statistic meteorology refers to monthly averages for temperature and relative humidity from November 2001 to June 2003 and detailed measurements for wind speed and directions during the aerosols sampling periods. The data has been collected at the meteorological station of Mykonos. According to the Service experts the temperature maximums should be lower in Delos while the wind data should be in accordance. The wind speed and direction data has been collected by four hours intervals (starting at 00:00), thus there are six measurements daily. The data of x axis in charts C5-C12 refer to relative ascending numbering. The absolute values start at 00:00 of the starting date and end at 20:00 of the last day as referred on the chart title. Details of the station's specifications can be found in the directory www.hnms.gr. Accordingly detailed data acquired by the Hellenic centre of marine research (Mykonos buoy) can be found in www.poseidon.gr.

IIIA. Offloaded charts from the meteorological station in Delos



```
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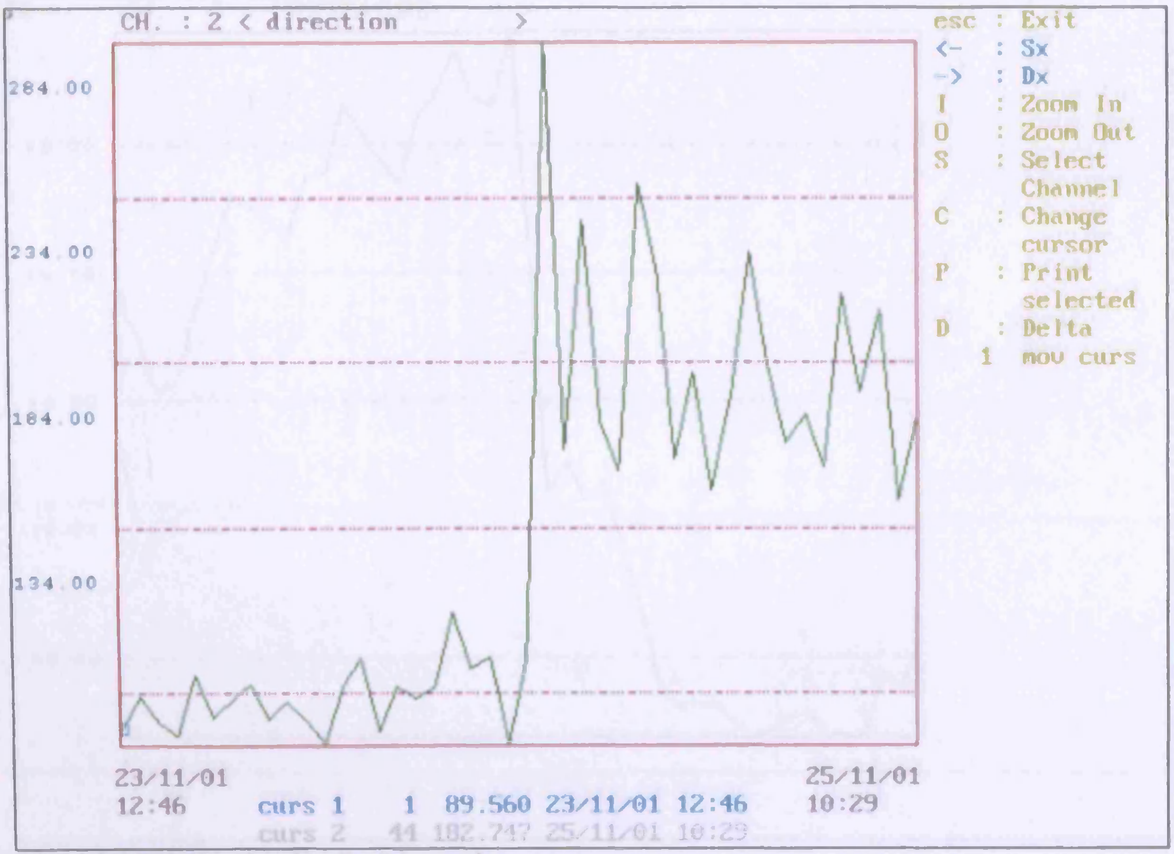
curs 2   44   5.556 25/11/01 10:29
```

Chart 1 Wind speed (m/s)



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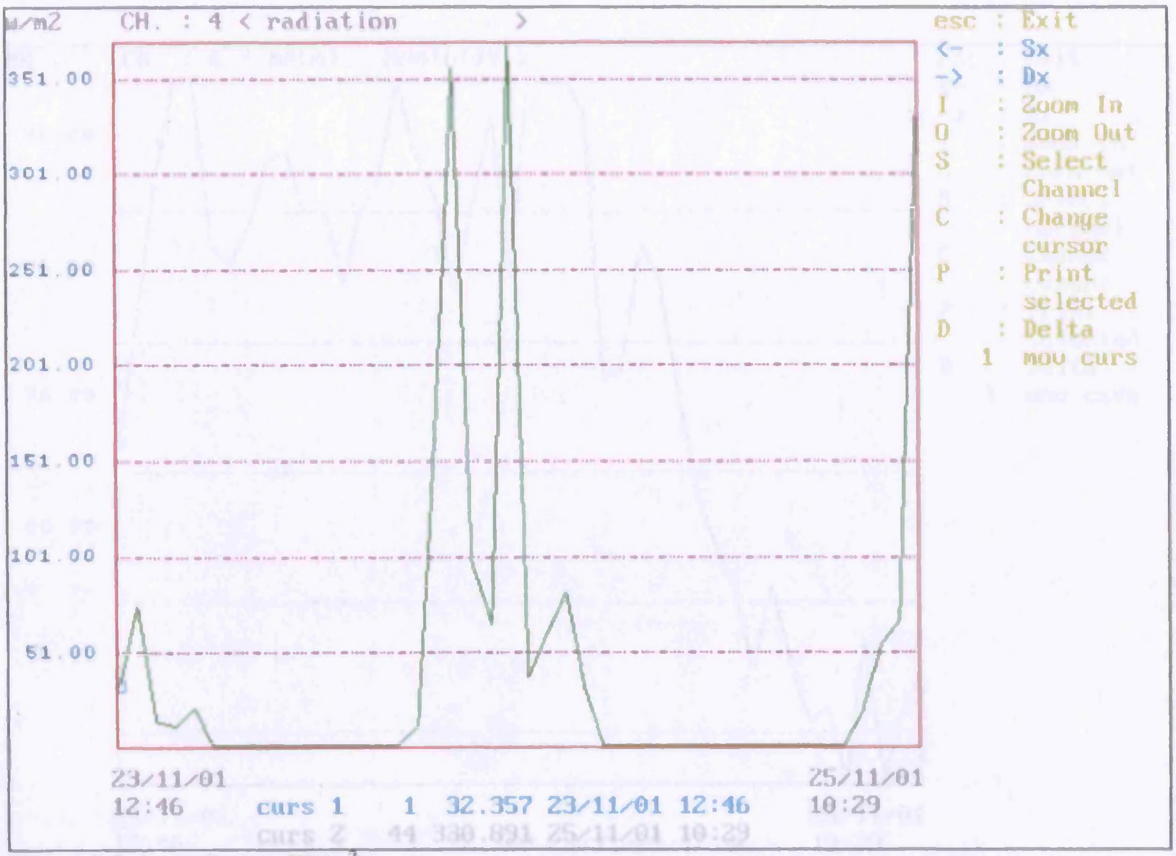
curs 2   44 182.747 25/11/01 10:29
```

Chart 2 Wind direction (cardinal degrees)



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curs 2   44 330.891 25/11/01 10:29
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Chart 3 Solar radiation (W/m^2)

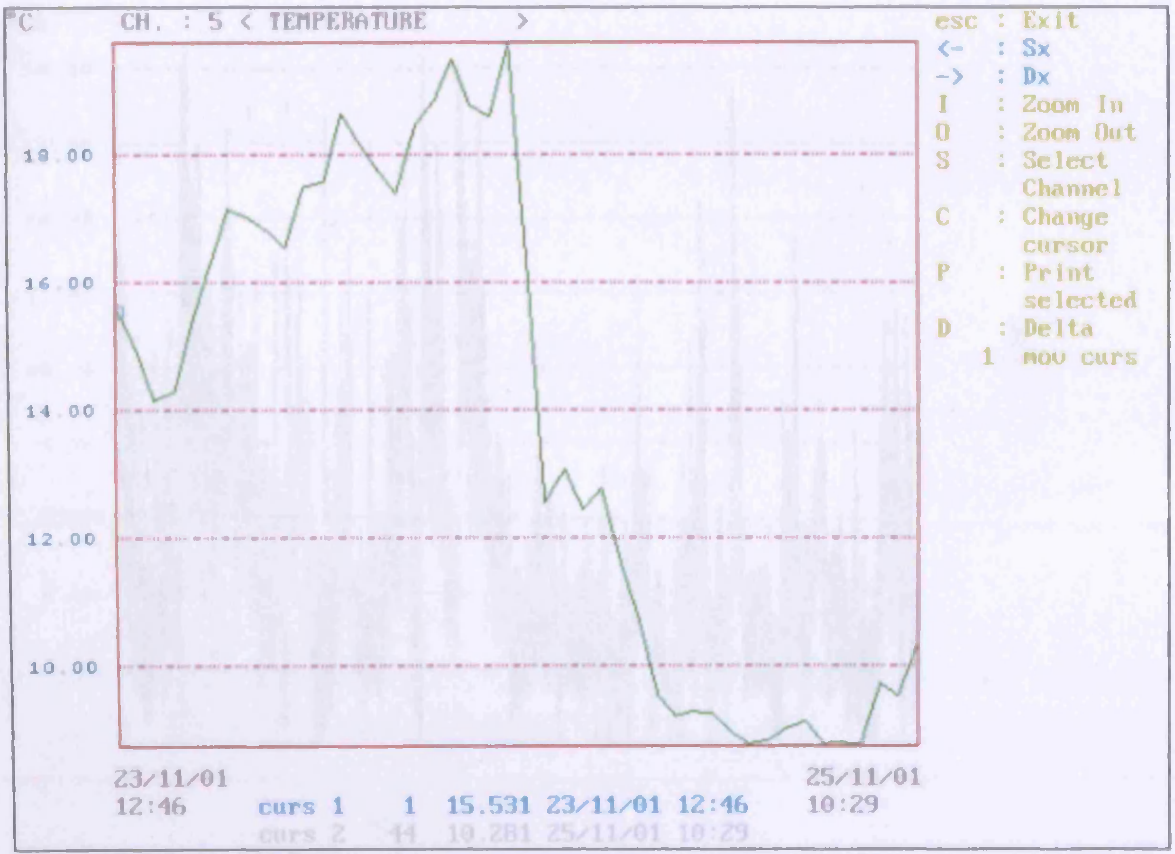

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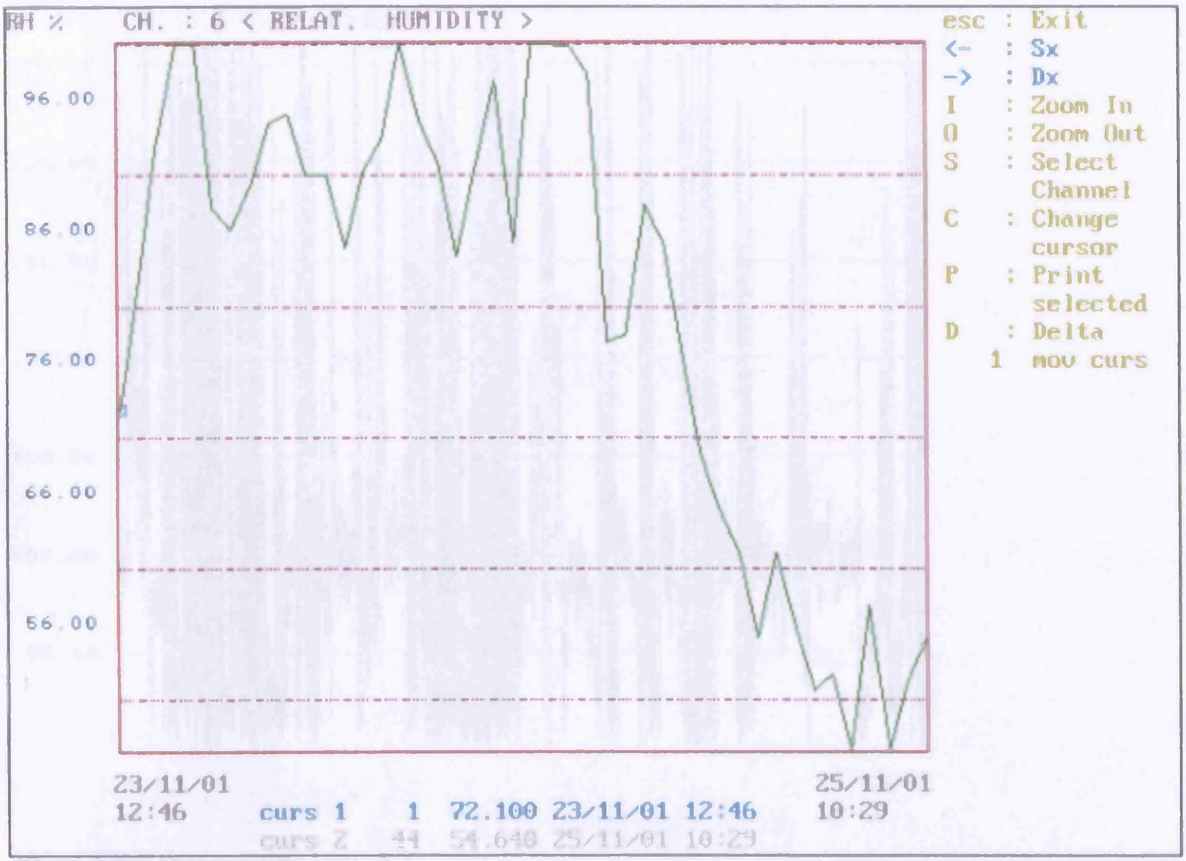
Chart 4 Temperature (C^o)



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curs 2    44  54.640 25/11/01 10:29
```

Chart 5 Relative humidity (%)

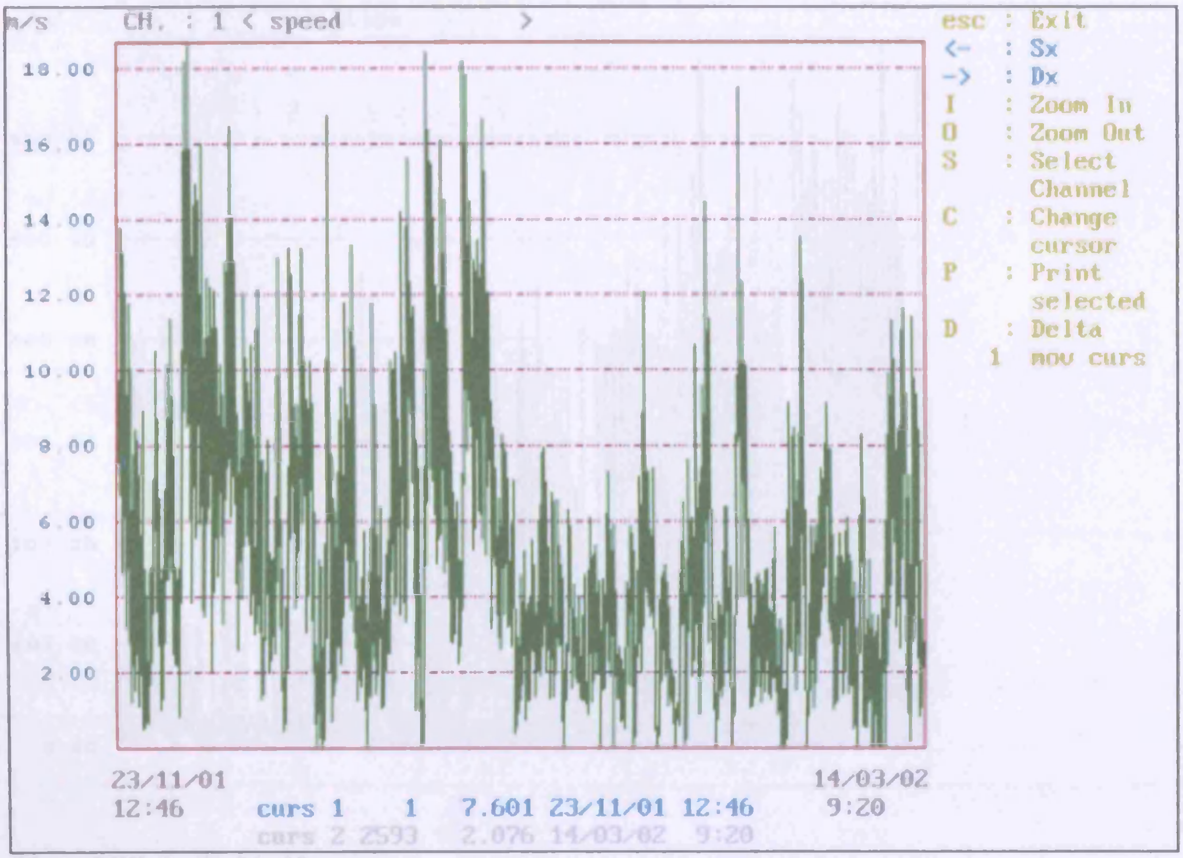

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Chart 6 Wind speed (m/s)

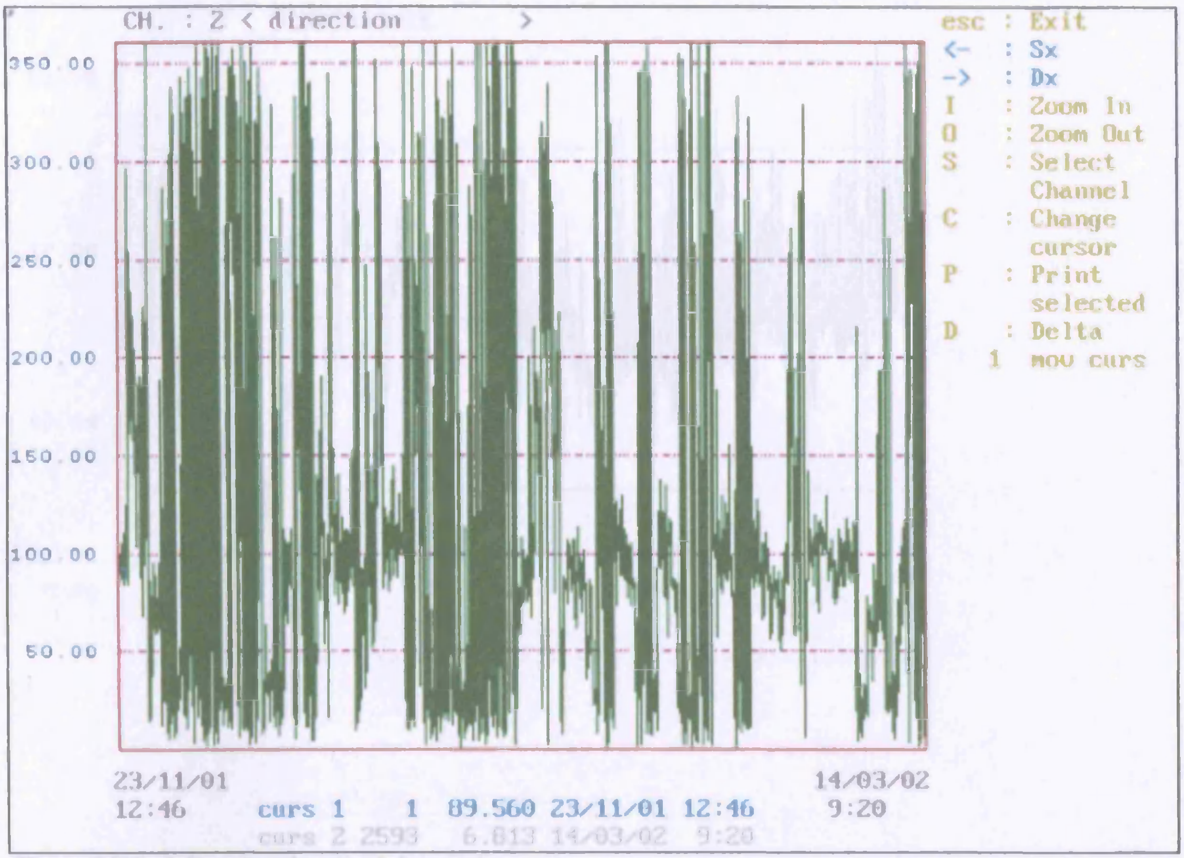

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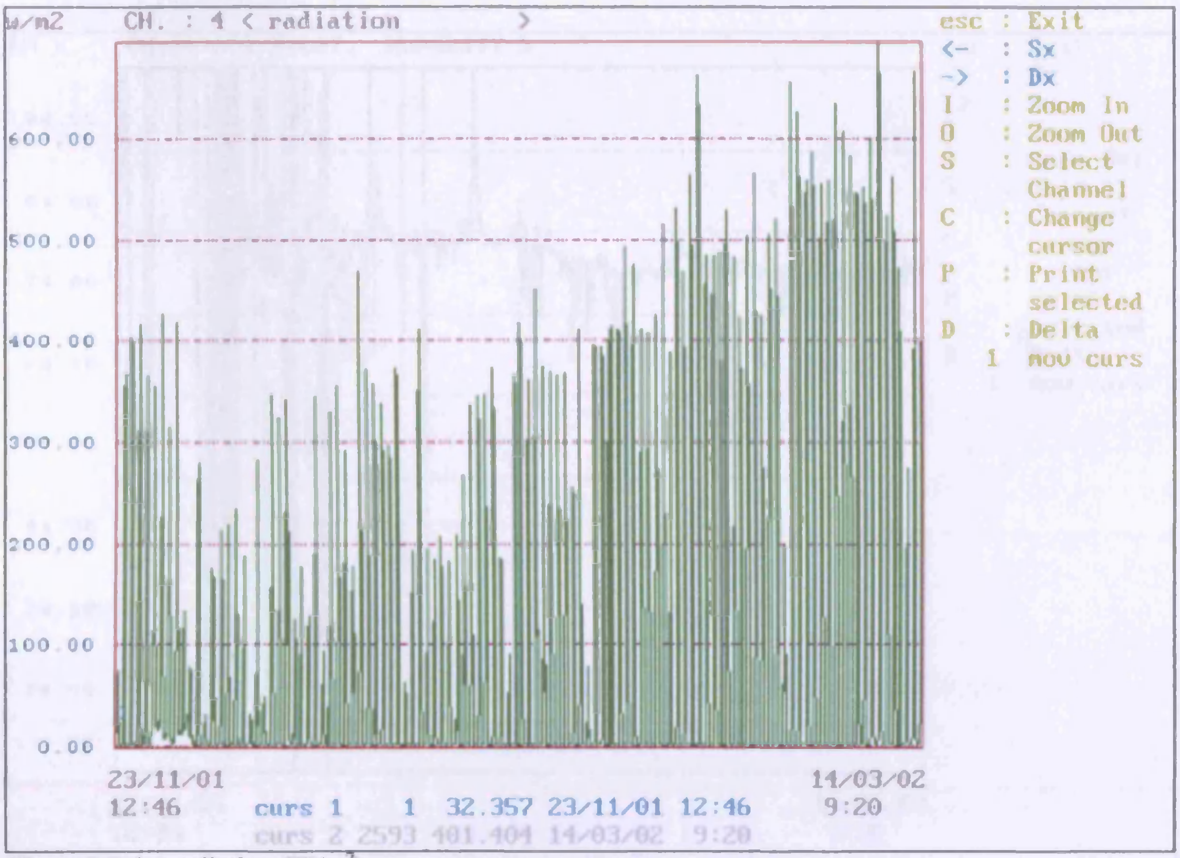
Chart 7 Wind direction (cardinal degrees)



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curs 2 2593 401.404 14/03/02  9:20
```

Chart 8 Solar radiation (W/m^2)

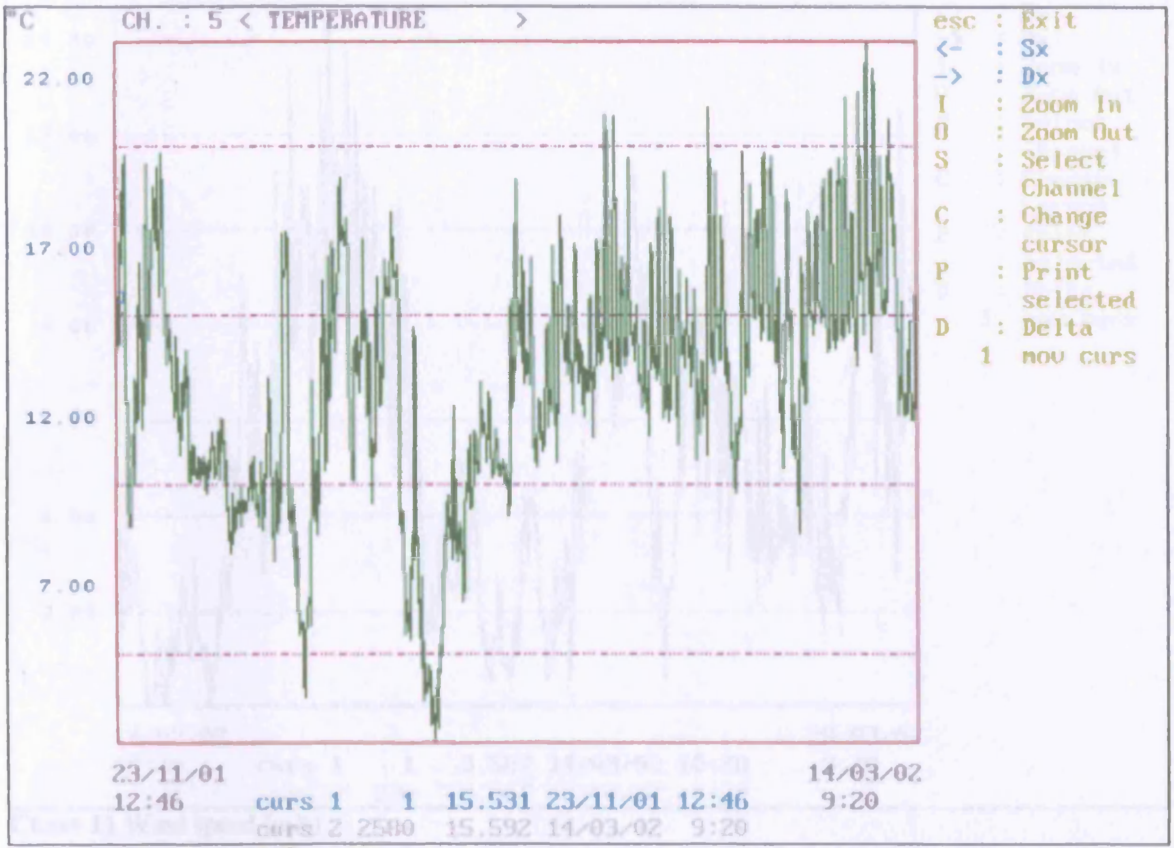

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Chart 9 Temperature (C°)

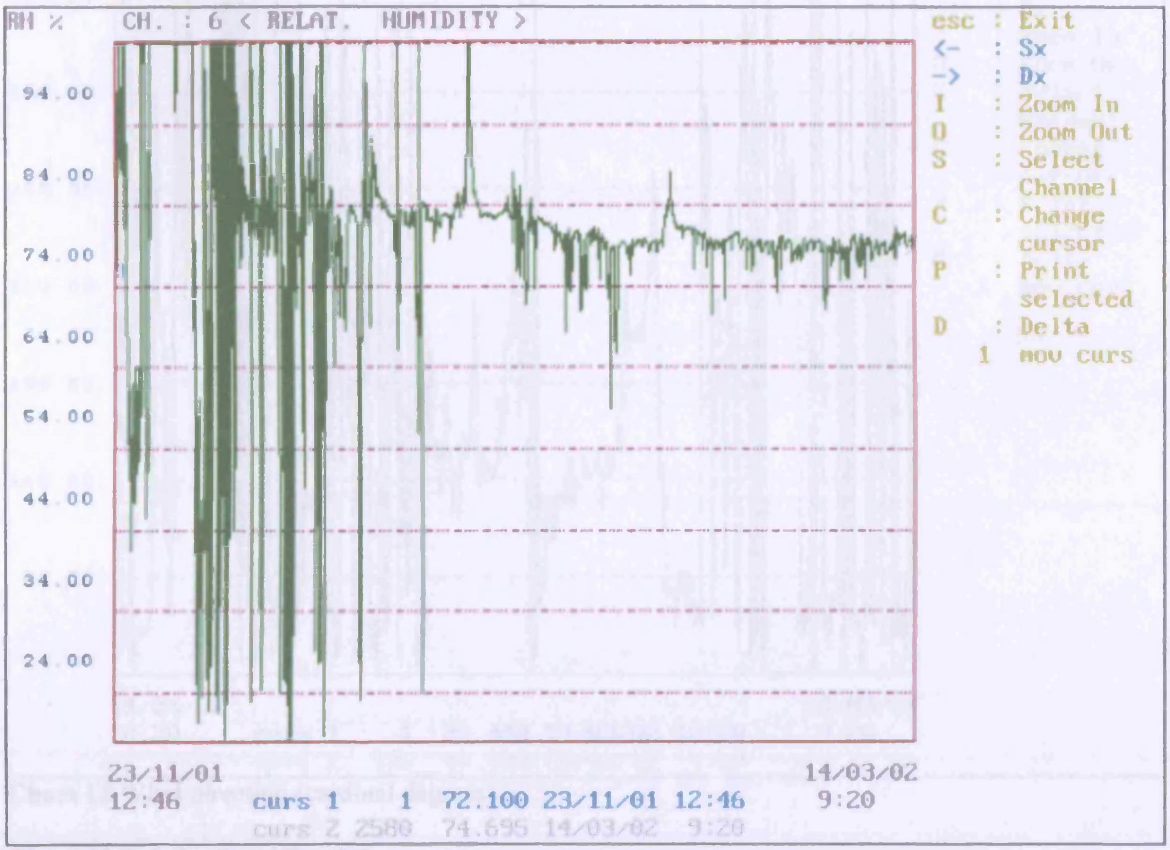

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Chart 10 Relative humidity (%)

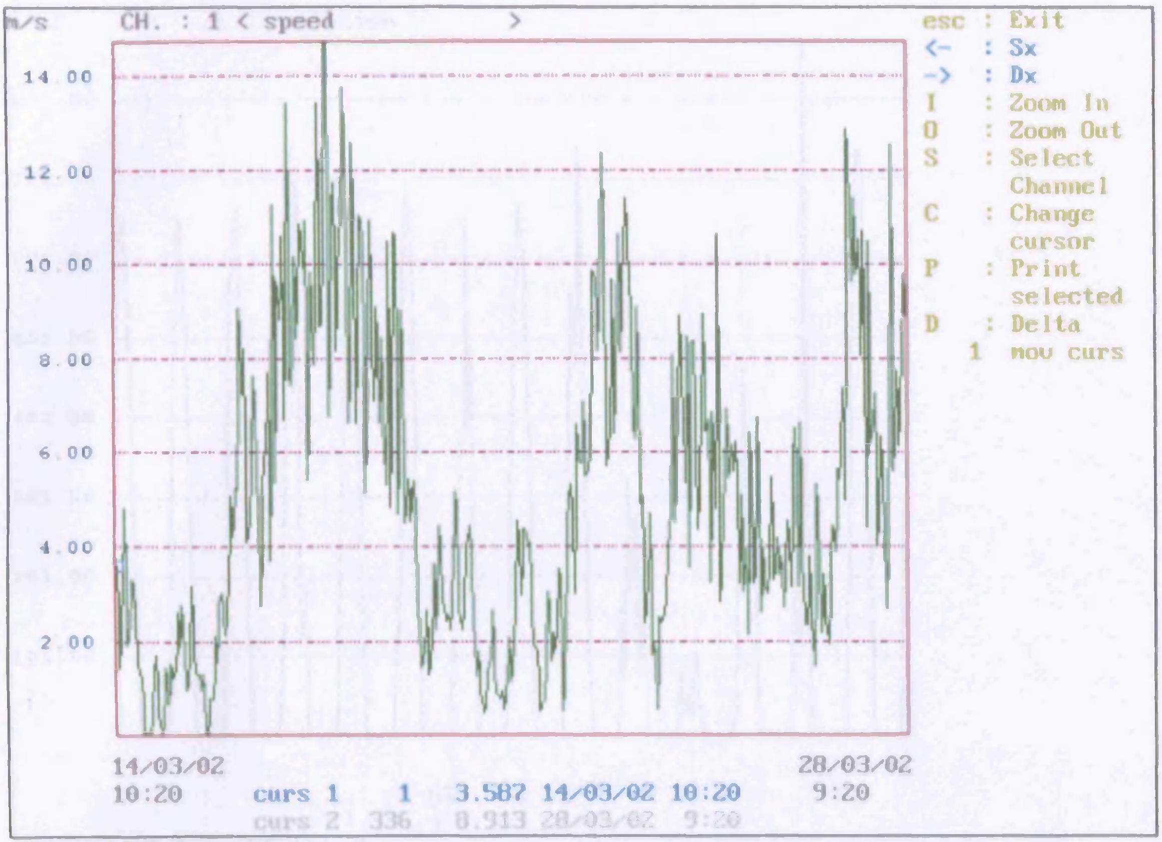

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Chart 11 Wind speed (m/s)

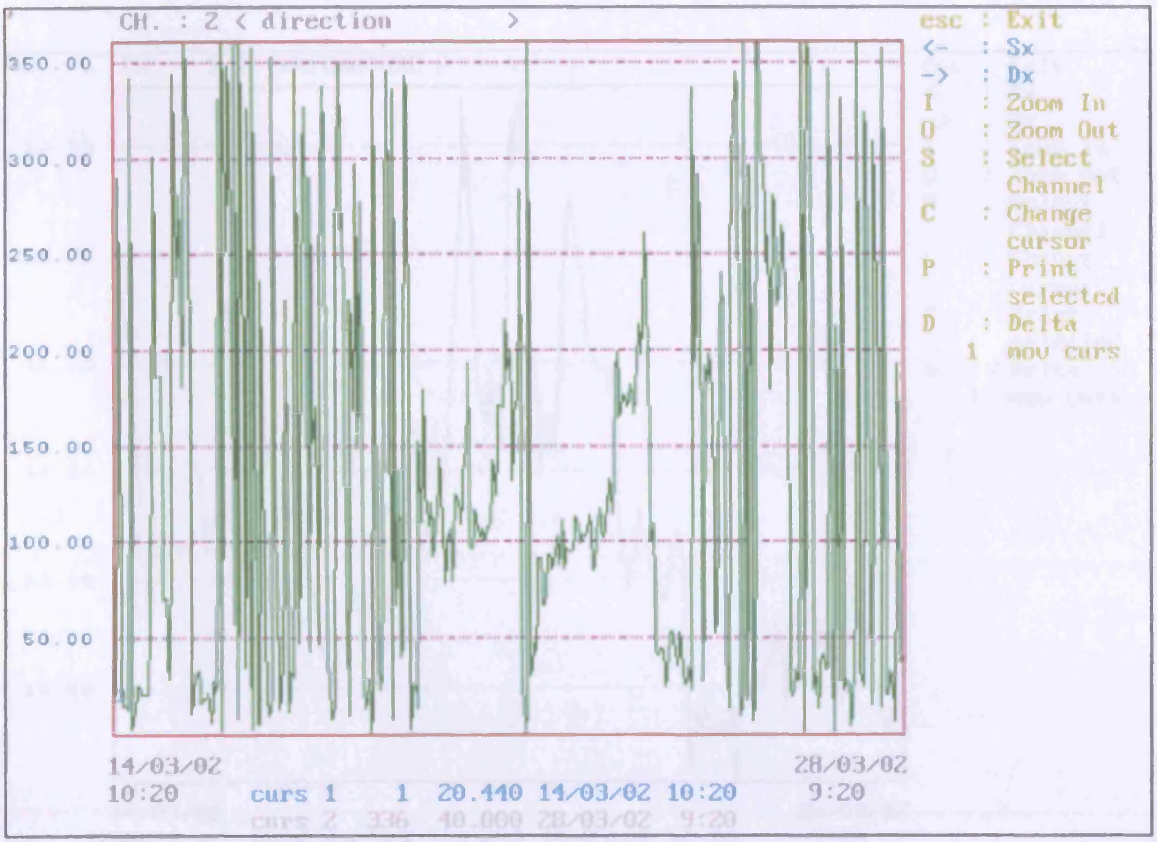

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Chart 12 Wind direction (cardinal degrees)

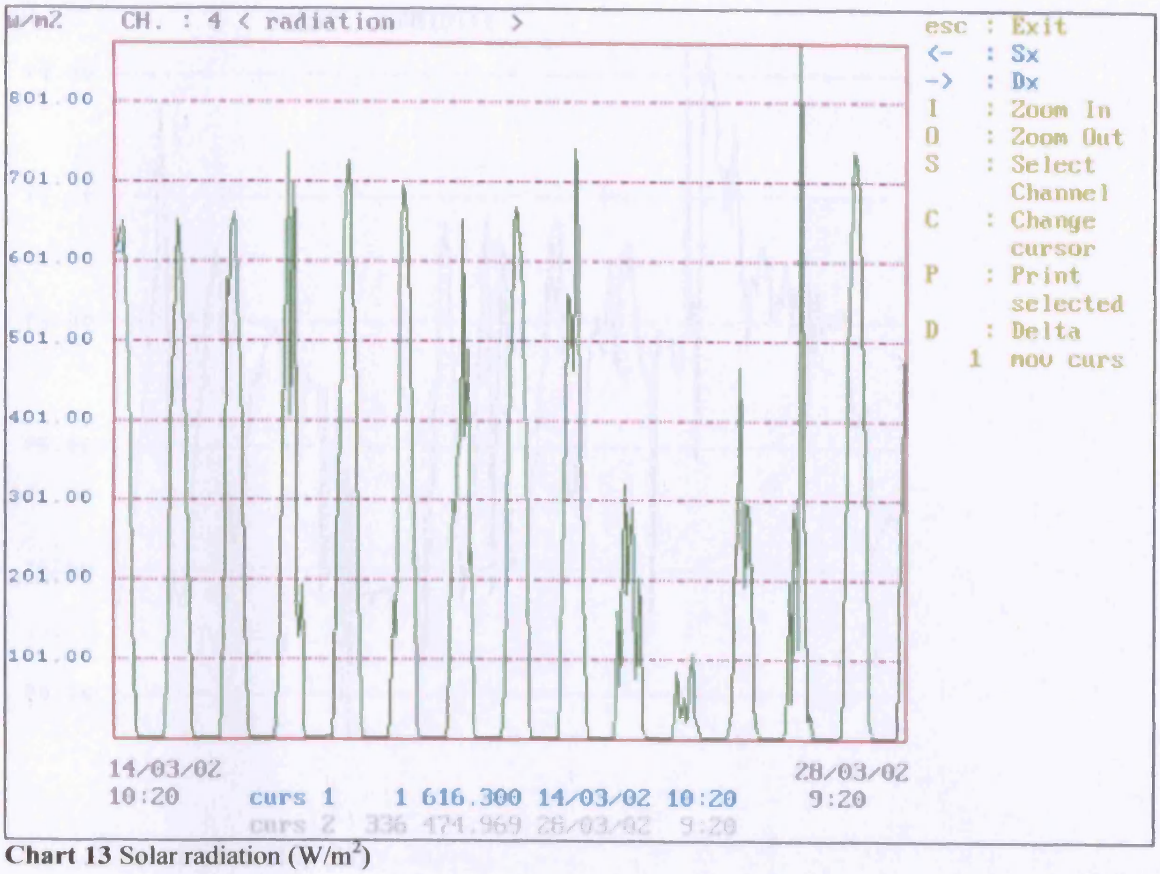

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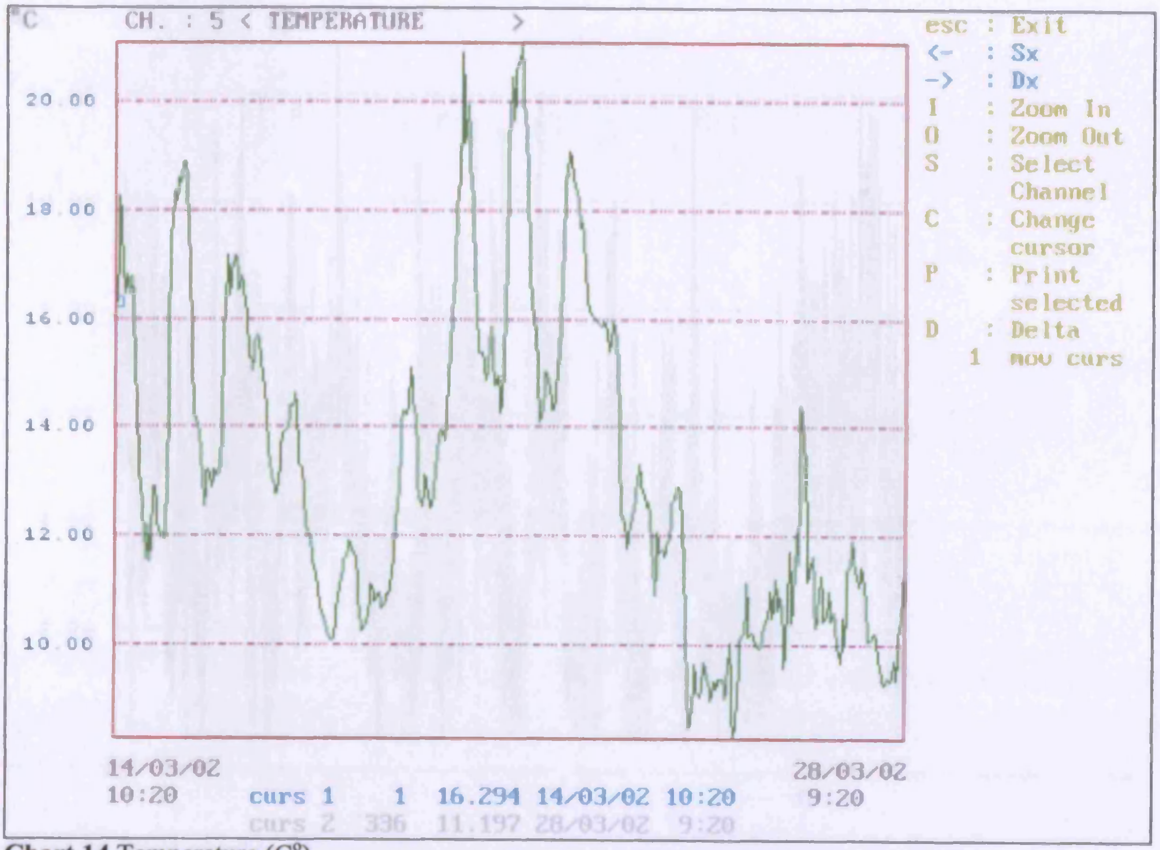
Chart 13 Solar radiation (W/m^2)



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```

Chart 14 Temperature (C^o)

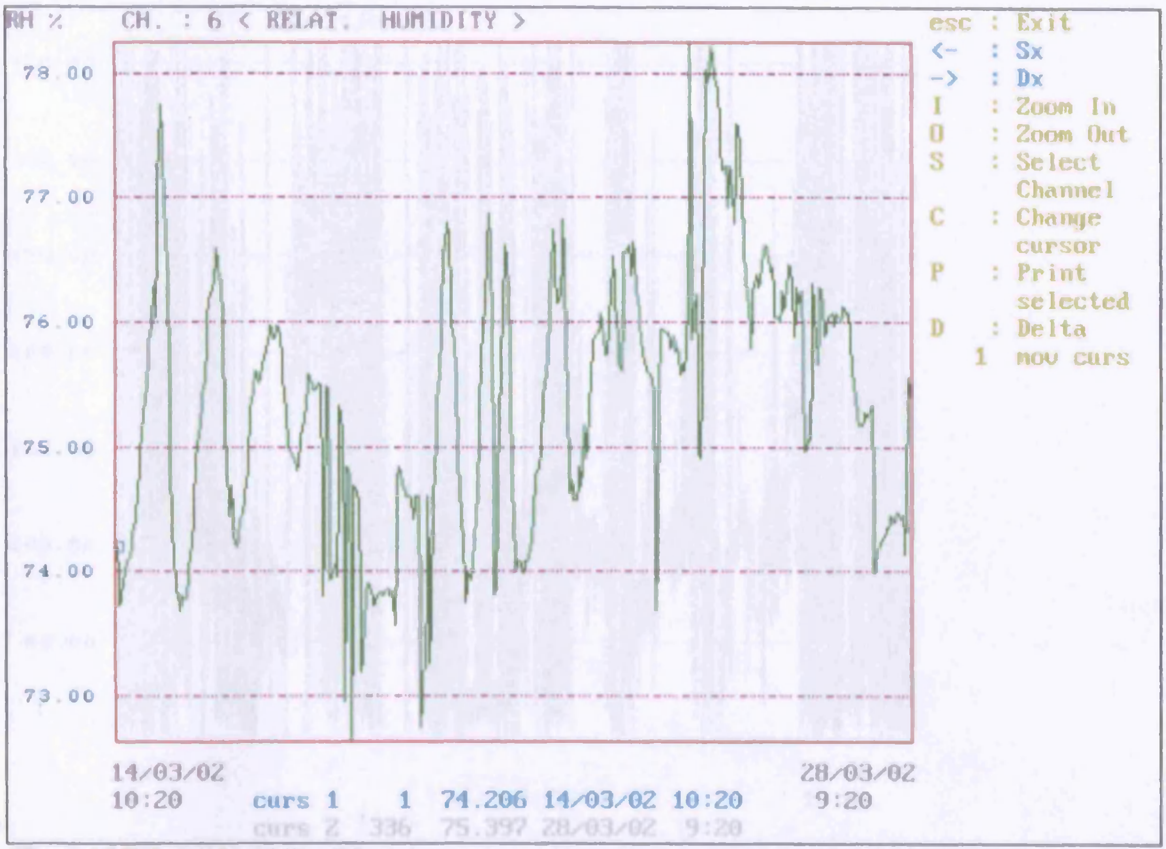

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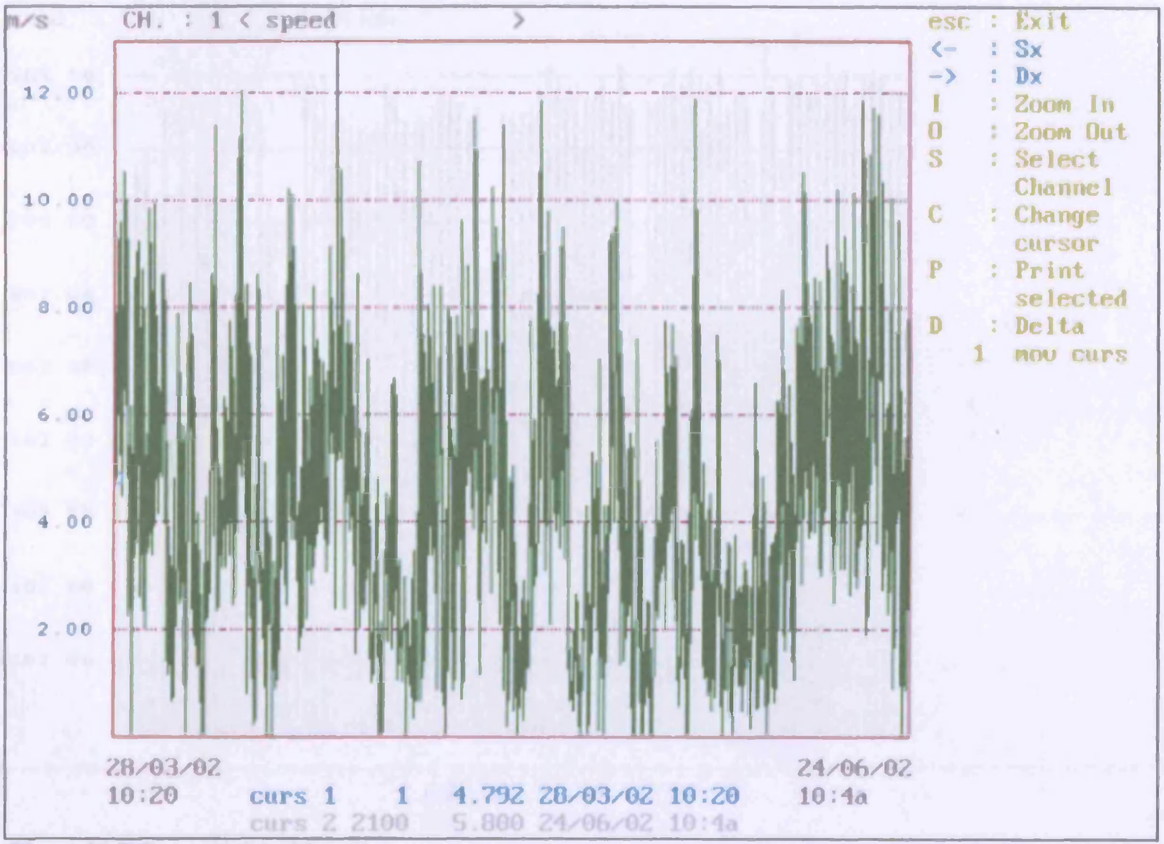
Chart 15 Relative humidity (%)



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curs 2  2100   5.800 24/06/02 10:4a
```

Chart 16 Wind speed (m/s)

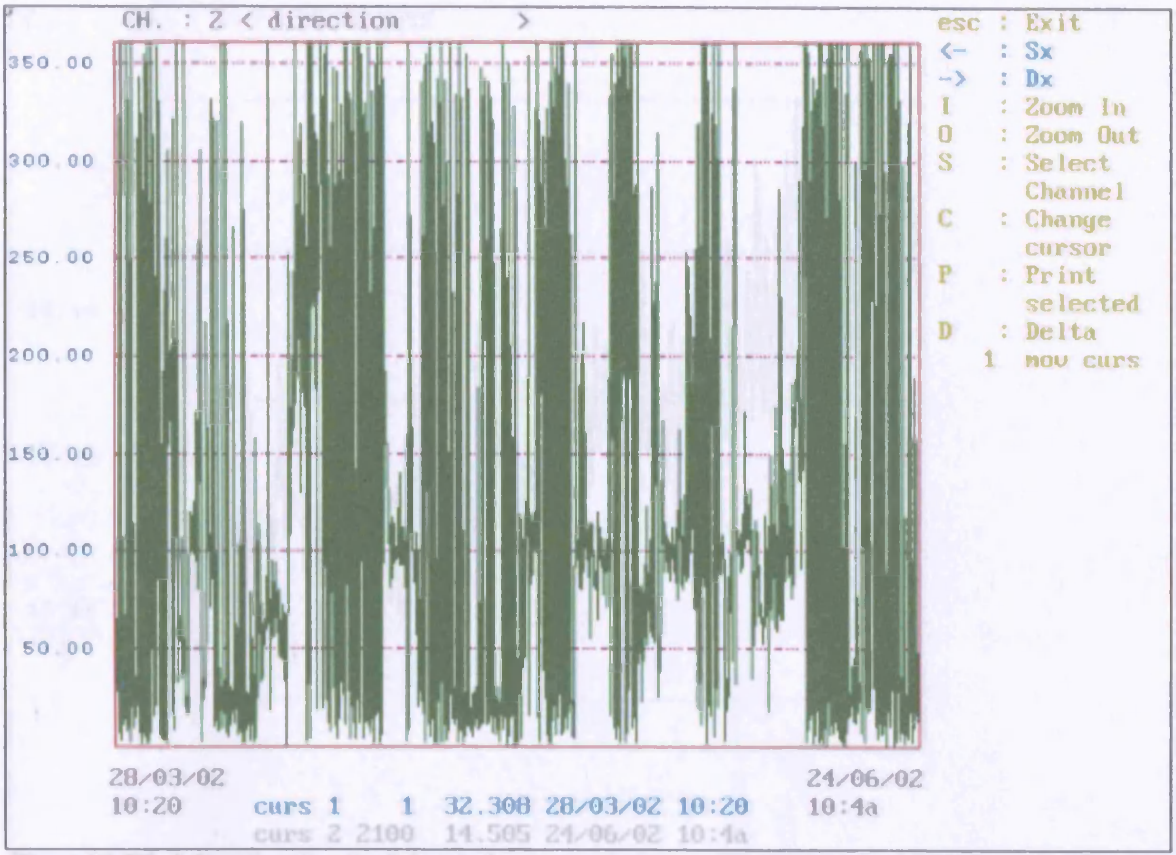


Chart 17 Wind direction (cardinal degrees)

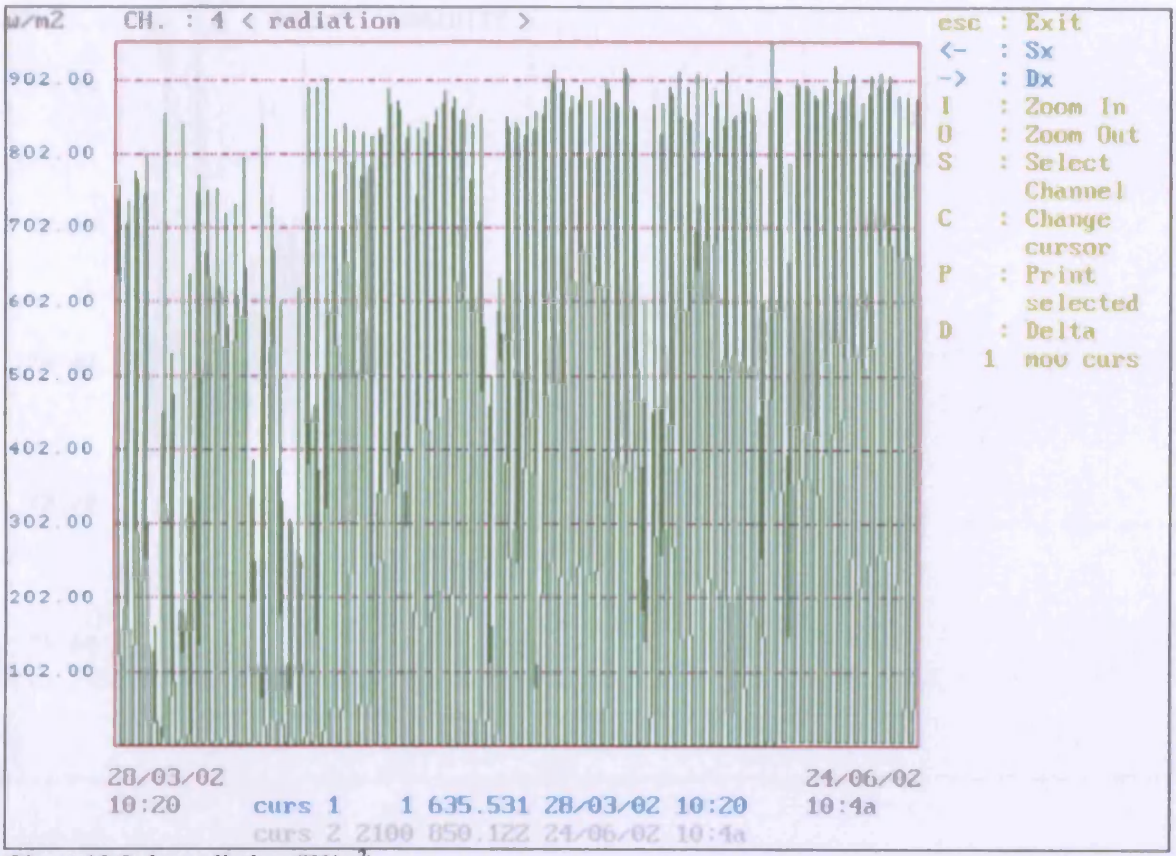
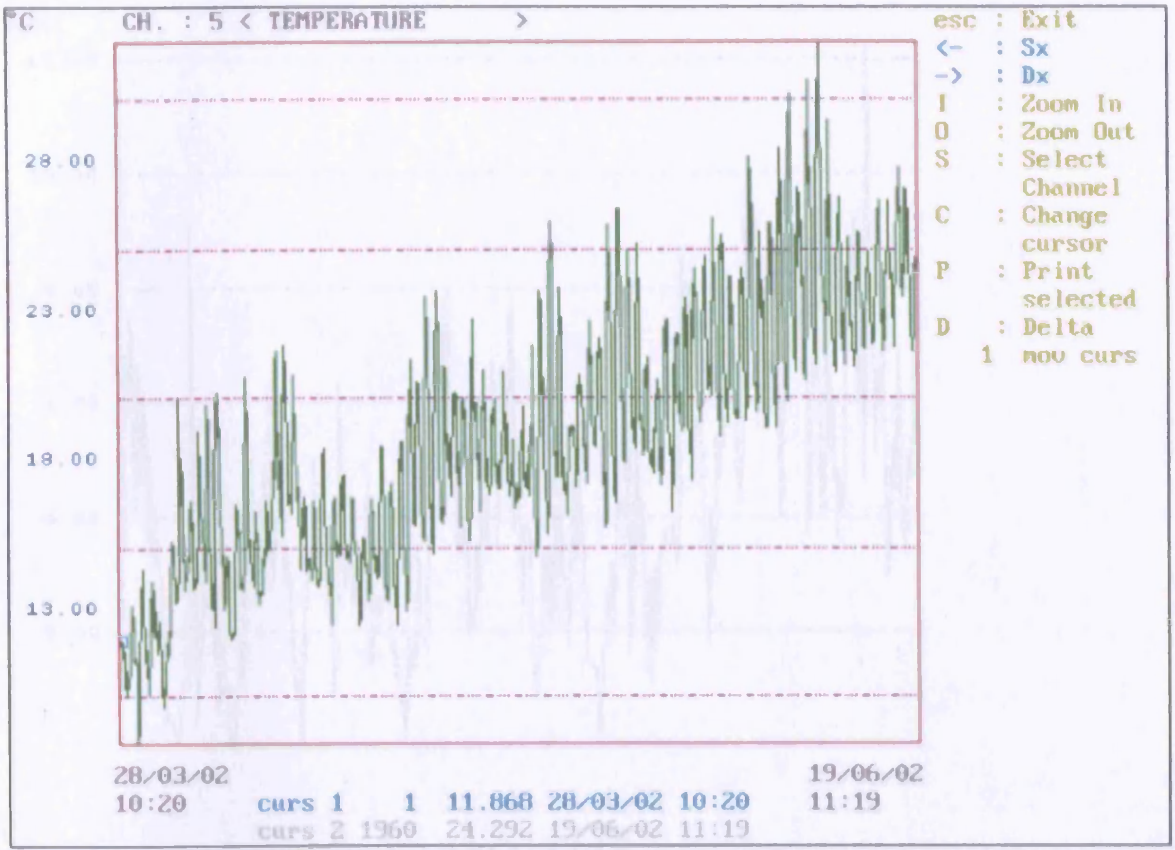
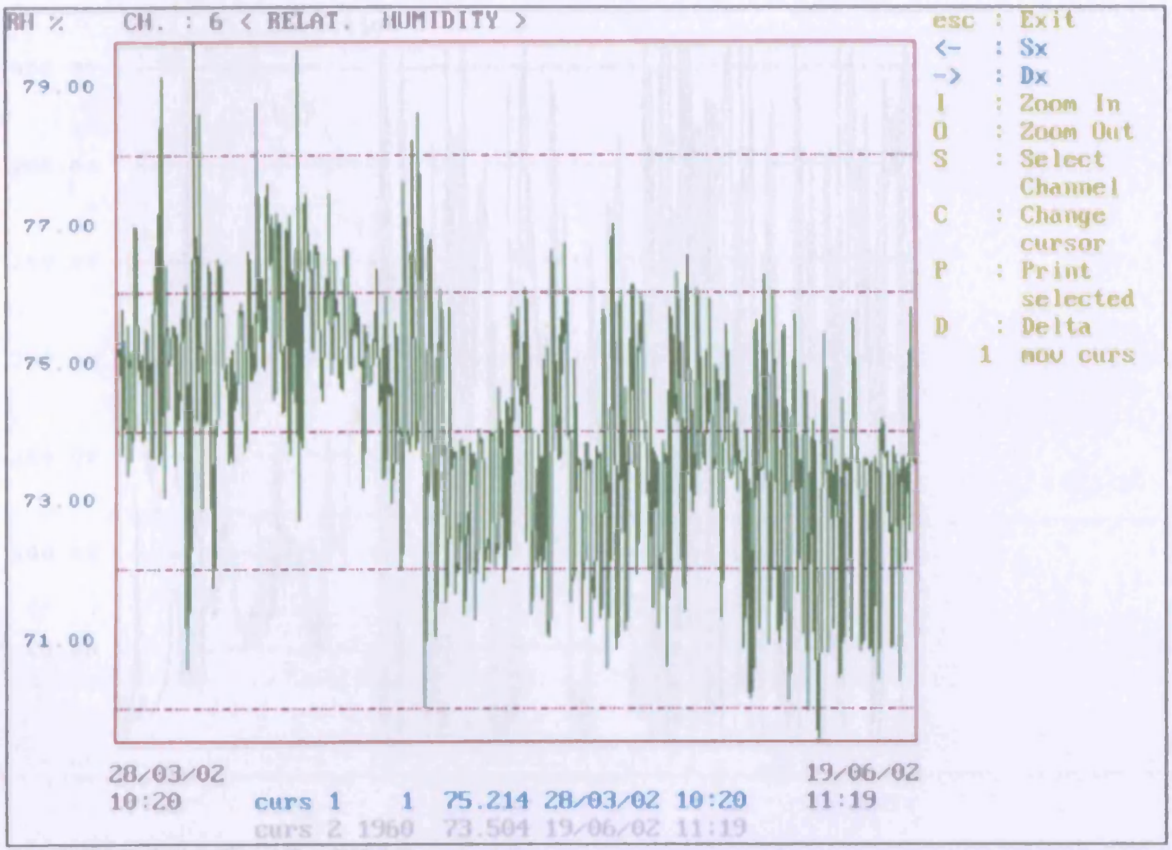


Chart 18 Solar radiation (W/m^2)



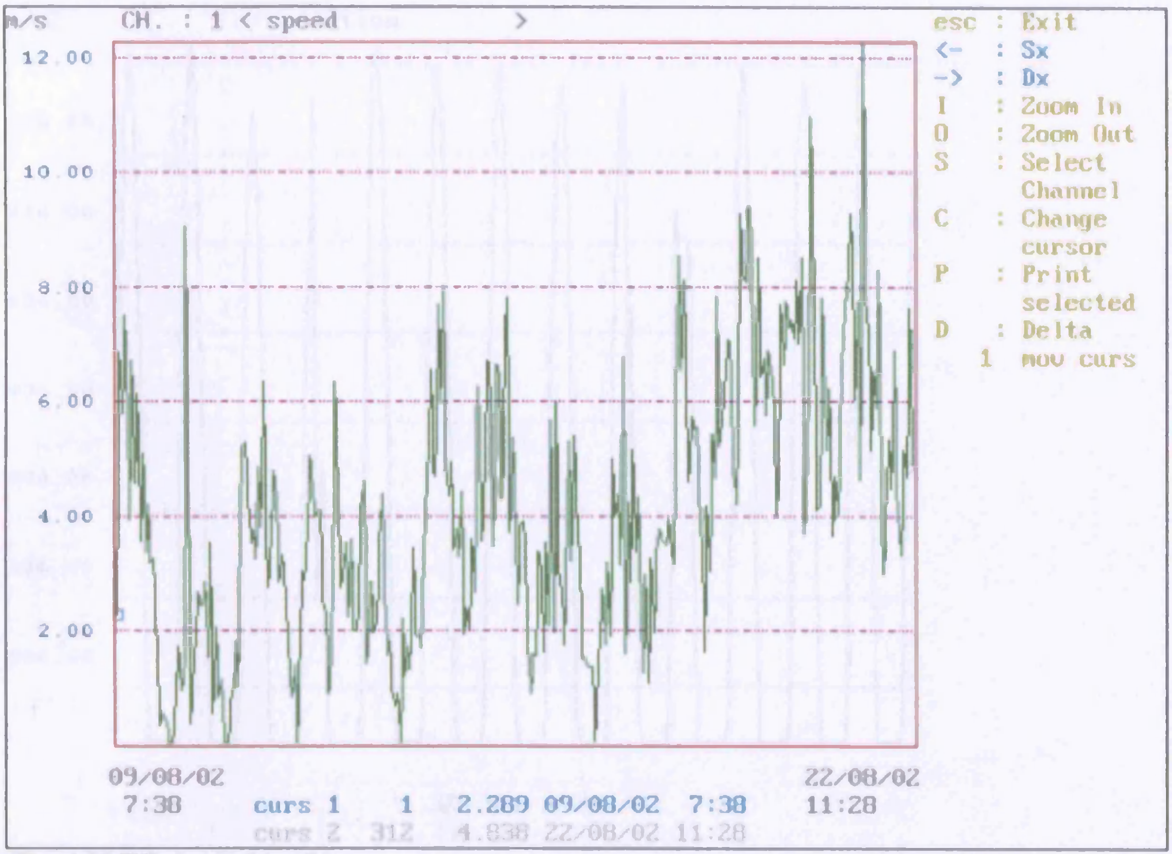
```
curs 1     1  11.868 28/03/02 10:20
curs 2 1960   24.292 19/06/02 11:19
```

Chart 19 Temperature (C^o)



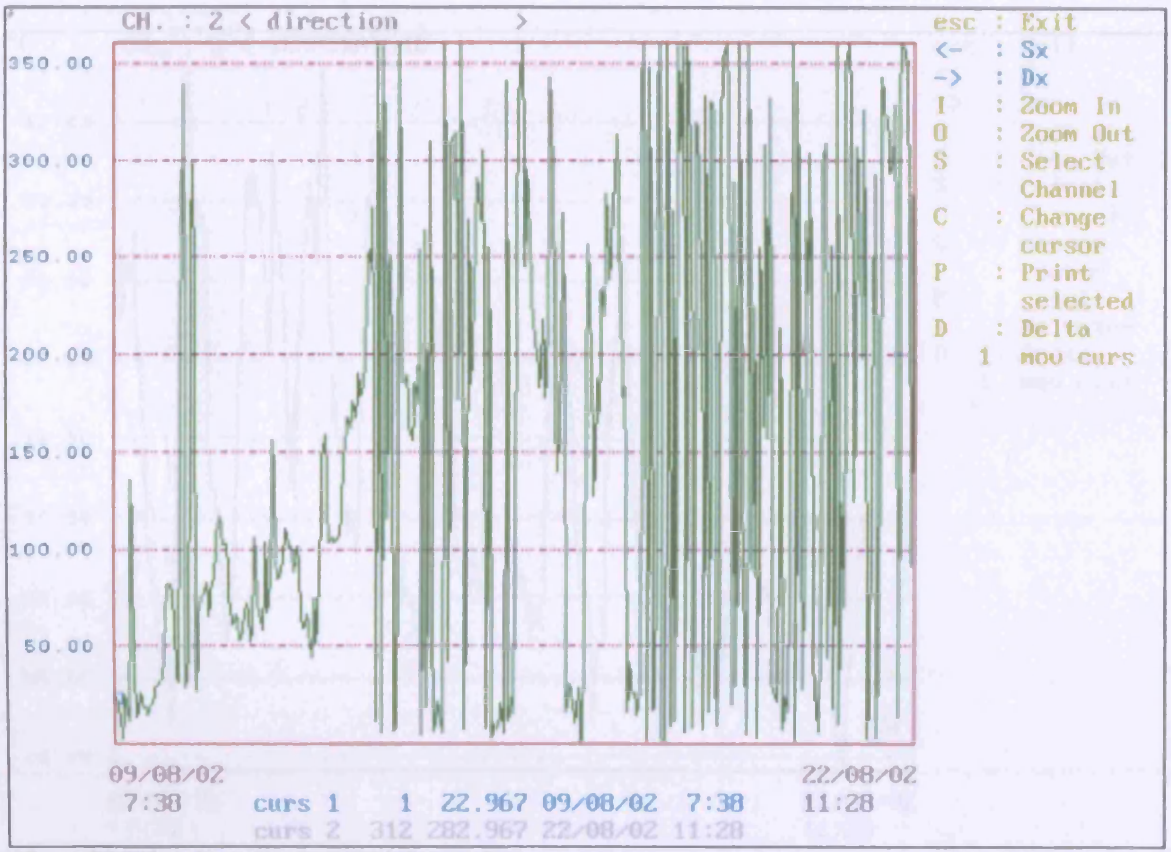
```
curs 1     1  75.214 28/03/02 10:20
curs 2 1960   73.504 19/06/02 11:19
```

Chart 20 Relative humidity (%)



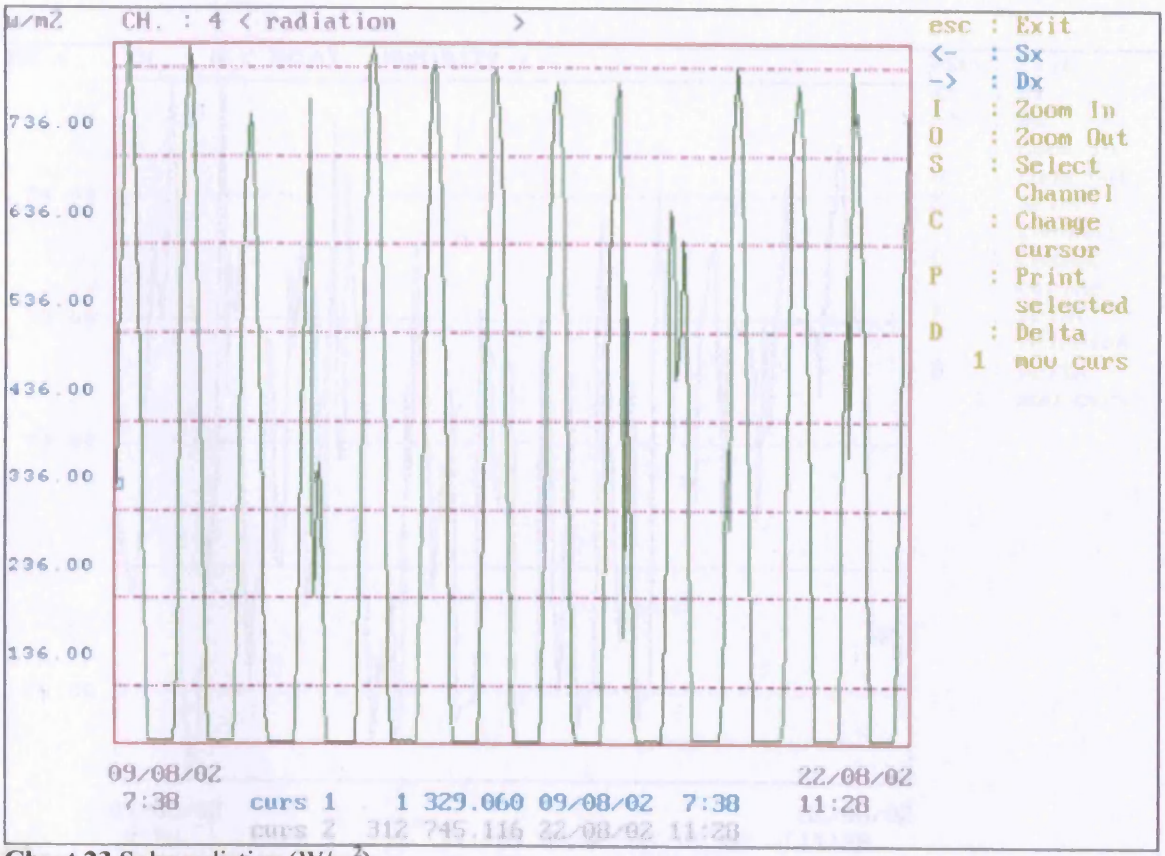
```
curs 1     1   2.289 09/08/02  7:38
curs 2   312   4.838 22/08/02 11:28
```

Chart 21 Wind speed (m/s)



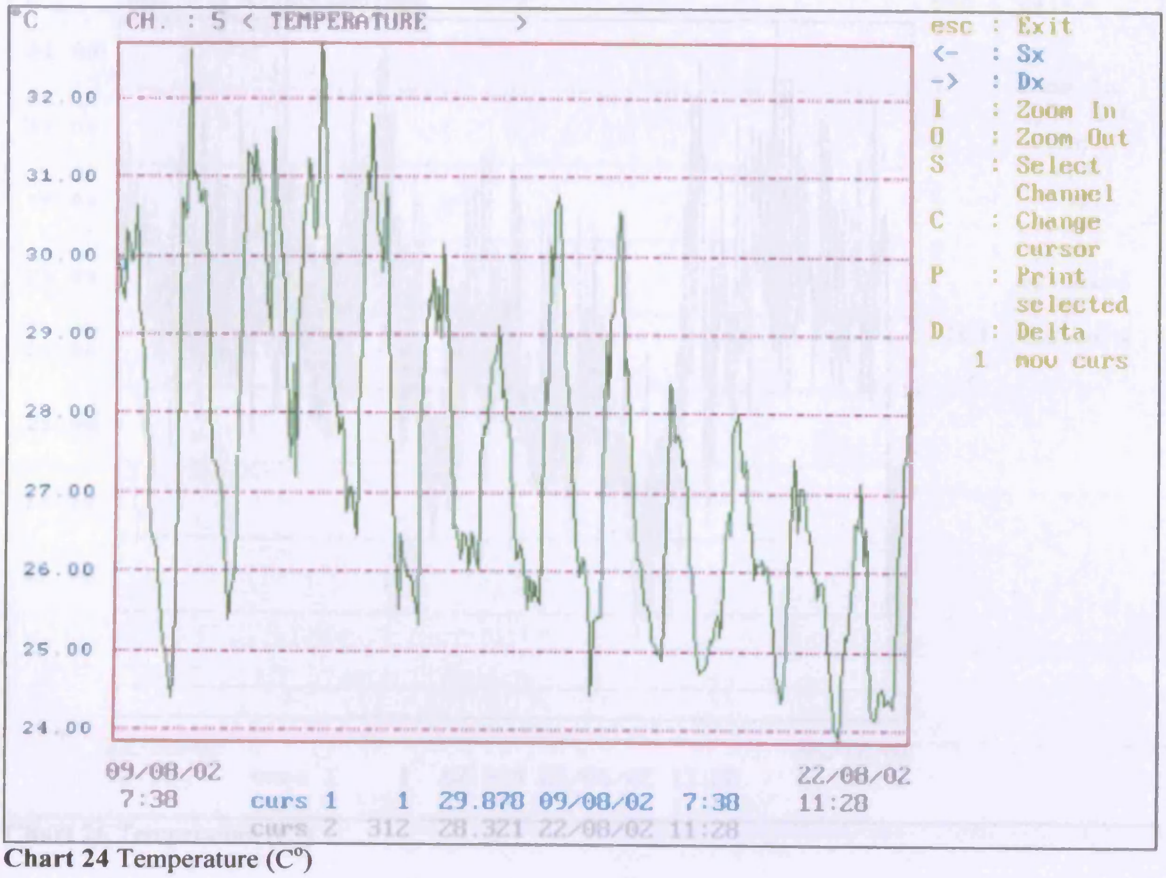
```
curs 1     1  22.967 09/08/02  7:38
curs 2   312 282.967 22/08/02 11:28
```

Chart 22 Wind direction (cardinal degrees)



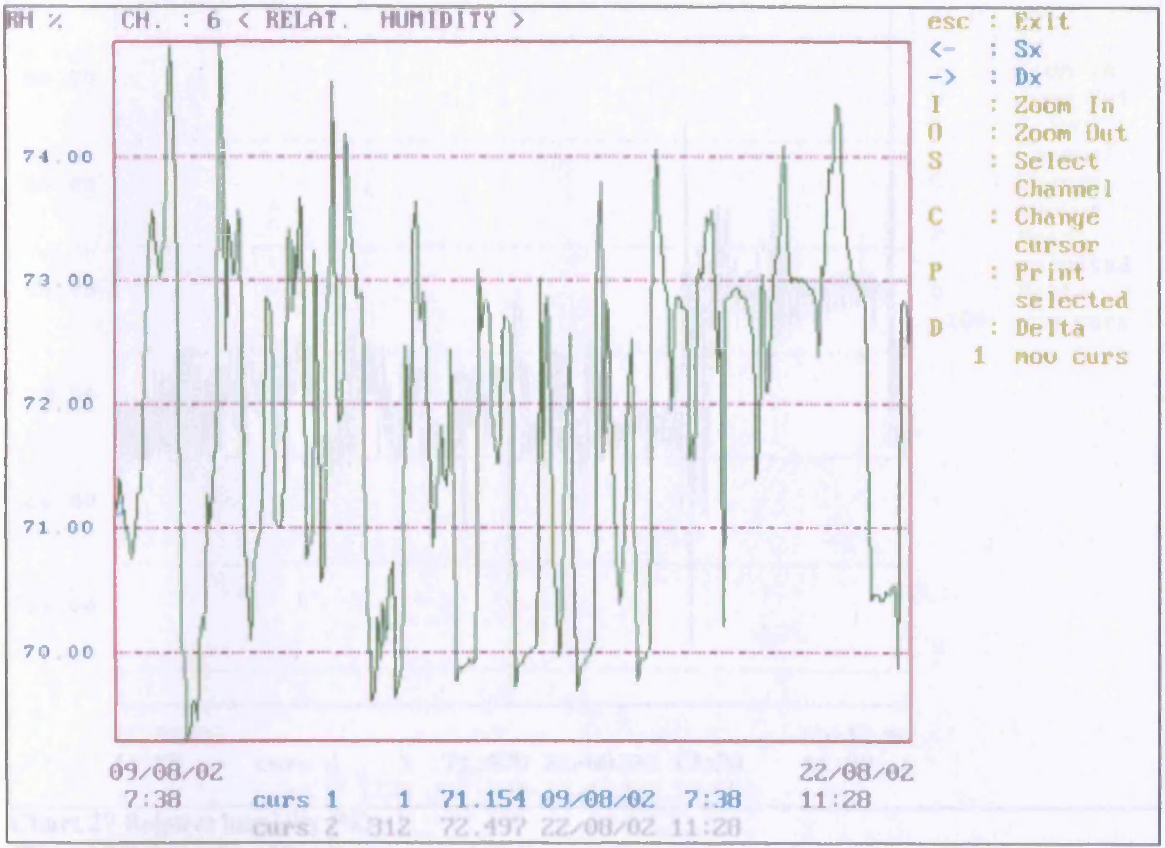
```
curs 1    1 329.060 09/08/02  7:38
curs 2  312 745.116 22/08/02 11:28
```

Chart 23 Solar radiation (W/m^2)



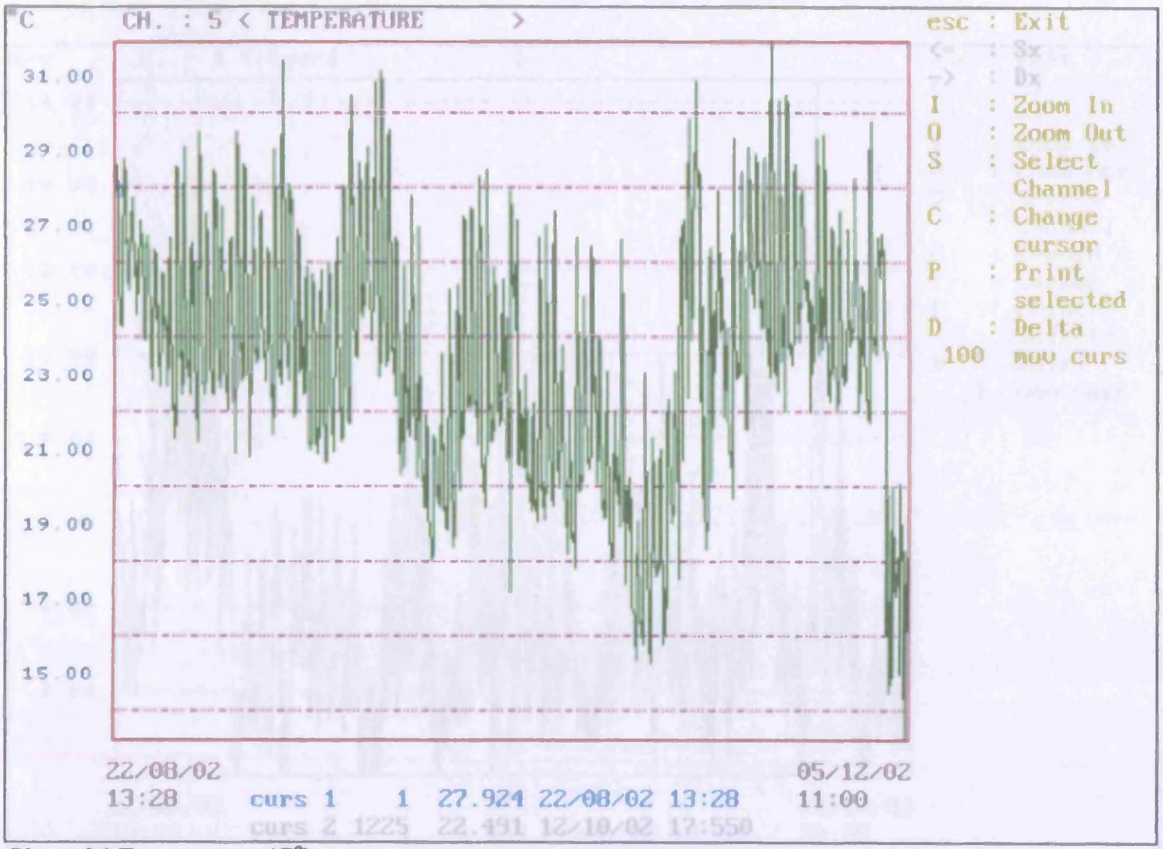
```
curs 1    1 29.878 09/08/02  7:38
curs 2  312 28.321 22/08/02 11:28
```

Chart 24 Temperature (C^o)



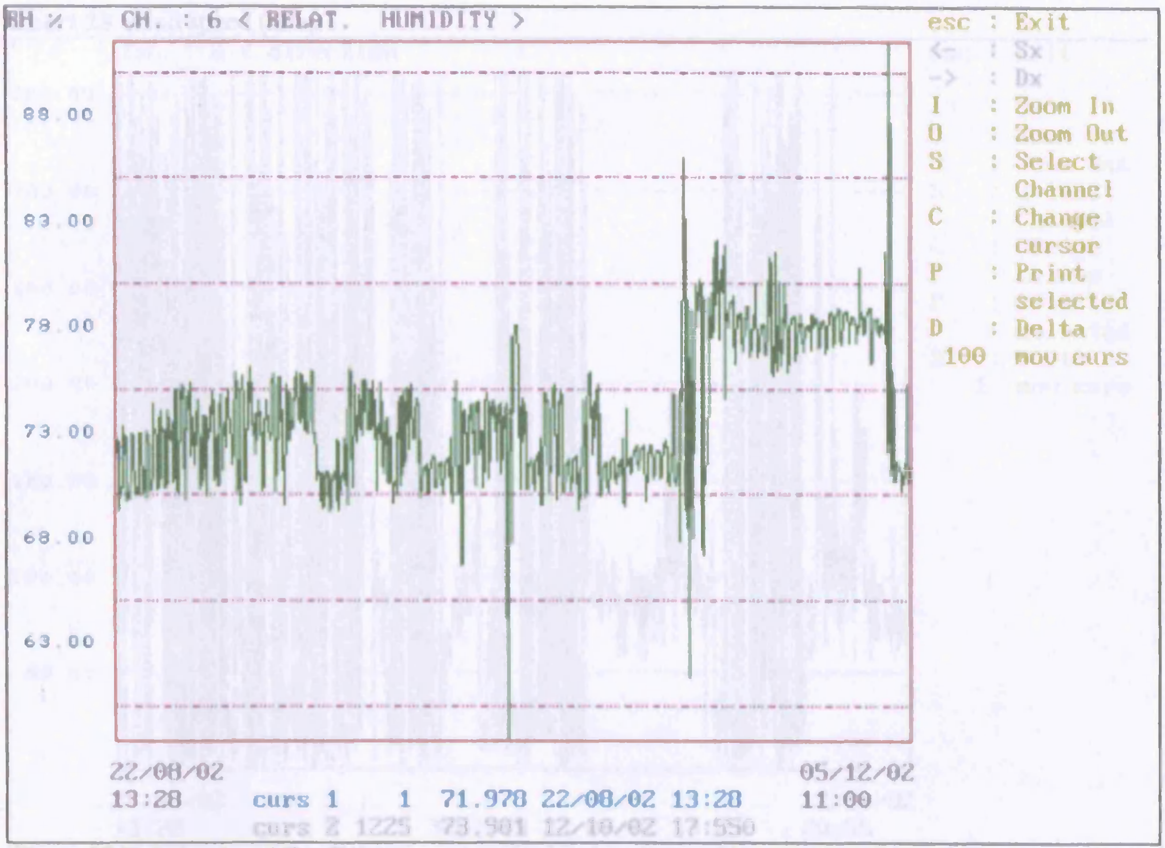
```
curs 1     1  71.154 09/08/02  7:38
```

Chart 25 Relative humidity (%)



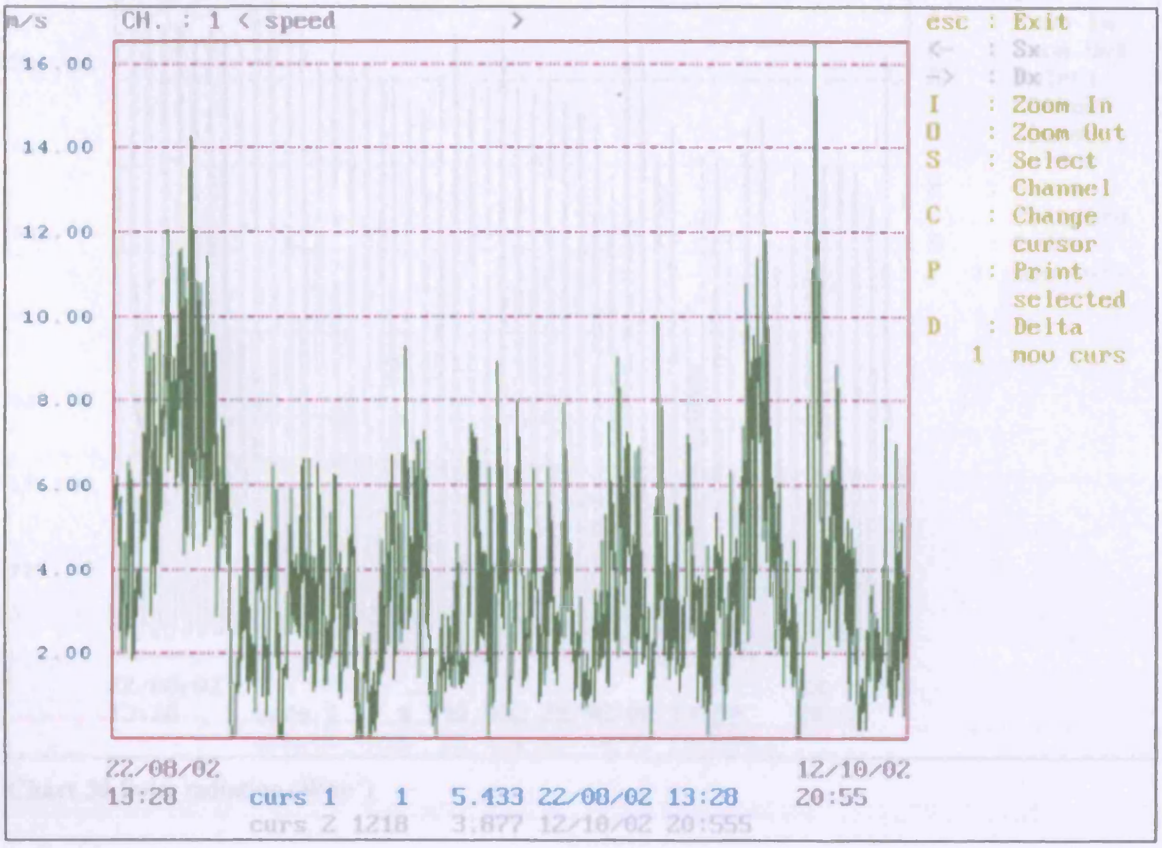
```
curs 1     1  27.924 22/08/02 13:28
```

Chart 26 Temperature (C°)



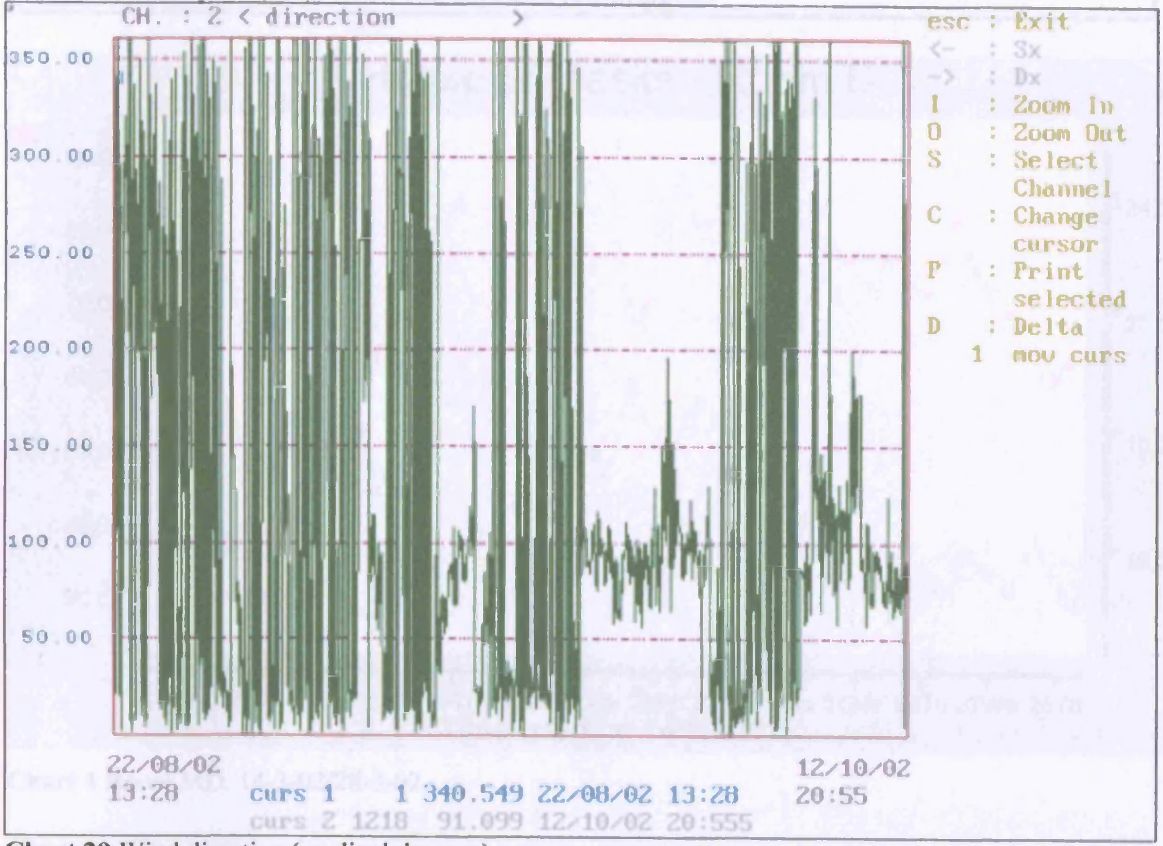
```
curs 1     1  71.978 22/08/02 13:28
curs 2 1225   73.901 12/10/02 17:550
```

Chart 27 Relative humidity (%)



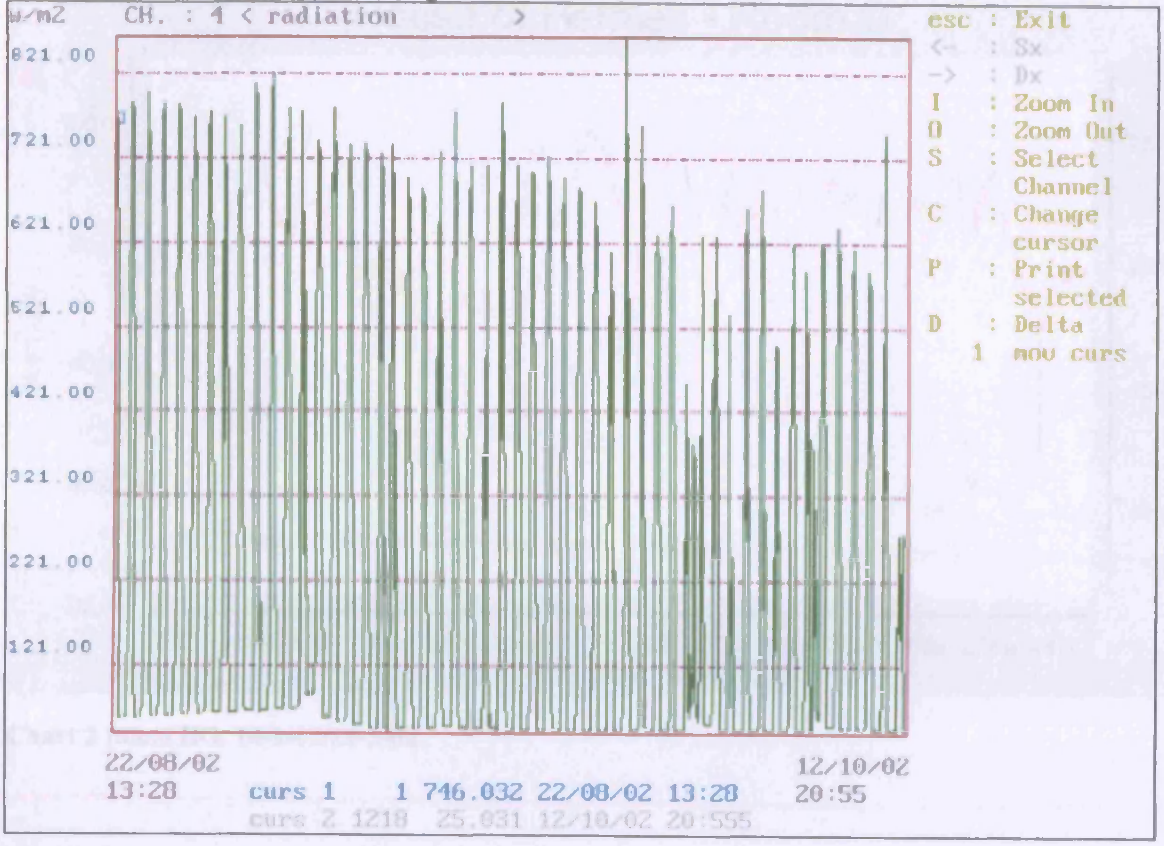
```
curs 1     1   5.433 22/08/02 13:28
curs 2 1218    3.877 12/10/02 20:555
```

Chart 28 Wind speed (m/s)



```
curs 1      1 340.549 22/08/02 13:28
curs 2 1218   91.099 12/10/02 20:555
```

Chart 29 Wind direction (cardinal degrees)



```
curs 1      1 746.032 22/08/02 13:28
curs 2 1218   25.031 12/10/02 20:555
```

Chart 30 Solar radiation (W/m^2)

IIIB. Offloaded charts from the indoors dataloggers

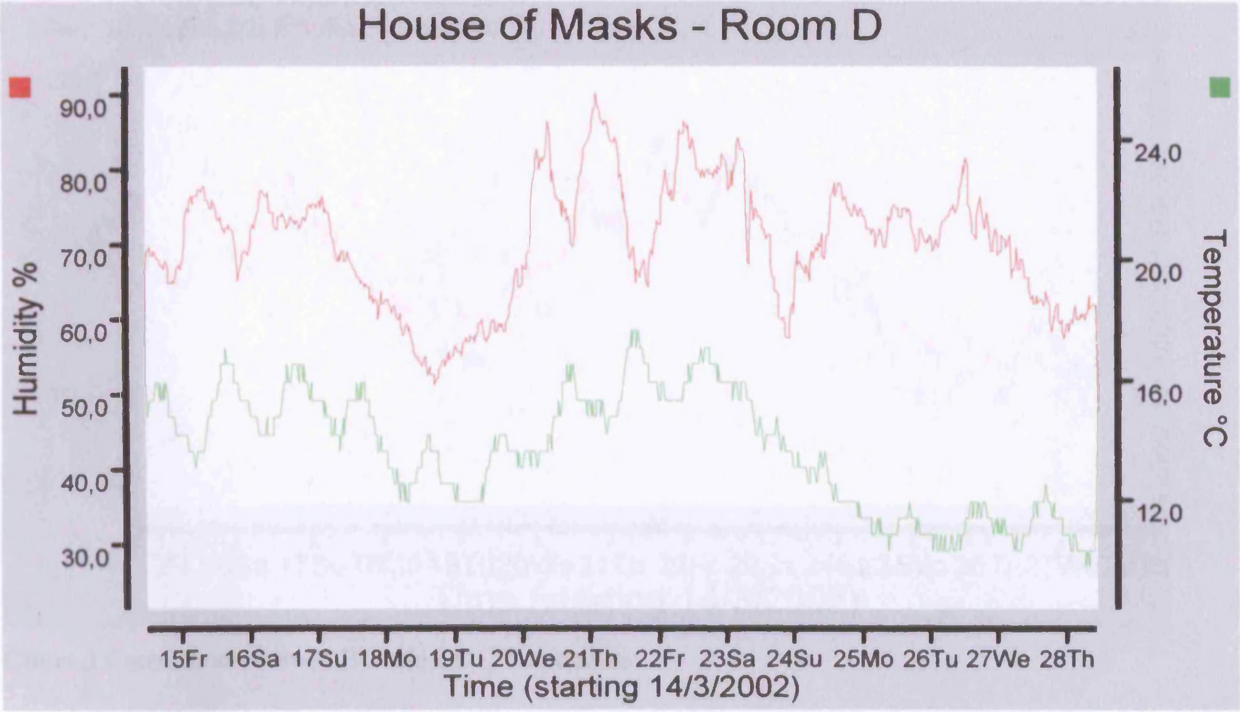


Chart 1 Room MD. 14-3-02/28-3-02

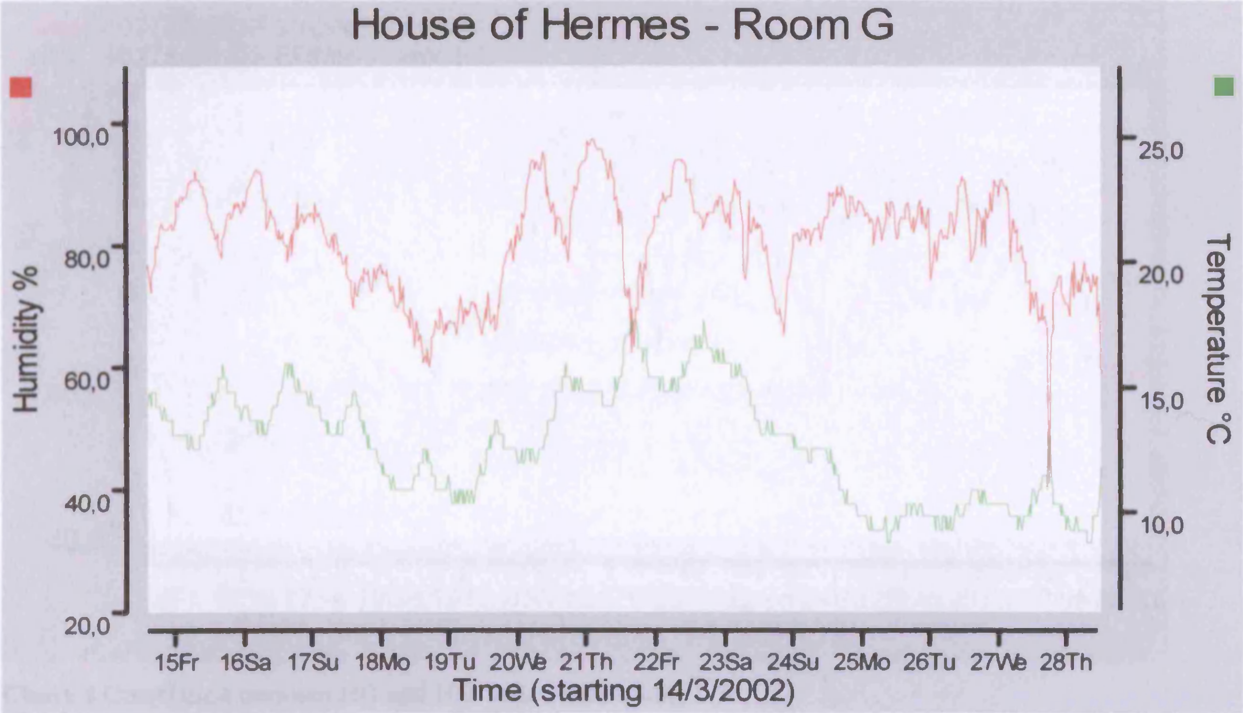


Chart 2 Room HG. 14-3-02/28-3-02

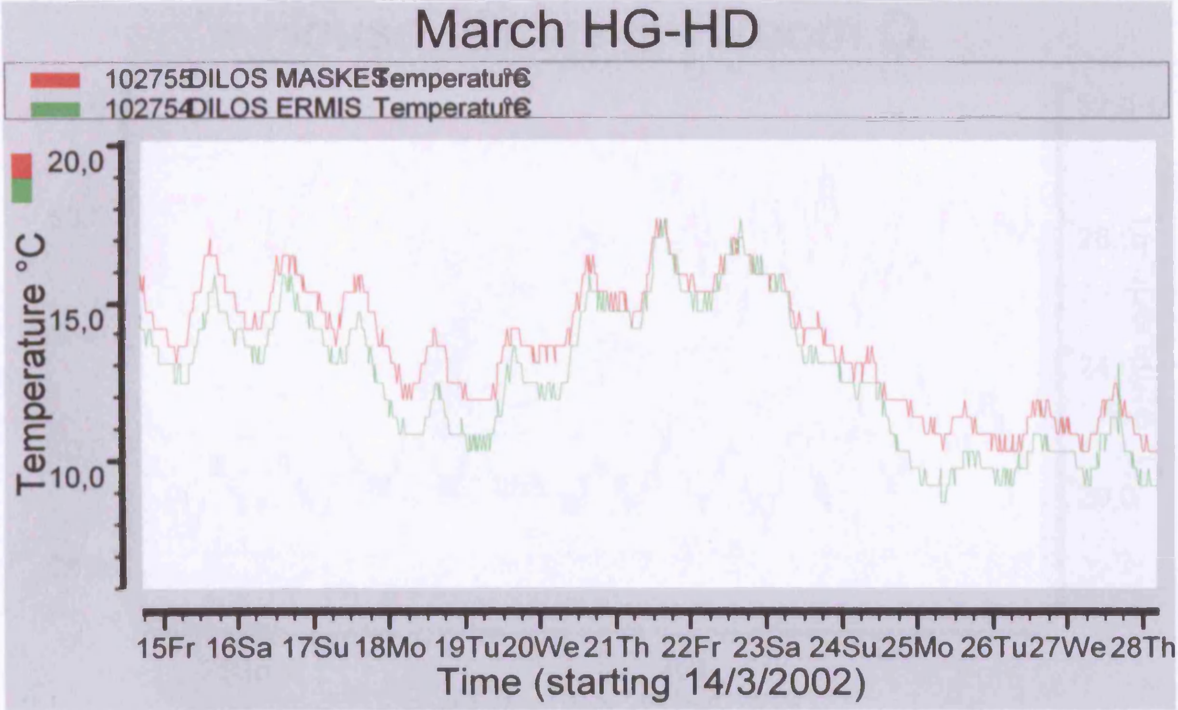


Chart 3 Correlation between HG and HD. Temperature

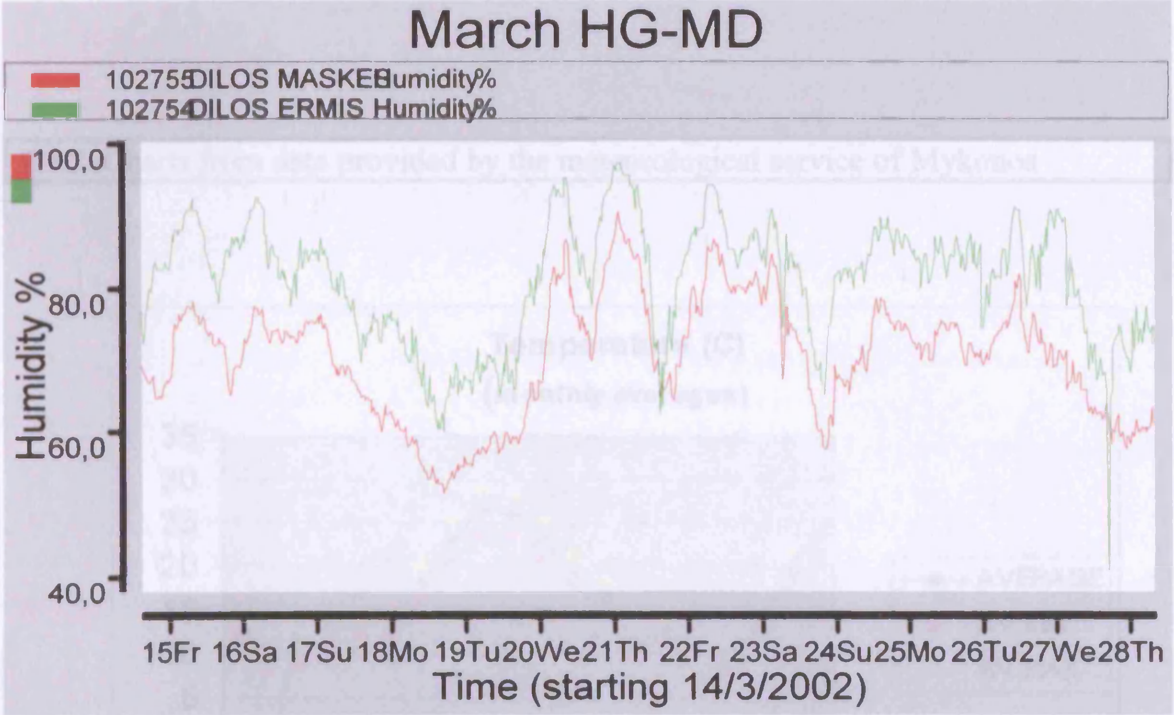


Chart 4 Correlation between HG and HD. Relative humidity

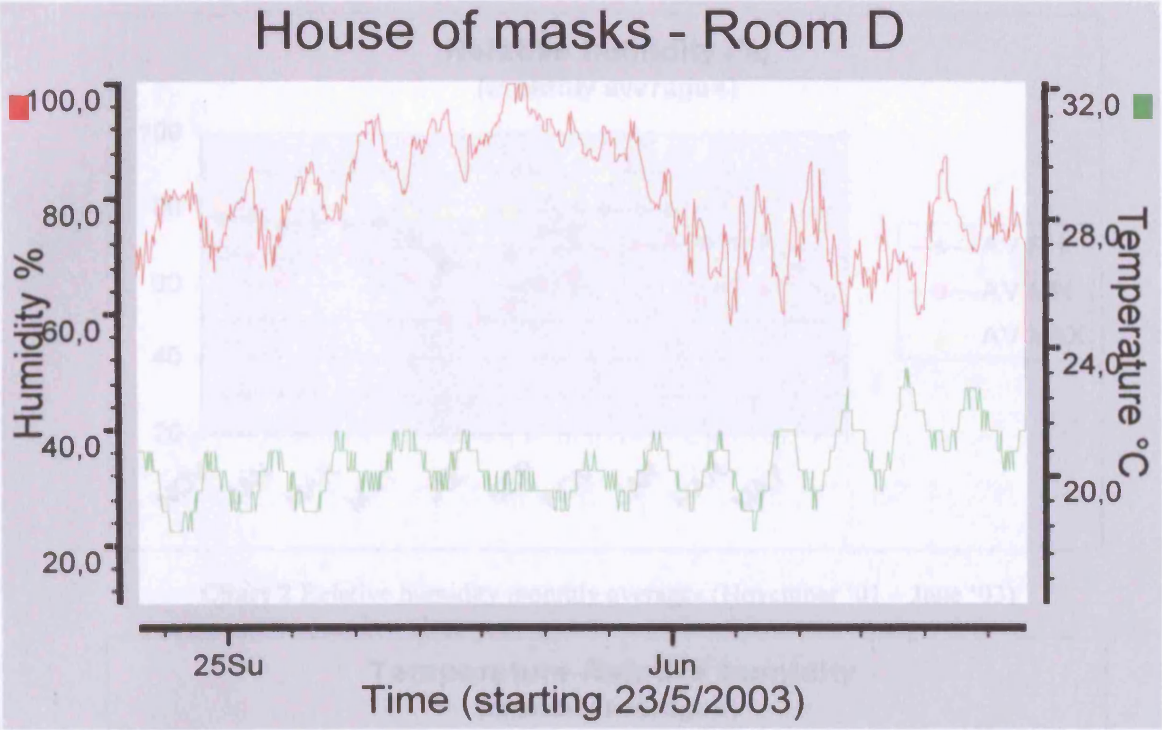


Chart 5 Room MD. 23-5-03/6-6-03

IIIC. Charts from data provided by the meteorological service of Mykonos

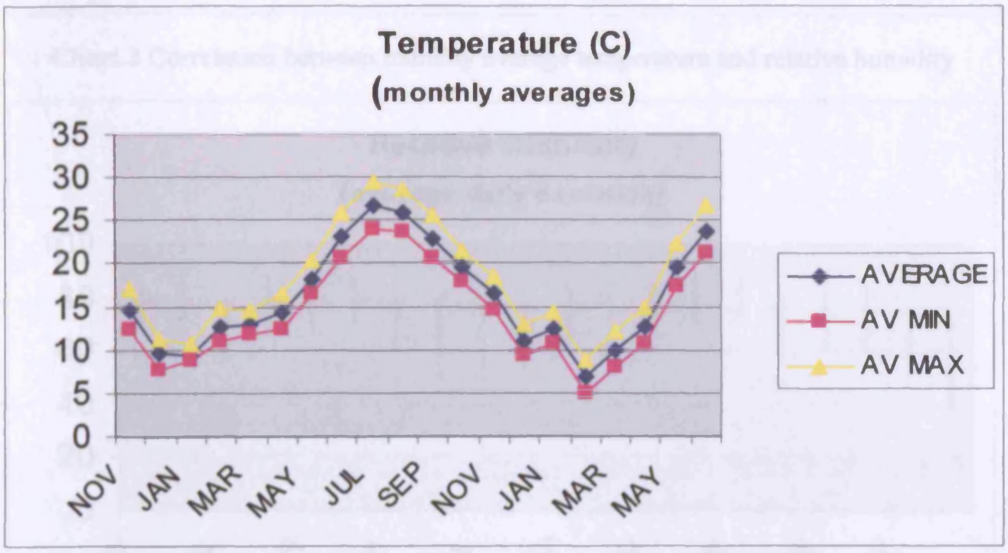


Chart 1 Temperature monthly averages (November '01 – June '03)

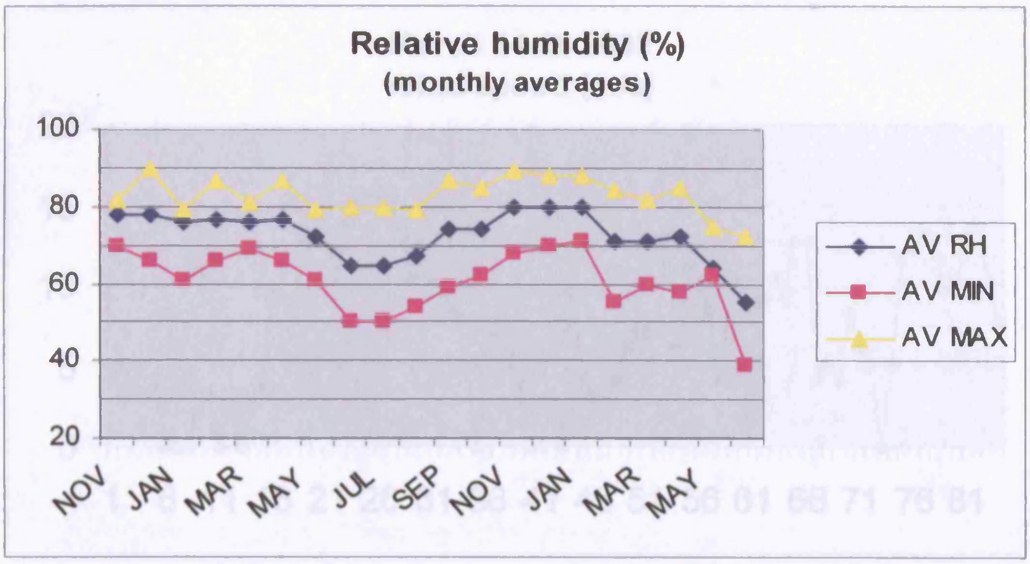


Chart 2 Relative humidity monthly averages (November '01 – June '03)

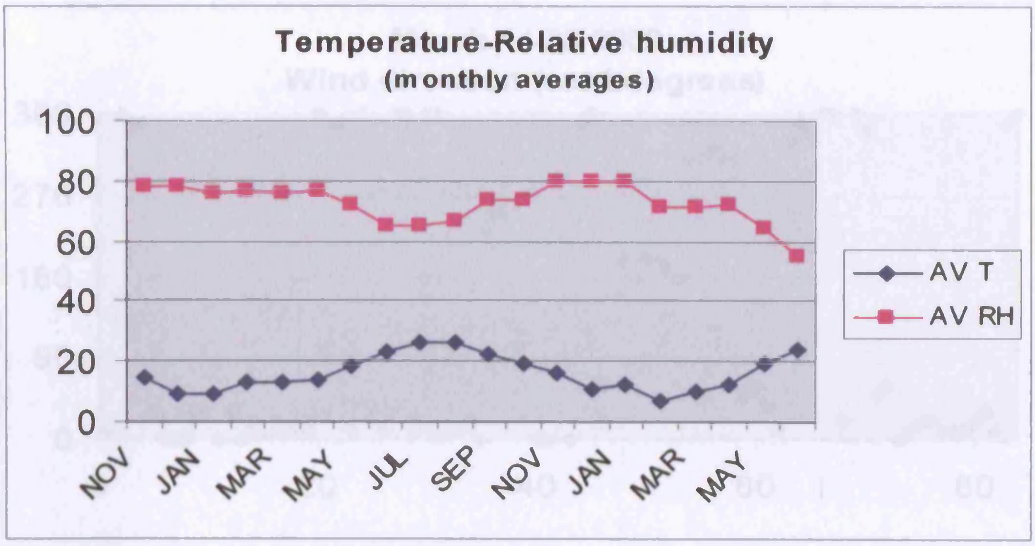


Chart 3 Correlation between monthly average temperature and relative humidity

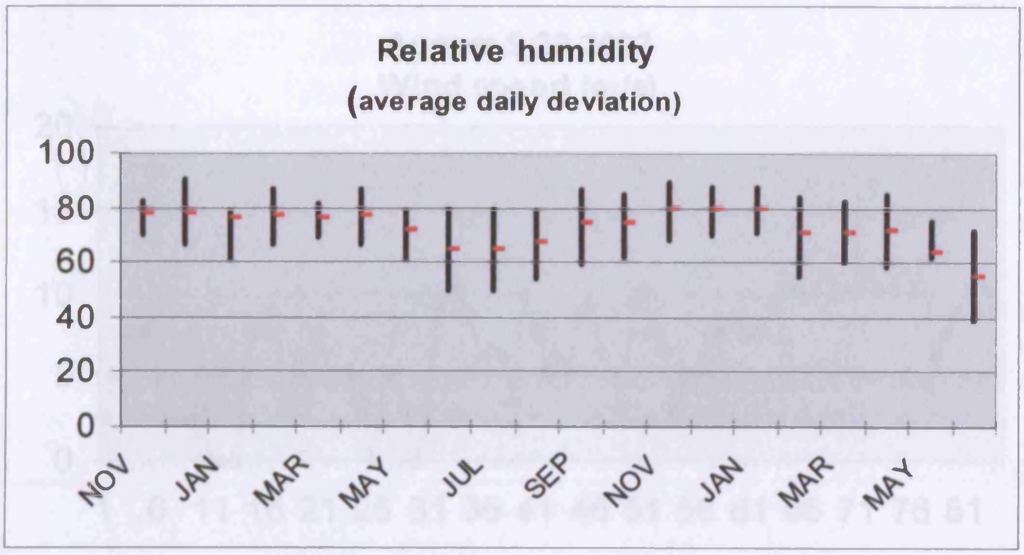


Chart 4 Relative humidity average daily deviation (min-max). Red dot marks monthly average

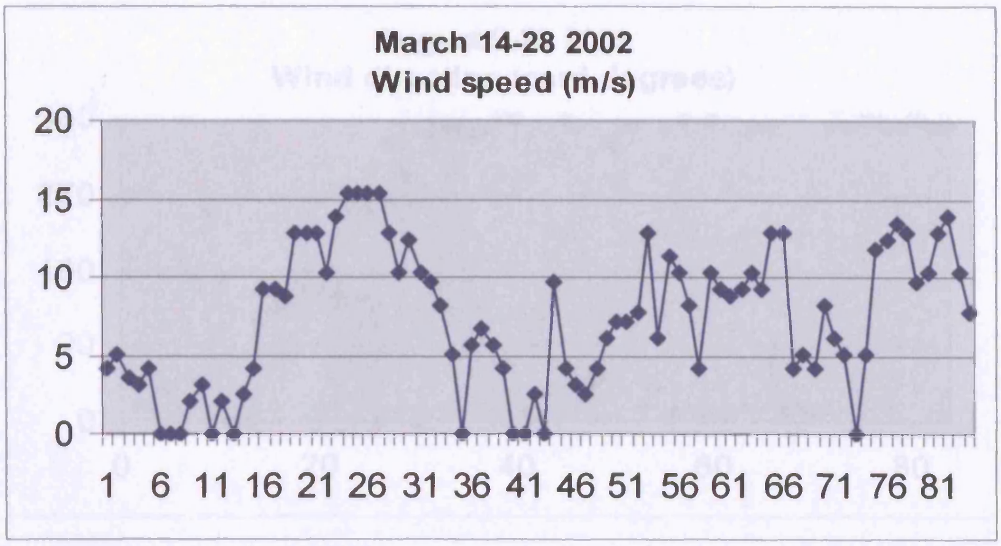


Chart 5 Wind speed (m/s)

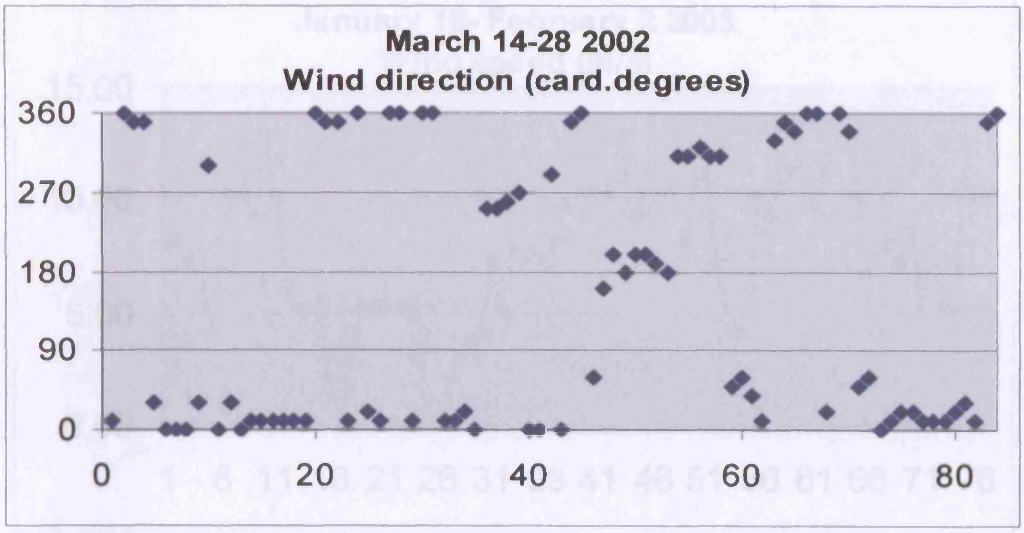


Chart 6 Wind direction (cardinal degrees)

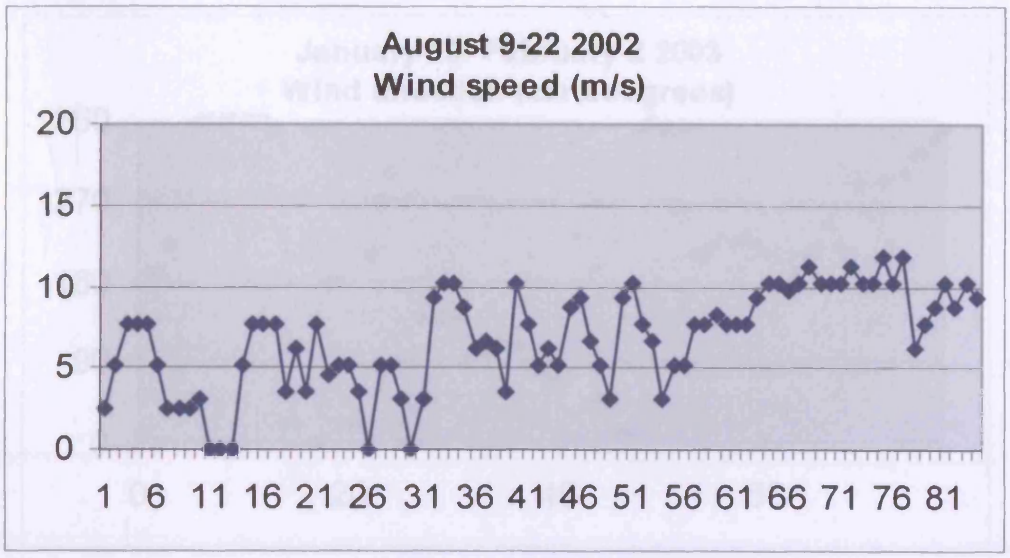


Chart 7 Wind speed (m/s)

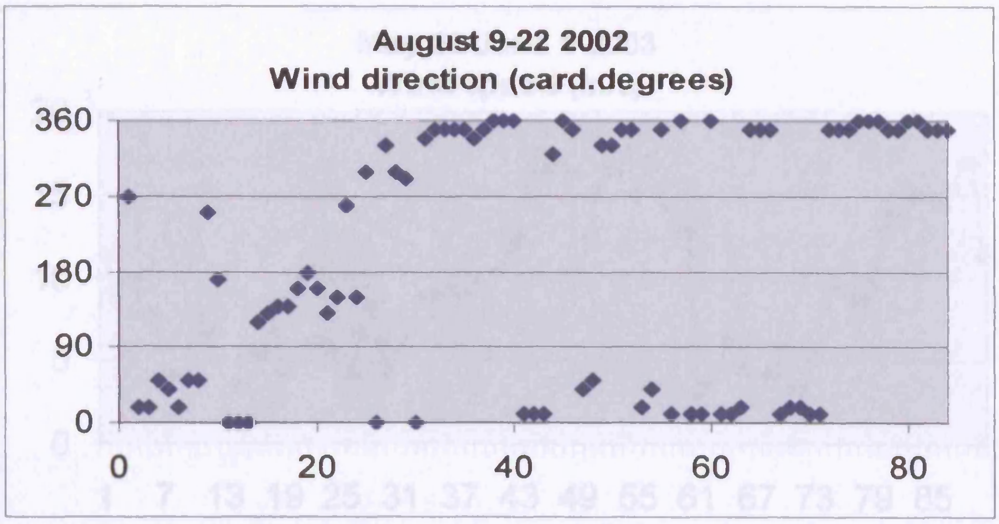


Chart 8 Wind direction (cardinal degrees)

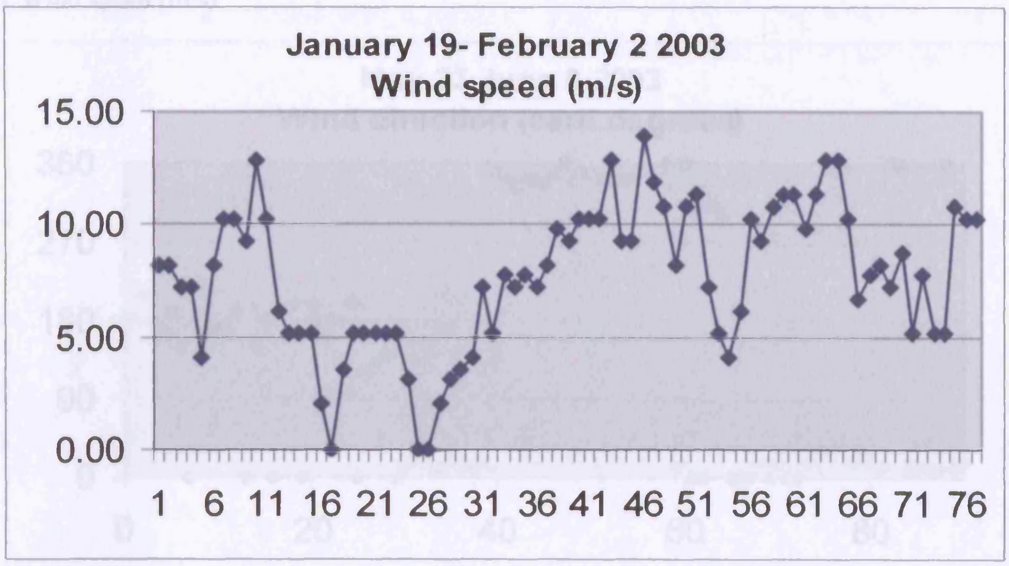


Chart 9 Wind speed (m/s)

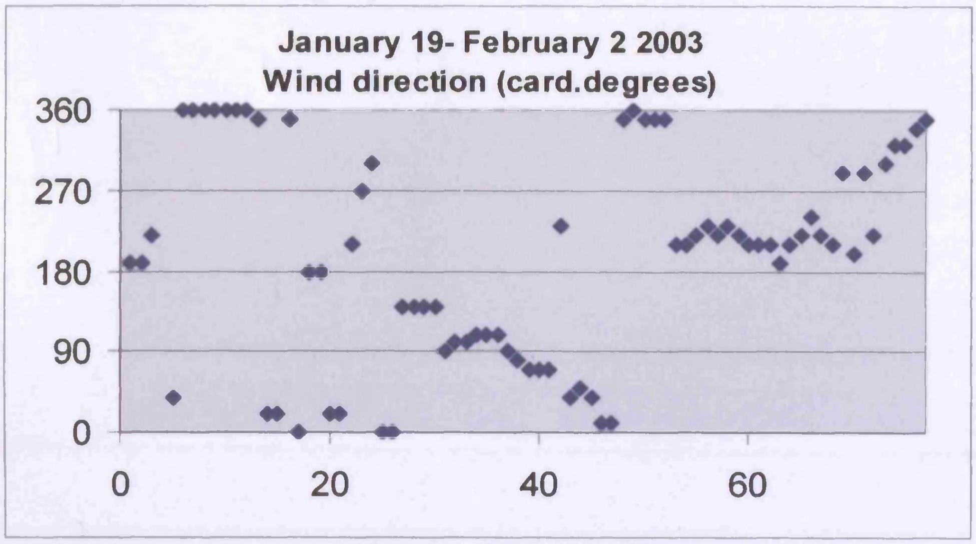


Chart 10 Wind direction (cardinal degrees)

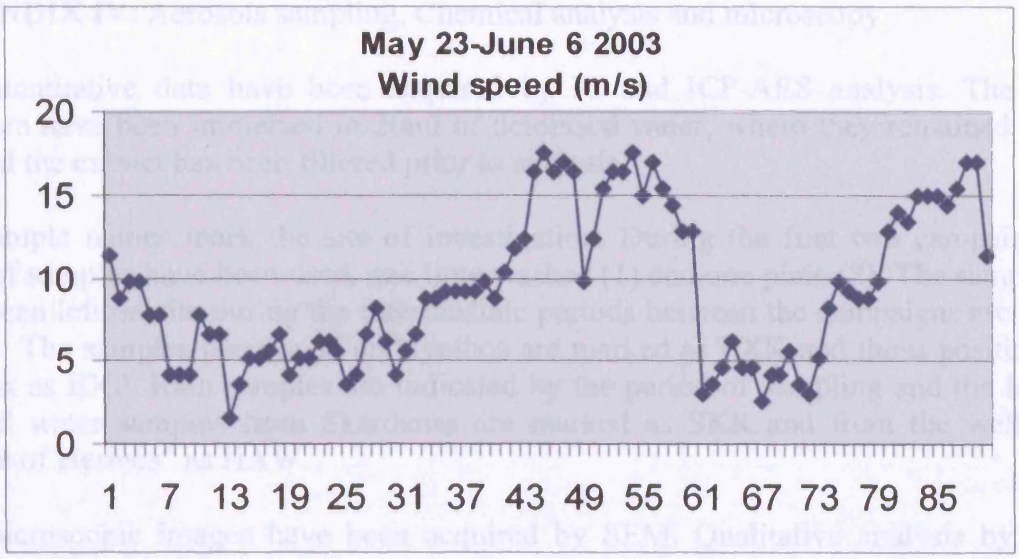


Chart 11 Wind speed (m/s)

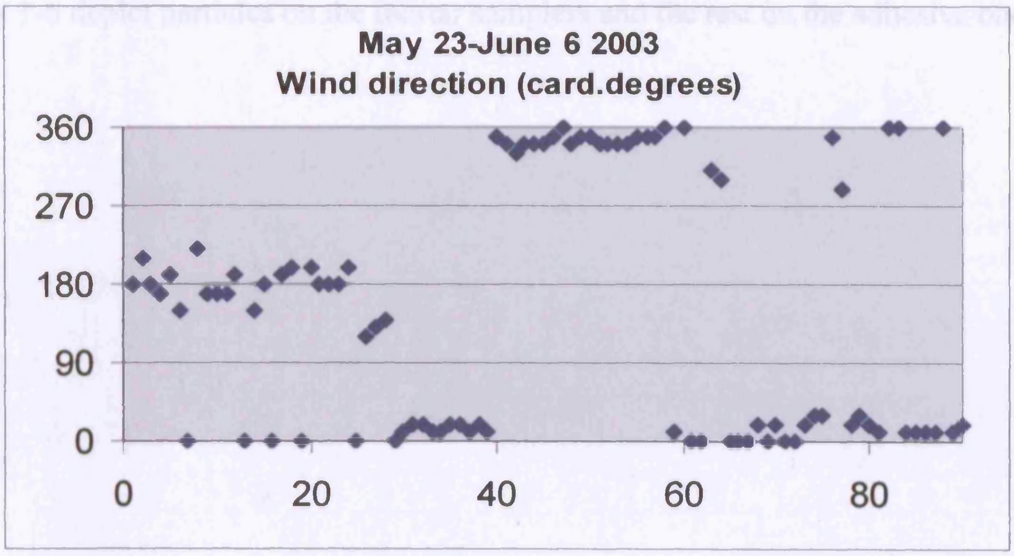


Chart 12 Wind direction (cardinal degrees)

APPENDIX IV: Aerosols sampling. Chemical analysis and microscopy

The quantitative data have been acquired by IC and ICP-AES analysis. The mortar samplers have been immersed in 20ml of deionised water, where they remained for one day and the extract has been filtered prior to analysis.

The sample names mark the site of investigation. During the first two campaigns two types of samples have been used, one lime washed (1) and one plain (2). The samples that have been left on site during the intermediate periods between the campaigns are marked with L. The samples positioned on Kynthos are marked as EXK and those positioned on the port as EXP. Rain samples are indicated by the period of sampling and the location. Ground water samples from Skardanas are marked as SKR and from the well of the "House of Hermes" as HAW.

The microscopic images have been acquired by SEM. Qualitative analysis by EDAX served only as indicator of the species composition. Since the mortar samplers are absorbent special non porous and adhesive samplers have been used for microscopy. Figures 1-6 depict particles on the mortar samplers and the rest on the adhesive ones.

Table 1

March 14-28 2002 (ppm)							
Room	**Na**	**Mg**	**K**	**Cl**	**NO3**	**SO4**	**Sum**
HD1	46.36	1.82	0.87	84.53	4.86	15.22	153.66
HD2	45.81	5.31	0	72.61	6.55	26.84	157.12
av	46.085	3.565	0.435	78.57	5.705	21.03	155.39
HG1	10.23	0.05	0.3	11.74	3.15	5.44	30.91
HG2	6.49	0.23	0.59	7.99	3.07	5.07	23.44
av	8.36	0.14	0.445	9.865	3.11	5.255	27.175
MA2	16.26	1.81	0.07	14.11	4.58	6.54	43.37
MA3	18.73	0.68	0.09	20.49	3.21	11.49	54.69
av	17.495	1.245	0.08	17.3	3.895	9.015	49.03
MD1	11.59	0.12	2.02	11.66	4.48	7	36.87
MD2	13.22	1.75	3.04	12.31	5.27	11.66	47.25
av	12.405	0.935	2.53	11.985	4.875	9.33	42.06

Table 2

August 9-22 2002 (ppm)							
Room	**Na**	**Mg**	**K**	**Cl**	**NO3**	**SO4**	**Sum**
MD1	4.47	0.55	0.11	4.868	1.831	0	11.829
MD2	3.29	0.34	0.59	4.833	0.862	1.727	11.642
av	3.88	0.445	0.35	4.8505	1.3465	0.8635	11.7355
MA1	2.93	0.61	0.78	6.9	1.4	3.81	16.43
MA2	6.02	0.77	0.01	10.552	0	4.224	21.576
av	4.475	0.69	0.395	8.726	0.7	4.017	19.003
HG1	3.51	0.95	0.34	8.67	0.37	0.5	14.34
HG2	3.14	0.83	0.73	8.2	0.71	1.21	14.82
av	3.325	0.89	0.535	8.435	0.54	0.855	14.58
HD1	21.71	0.28	0.87	41.27	0	4.02	68.15
HD2	26.72	0.04	0.66	33.4	0	8.2	69.02
av	24.215	0.16	0.765	37.335	0	6.11	68.585

Table 3

January 19- February 2 2003							
Room	**Na**	**Mg**	**K**	**Cl**	**NO3**	**SO4**	**SUM**
HD	51.22	2.4	1.02	81.511	4.587	19.399	160.137
HG	4.01	0.55	0.03	6.957	2.028	4.181	17.756
MA	4.12	1.47	0.77	10.072	0	4.863	21.295

MD	3.41	0	0	5.162	1.544	2.026	12.142
SUM	62.76	4.42	1.82	103.702	8.159	30.469	211.33

Table 4

May 23 - June 6 2003							
Room	**Na**	**Mg**	**K**	**Cl**	**NO3**	**SO4**	sum
HD	90.95	2.94	4.07	163.32	1.1	20.01	282.39
HG	23.34	2.03	0.67	40.1	2.13	6.54	74.81
MA	19.05	1.8	1.32	31.94	0.03	10.55	64.69
MD	10.11	2.37	0.72	23.21	0.49	3.07	39.97
sum	143.45	9.14	6.78	258.57	3.75	40.17	461.86

Table 5

Supplementary samples							
Room	**Na**	**Mg**	**K**	**Cl**	**NO3**	**SO4**	**sum**
May 23-June 6 2003							
EXP1	1003.75	69.23	27.93	1803.07	5.69	230.91	3140.58
EXP2	878.18	60.33	42.80	1578.64	5.71	199.46	2765.12
Jan 19 -Feb 6 2003							
EXP	647.07	54.26	28.01	1338.30	4.70	117.40	2189.74
EXK	63.22	1.90	1.26	131.80	4.92	19.95	223.05
Aug 02-Jan 03 (ppm)							
HDL	178.93	15.79	8.37	351.28	27.56	71.96	653.89
Feb 03-May 03 (ppm)							
MAL	80.35	4.18	5.70	143.30	2.01	26.27	261.81
HDL	199.01	6.81	7.07	379.45	6.98	61.03	660.35
HGL	69.82	2.57	2.59	111.56	0.90	23.10	210.54
EXPL	6214.24	245.63	206.31	13127.30	40.32	1753.50	21,587.30

Table 6

Rain samples							
	Ca	**Na**	**Mg**	**K**	**Cl**	**NO3**	**SO4**
NOVD	5.3	33.31	3.86	2.86	70.01	4.57	11.58
AUGD	7.28	219.61	24.44	15	362.583	0	54.351
OCTD	0.35	11.84	0.36	0.8	8.94	0.215	1.532
JULD	2.74	6.14	0.83	0.49	10.452	1.331	3.774
AUGA	2.58	1.66	0.31	1.17	2.802	1.669	3.363
JULA	0.22	0.07	0.02	0.15	0.487	0.2	1.325
Ground water samples							
	Ca	**Na**	**Mg**	**K**	**Cl**	**NO3**	**SO4**
SKR	1.51	10.9	1.08	0.43	18.848	0	4.586
HAW	2.62	11.2	2.79	0	20.17	3.2	1.034

Table 7

EF values (Na as indicator element)					
March 14-28 2002					
Room	**Cl**	**SO4**	**Mg**	**K**	
HD	0.9	1.8	0.6	0.3	
HG	0.7	2.5	0.1	1.5	
MA	0.5	2.1	0.6	0.1	
MD	0.5	3.0	0.6	5.8	
August 9-22 2002					
Room	**Cl**	**SO4**	**Mg**	**K**	
HD	0.9	1.0	0.1	0.9	
HG	1.4	1.0	2.2	4.6	
MA	1.1	0.9	1.3	2.5	
MD	0.7	3.6	1.0	2.6	
January 19- February 2 2003					
Room	**Cl**	**SO4**	**Mg**	**K**	
HD	0.9	1.5	0.4	0.6	
HG	1.0	4.2	1.1	0.2	
MA	1.4	4.7	3.0	5.3	
MD	0.8	2.4	0.0	0.0	
HDL	1.1	1.6	0.7	1.3	
EXP	1.2	0.7	0.7	1.2	
May 23 - June 6 2003					
Room	**CL**	**SO4**	**Mg**	**K**	
HD	1.0	0.9	0.3	1.3	
HG	1.0	1.1	0.7	0.8	
MA	0.9	2.2	0.8	2.0	
MD	1.3	1.2	2.0	2.0	
Supplementary samples					
MAL	1.0	1.3	0.4	2.0	
HDL	1.1	1.2	0.3	1.0	
HGL	0.9	1.3	0.3	1.1	
EXP2	1.0	0.9	0.6	1.4	
EXP1	1.0	0.9	0.6	0.8	
EXPL	1.2	1.1	0.3	0.9	
Rain samples					
	CL	**SO4**	**Mg**	**K**	**Ca**
NOVD	1.2	1.4	1.0	2.5	0.8
AUGD	0.9	1.0	0.9	2.0	0.2
JULD	0.9	2.5	1.1	2.3	2.1
AUGA	0.9	8.1	1.6	20.1	7.4
JULA	3.9	75.7	2.4	61.2	15.0
Ground water					
SKR	1.0	1.7	0.8	1.1	0.7
HAW	1.0	0.4	2.1	0.0	2.0

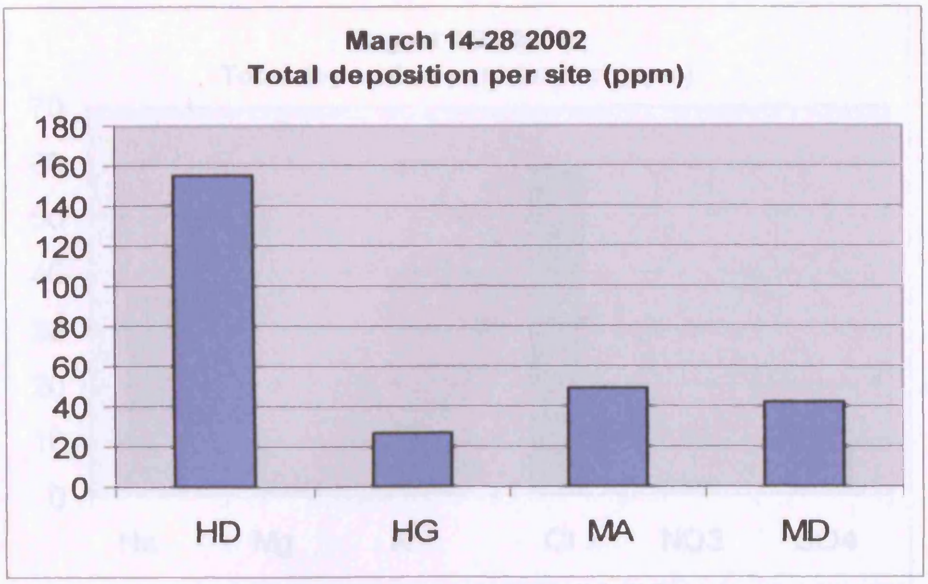


Chart 1

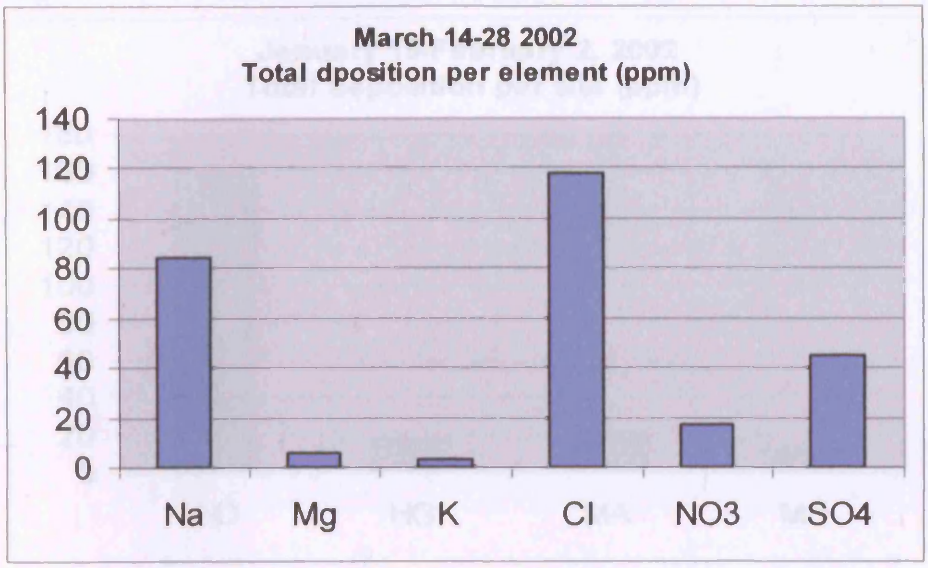


Chart 2

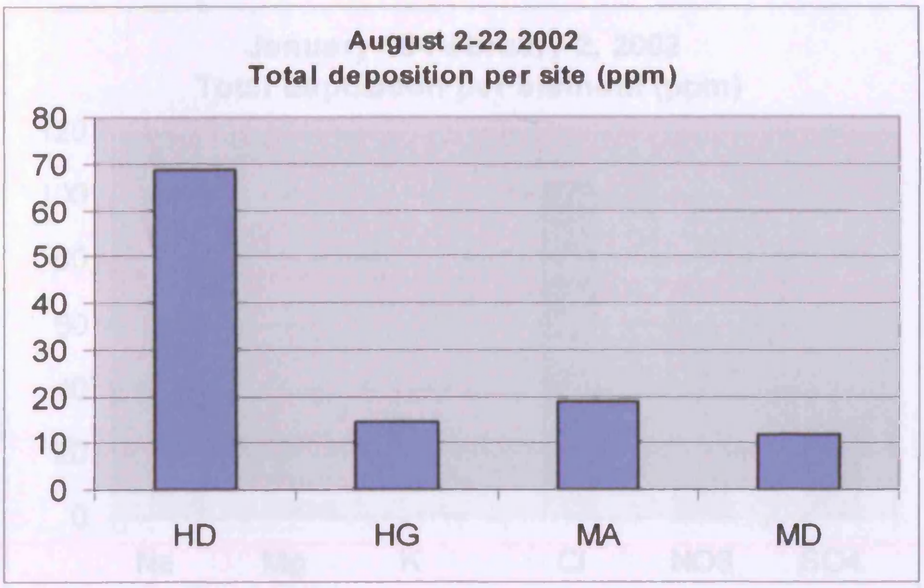


Chart 3

Chart 4

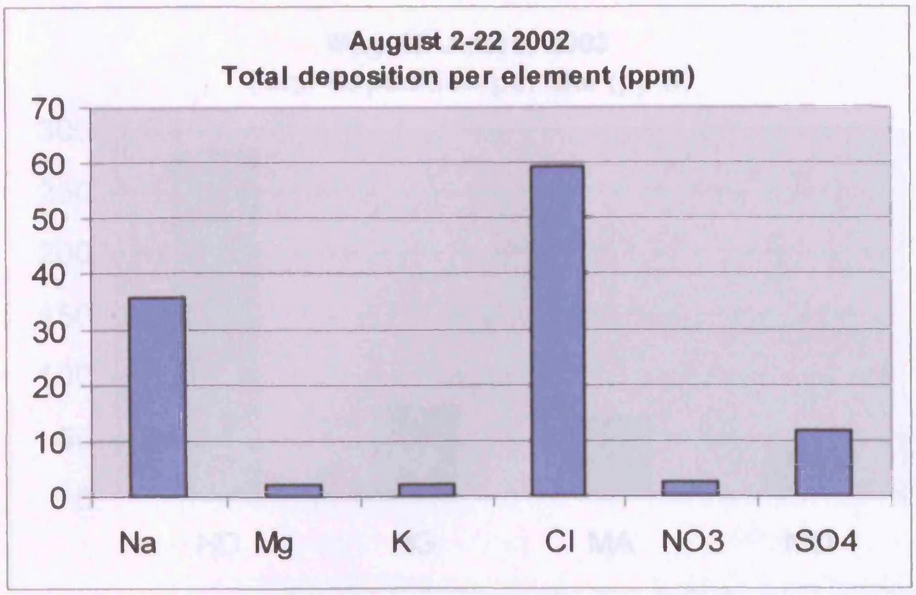

August 2-22 2002
Total deposition per element (ppm)

Chart 5

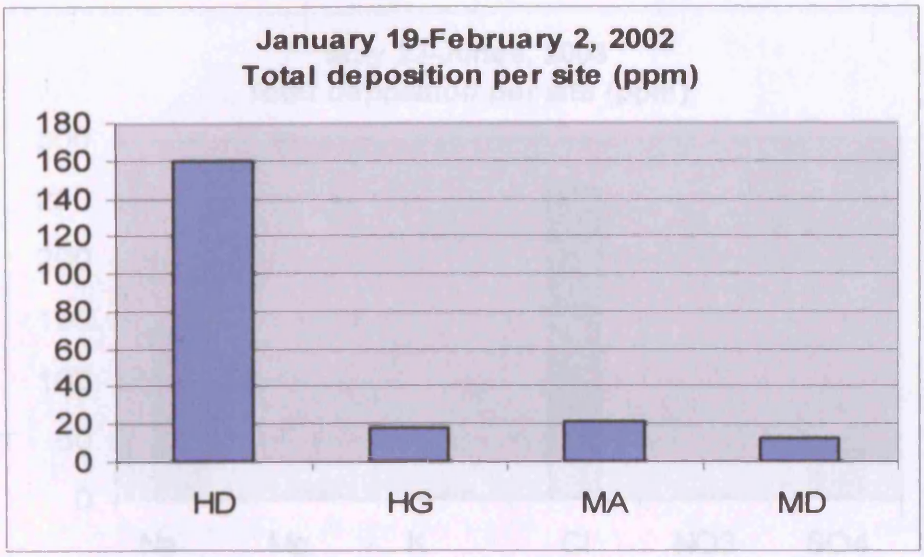
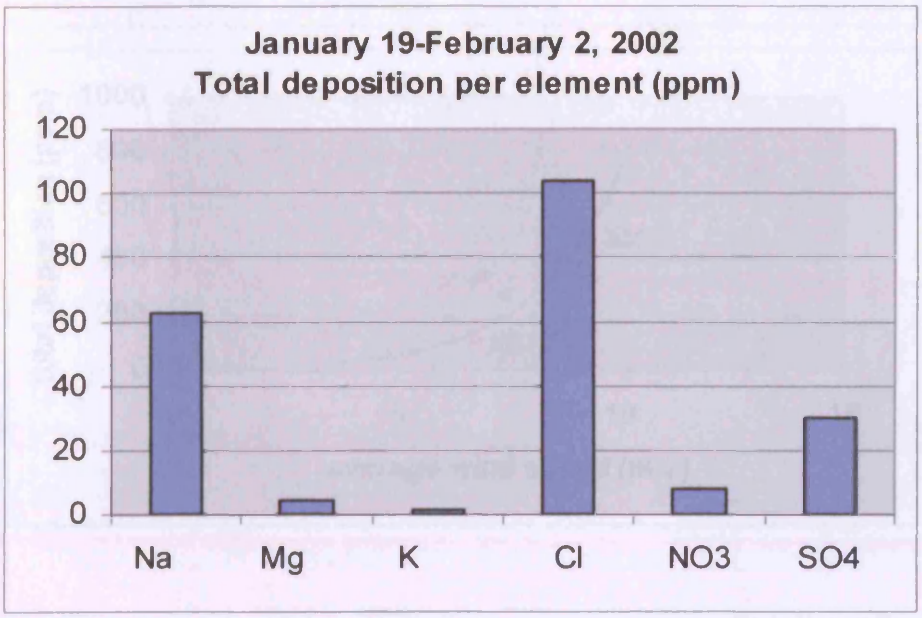

January 19-February 2, 2002
Total deposition per site (ppm)

Chart 6


January 19-February 2, 2002
Total deposition per element (ppm)

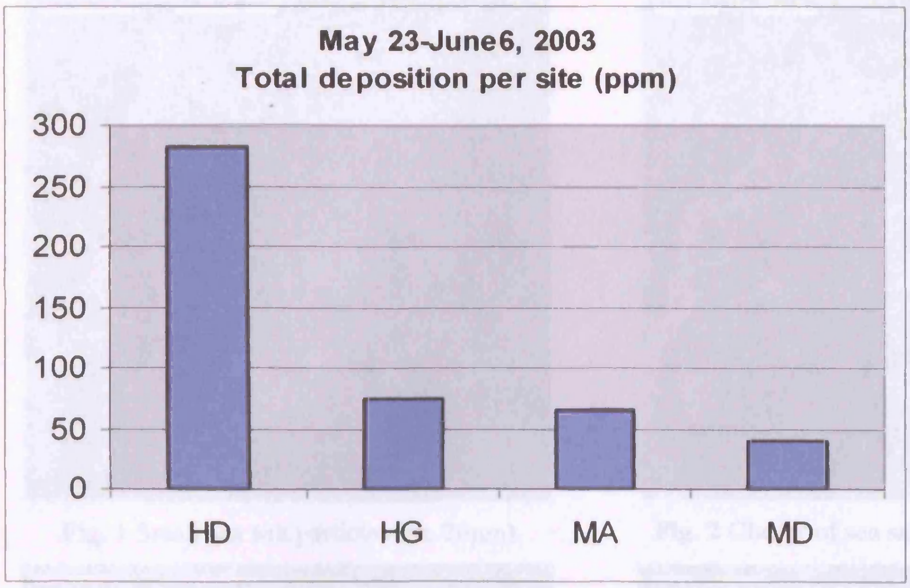


Chart 7

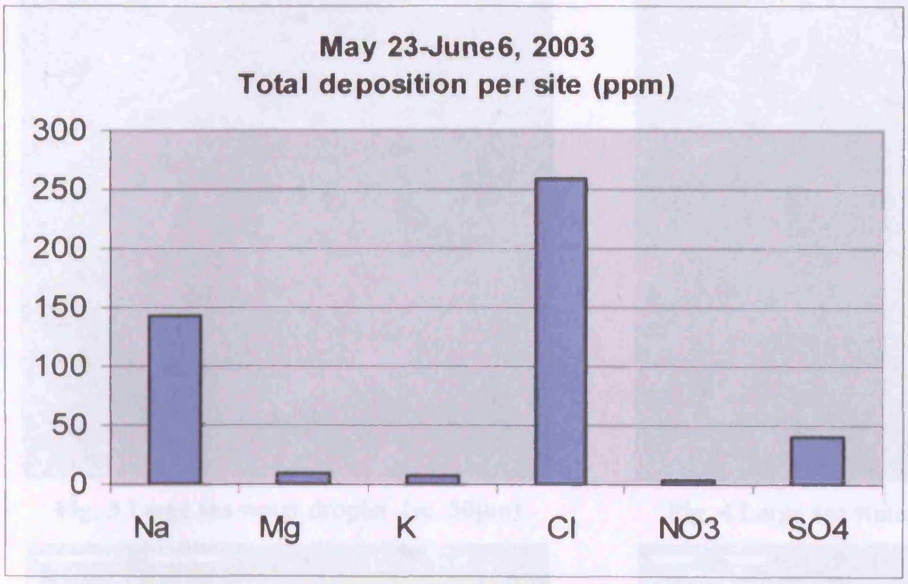


Chart 8

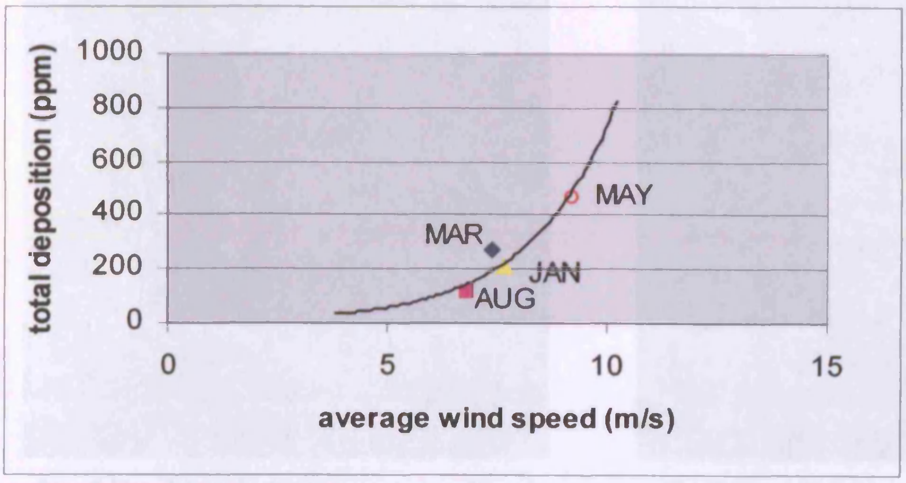


Chart 9

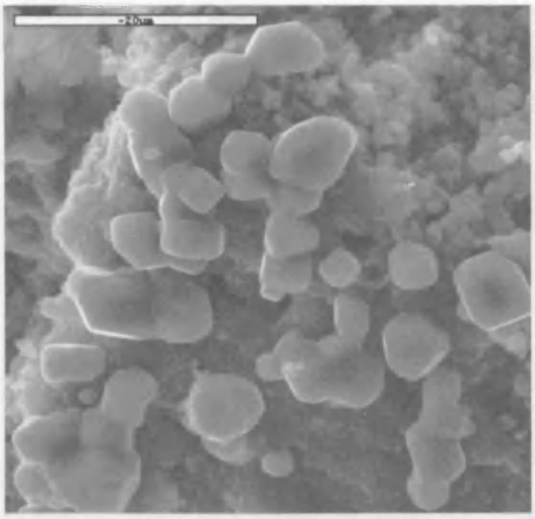


Fig. 1 Small sea salt particles (sc. 20μm)

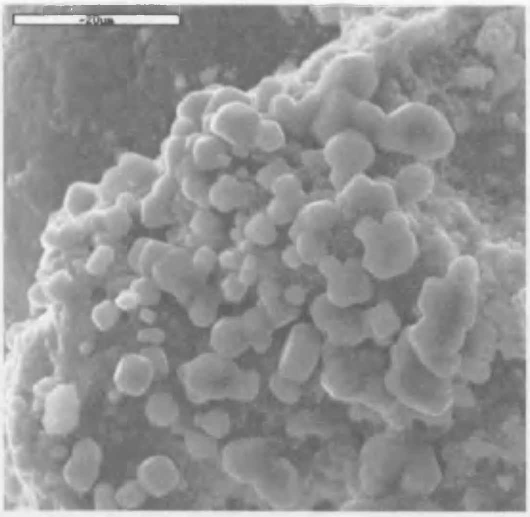


Fig. 2 Cluster of sea salt particles (sc. 20μm)

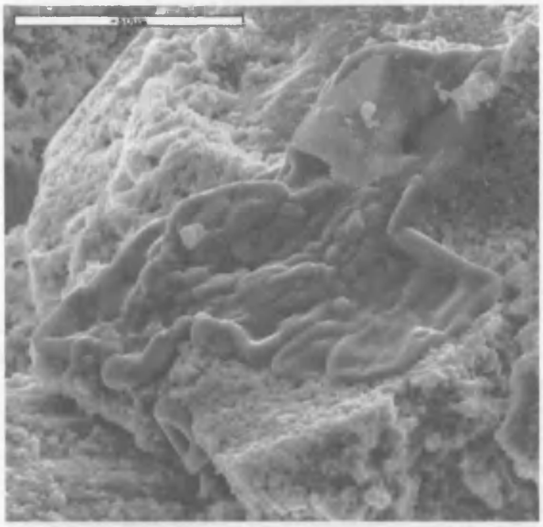


Fig. 3 Large sea water droplet (sc. 50μm)

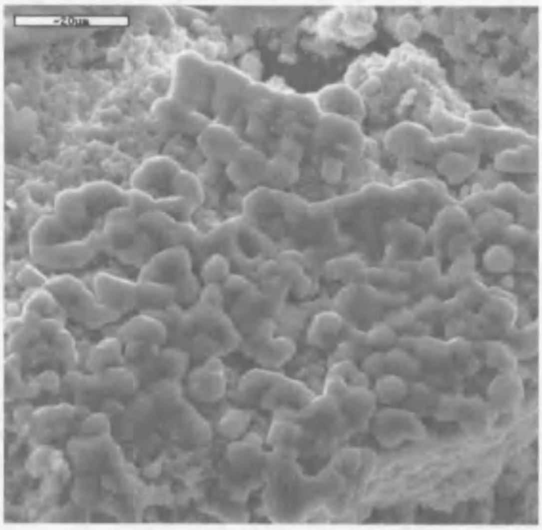


Fig. 4 Large sea water droplet (sc. 20μm)

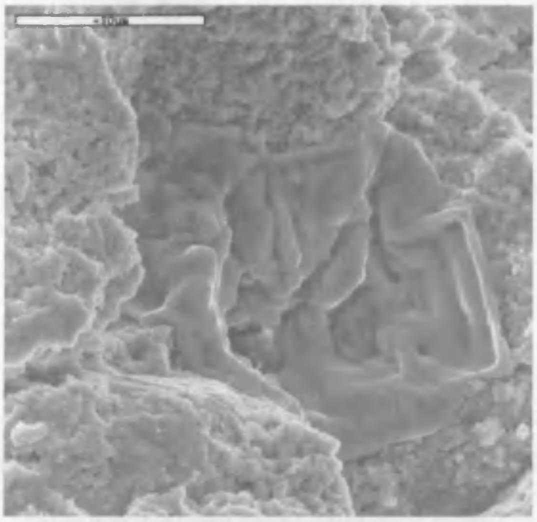


Fig. 5 Droplet sucked into a pore (sc. 50μm)

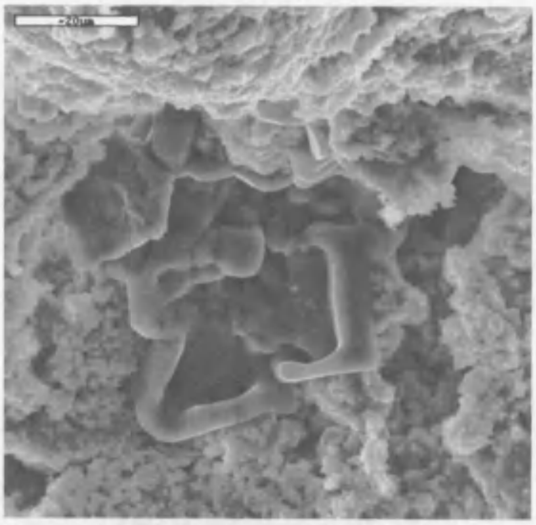


Fig. 6 Sea salt particle in a pore (sc. 20μm)

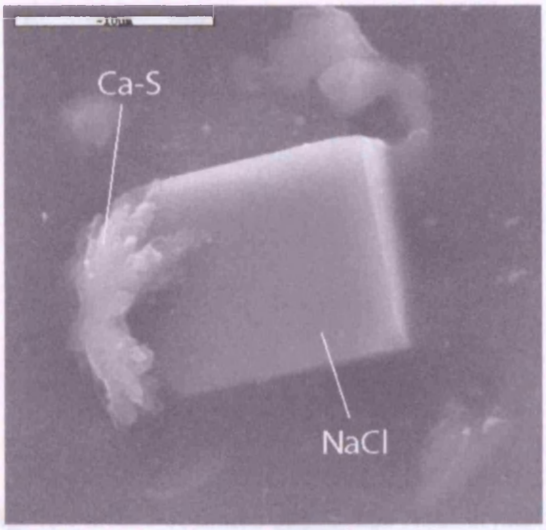


Fig. 7 Typical sea salt particle (sc. 20µm)

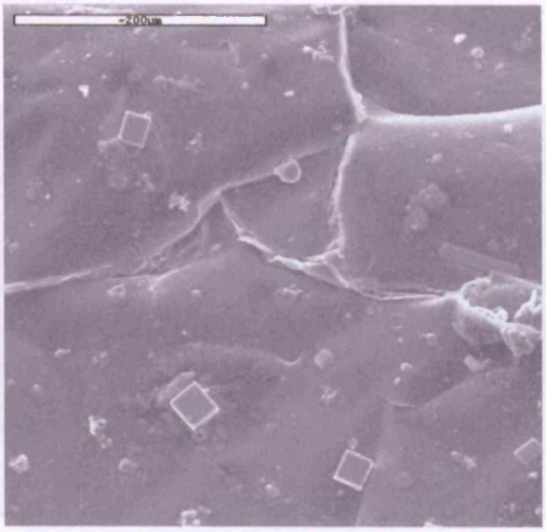


Fig. 8 Various particles. The distribution on the sampler is quite dense (sc. 200µm)

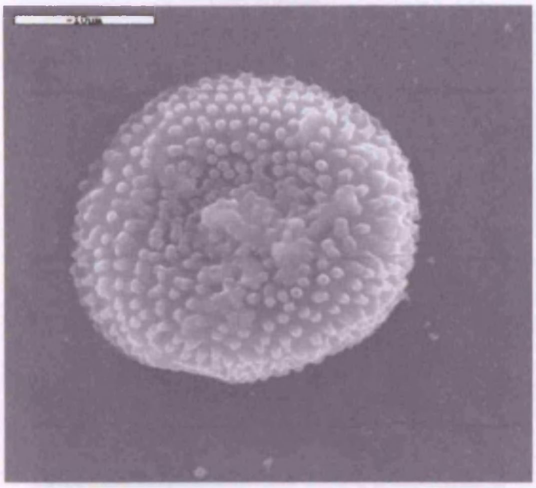


Fig. 9 Particle of biological origin, rich in P. Probably pollen (sc.10µm)

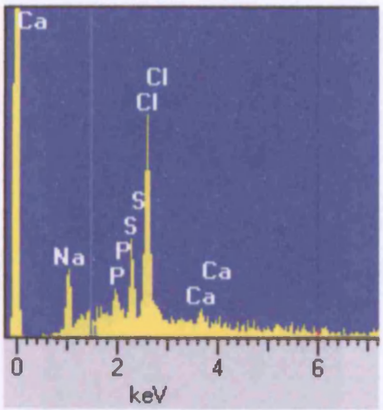


Fig. 10 Spectrum of fig.9

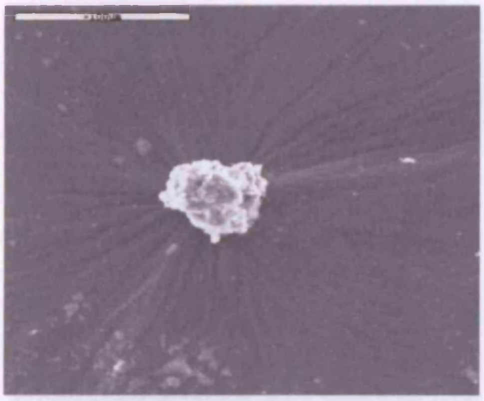


Fig. 11 Particle of terrigenous origin, rich in Ca, Si, Mg, Al, Fe and Ti. The force of the deposition impact is depicted on the sampler's surface (sc. 100µm)

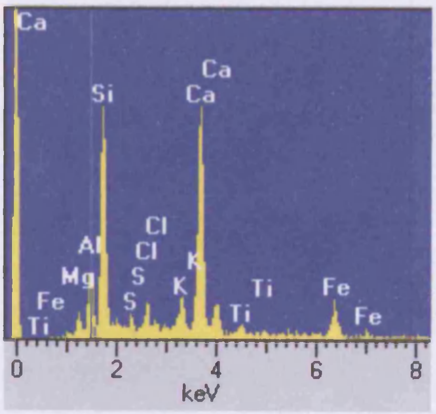


Fig. 12 Spectrum of fig. 11

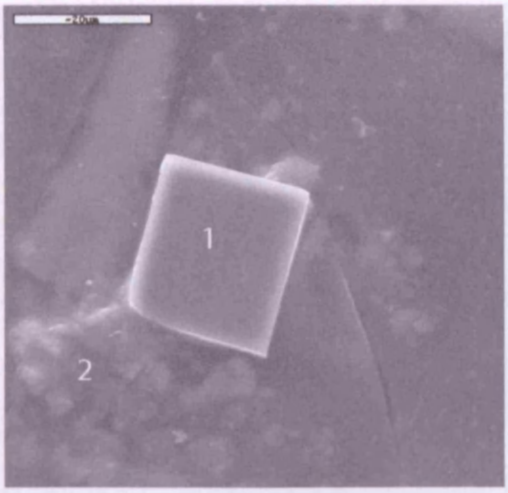


Fig. 13 Particle of mixed origin. The NaCl crystal is surrounded by amorphous particles containing primarily Si along with Ca, Mg, Fe, K, Al, P and S (sc. 20μm)

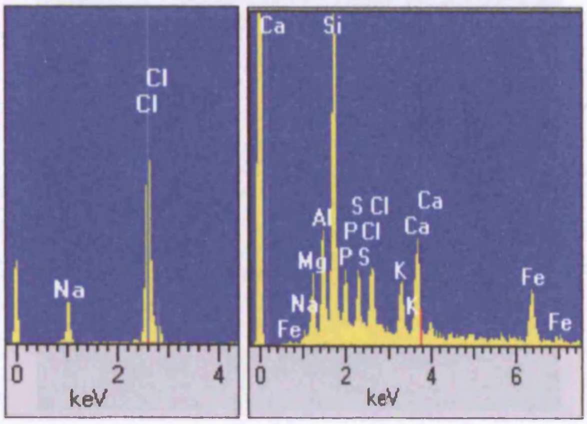


Fig. 14 Spectra 1and 2 of fig. 13

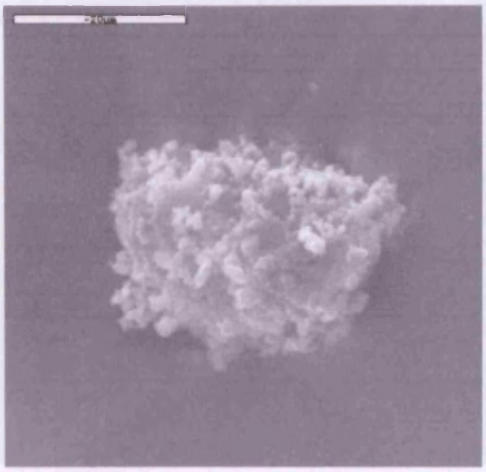


Fig. 15 Calcareous particle, rich in S. Probably resuspended weathering product (sc. 20μm)

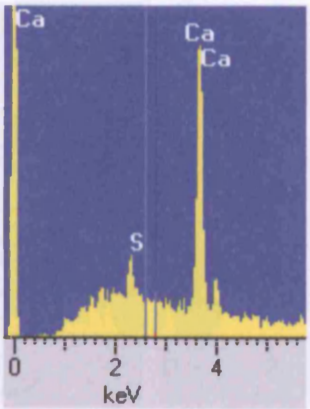


Fig. 16 Spectrum of fig. 15

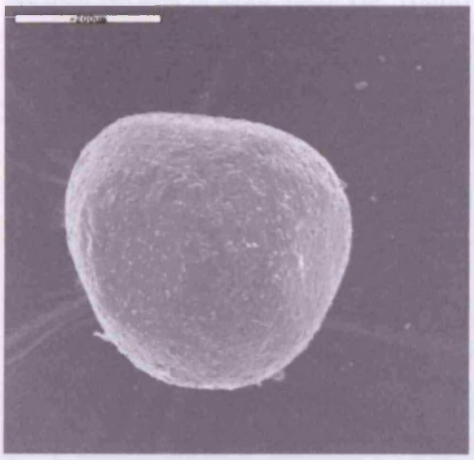


Fig. 17 Large siliceous particle (sc. 200μm)

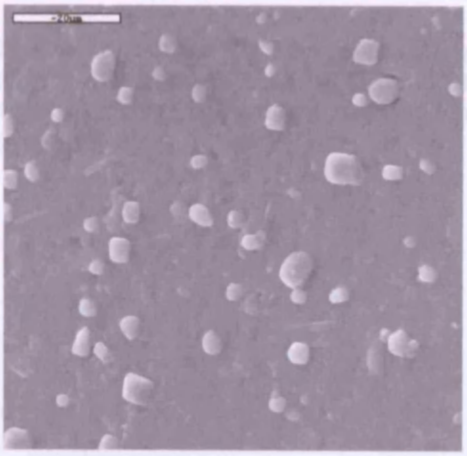


Fig. 18 Detail of fig17. NaCl particles (sc. 20μm)

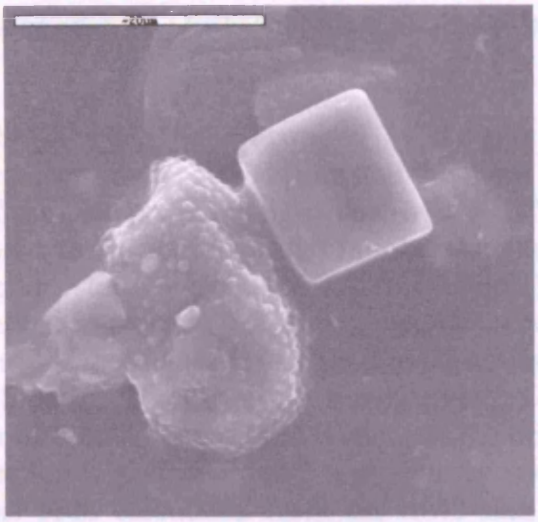


Fig. 19 Mixed particle of marine and biological origin (sc. 20µm)

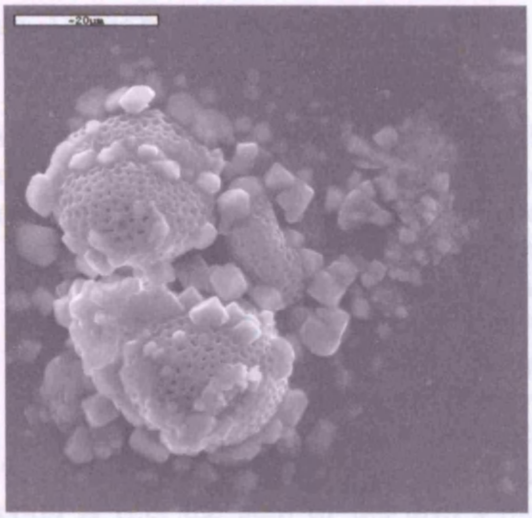


Fig. 20 NaCl particles crystallized on pollen (sc. 20µm)

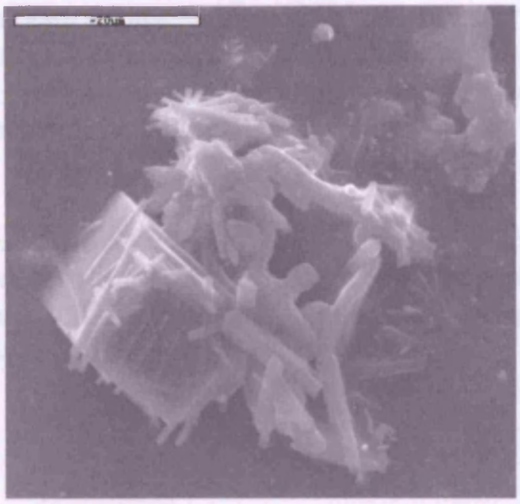


Fig. 21 Particle of marine origin. The cubic crystal is NaCl, the whiskers Ca-S and the amorphous crystals are rich in Mg-Cl-S-P (sc. 10µm)

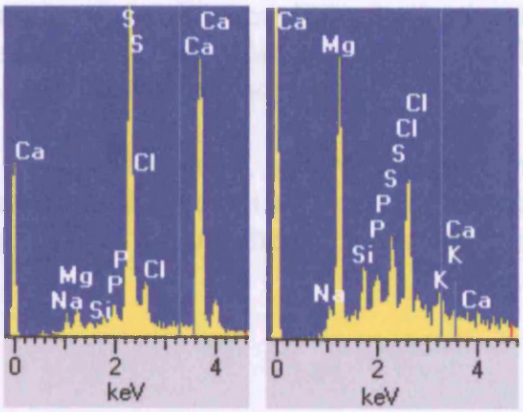


Figure22 Spectra of fig. 21

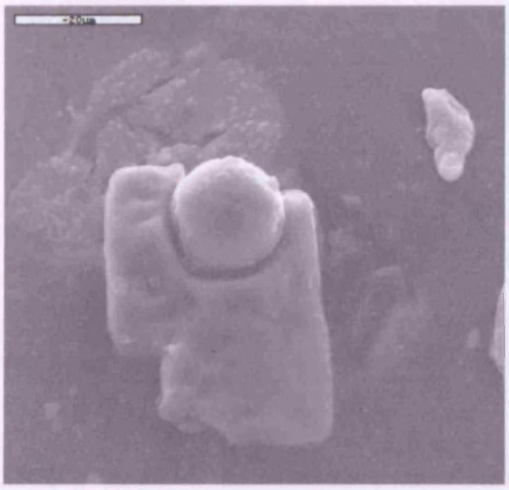


Fig. 23 The shape of the NaCl crystal has changed as a consequence of the presence of the unidentified spherical particle indicating that it preexisted in the sea water droplet.

Appendix V: Drills analytical and calculated data. Tables and charts

The data has been acquired by IC and ICP-AES analysis. The columns of the tables represent the acquired ions and the rows the samples. The tables are organised in groups of samples per campaign. The row "**R-H**" indicates the location of the samples; the letters indicate the room and the numbers the height. The numbers on the row "**D**" indicate the depth (starting from the external sample). The row "**No**" is the analysis numbering and serves as reference. The row "**total**" in section **A** represents the total ionic content as the sum of the quantities in each row and the row "**W**" represents the weight of the sample which has been used for the calculation of the % concentrations in section **B**. The rows "**sum**" indicate the total content of the drill per each ion the sum of the above column. In section B the rows "**av**" represent the average % concentration of each ion per drill and has been calculated from the rows sum of section **A** (i.e. the sum of the drill's ionic content and the sum of the samples weights consisting each drill). The column "**total**" of section **B** represents the % total salt content of each sample as the sum of the ionic % concentrations. In section **C** rows "**sum**" depict the sum of the drill's molar concentrations per each ion, column "**sum+**" the sum of the cations and column "**sum-**" the sum of the anions, the column "**ratio**" represents the ratio sum+/sum- indicating the electrochemical balance of each sample. The charts refer to data from the tables in section **B**. They are also organised in groups per campaign and sampling location.

(Supplementary samples legend: **cs** = concrete slab, **gr** = ground, **mos** = mosaic, **con** = conservation mortar. Sample **mosM** has been extracted after the nitrates contamination in May 2003. Sample **MDgr** has been extracted by the area around thee mosaics which has not been insulated)

V.A Raw data (ppm)

NOVEMBER 2001

No	R-H	D	Ca	Na	Mg	K	Cl	NO_3	SO_4	total	W
1	**MD1**	**4**	21.65	5.45	0.27	1.03	6.04	1.31	34.82	70.56	5.20
2		**3**	12.72	5.82	0.20	1.27	6.29	0.55	27.30	54.15	3.20
3		**2**	8.61	5.48	0.15	0.75	4.52	1.00	17.53	38.03	2.00
4		**1**	24.60	6.13	0.63	0.89	6.31	1.16	58.30	98.01	24.30
sum			67.58	22.88	1.25	3.94	23.15	4.01	137.94	260.75	34.70
5	**MD2**	**1**	13.14	6.43	1.36	1.25	10.24	2.13	26.19	60.74	21.60
6		**2**	11.46	4.77	0.35	0.88	4.48	0.91	28.83	51.68	4.00
7		**3**	7.20	6.13	0.28	1.11	5.16	0.67	18.16	38.71	2.60
sum			31.80	17.33	1.99	3.24	19.88	3.71	73.18	151.13	28.20
8	**MD3**	**1**	2.41	7.83	0.24	2.34	9.23	0.61	4.18	26.84	7.50
9		**2**	11.28	7.23	1.04	1.66	12.22	1.31	7.51	42.25	13.20
10		**3**	3.15	6.24	0.48	1.31	10.18	0.00	1.95	23.31	9.80
11		**4**	3.71	5.58	0.58	0.49	8.78	1.04	1.99	22.18	12.10
sum			20.55	26.88	2.34	5.80	40.41	2.96	15.64	114.58	42.60
12	**MA3**	**1**	14.22	6.49	1.31	1.03	10.01	0.00	5.92	38.98	32.70
13		**2**	18.73	20.54	4.72	3.48	32.78	18.32	7.33	105.90	65.40
14		**3**	18.01	14.24	3.08	1.87	22.50	0.00	3.62	63.32	50.80
sum			50.96	41.27	9.11	6.38	65.29	18.32	16.87	208.20	148.90
28	**HD3**	**1**	1.98	7.74	0.11	2.03	7.75	1.59	3.44	24.64	1.50
29		**6**	10.41	4.56	0.23	0.54	4.09	1.02	2.88	23.73	15.40
30		**5**	3.24	5.68	0.12	0.68	6.78	5.97	3.61	26.08	4.50
31		**4**	2.12	2.98	0.09	0.23	2.36	0.98	2.02	10.78	2.60
32		**3**	1.54	4.59	0.08	0.39	3.82	1.40	2.84	14.66	1.70
33		**2**	2.85	5.78	0.11	0.51	4.29	1.33	3.50	18.36	1.70
sum			22.14	31.33	0.74	4.38	29.08	12.28	18.29	118.24	27.40
34	**HD1**	**1**	1.18	4.04	0.10	0.37	4.02	1.03	2.80	13.54	2.40
35		**2**	1.76	5.07	0.14	0.41	4.32	1.08	2.94	15.71	4.40
36		**3**	1.64	3.64	0.09	0.05	2.73	1.04	2.41	11.60	2.60
37		**4**	3.64	4.42	0.25	0.21	7.14	2.45	3.21	21.33	12.20
38		**5**	6.17	8.66	0.69	0.43	12.67	1.71	5.20	35.53	54.80
sum			14.39	25.83	1.27	1.47	30.88	7.31	16.57	97.71	76.40
39	**HG3**	**1**	1.53	3.75	0.06	0.16	2.73	1.16	2.65	12.05	1.60
40		**2**	1.40	4.43	0.06	0.09	3.30	1.44	3.09	13.81	1.40
41		**3**	4.56	4.68	0.14	0.26	3.31	1.48	3.14	17.56	11.80
42		**4**	6.89	7.23	0.23	1.56	7.01	1.45	3.75	28.12	30.80
43		**5**	5.92	4.55	0.12	0.22	4.19	1.46	2.92	19.38	6.90
sum			20.30	24.64	0.61	2.29	20.54	6.99	15.54	90.91	52.50
44	**HG1**	**1**	1.44	6.68	0.06	0.14	2.62	0.96	5.56	17.46	2.00

45		**2**	9.95	3.26	0.07	0.15	3.23	1.05	24.82	42.53	4.30
sum			11.39	9.94	0.13	0.29	5.85	2.00	30.39	59.99	6.30

MARCH 2002

No	RH	D	Ca	Na	Mg	K	Cl	NO_3	SO_4	total	w
4	**HD3**	**1**	1.00	1.20	0.01	0.74	3.34	0.87	2.33	9.49	0.92
5		**2**	8.40	0.61	0.03	0.48	1.10	0.75	1.18	12.55	1.32
6		**3**	10.64	1.81	0.16	1.24	4.10	0.83	2.08	20.86	2.92
7		**4**	10.93	1.22	0.17	0.76	2.75	0.91	2.63	19.37	3.48
8		**5**	16.51	1.61	0.18	1.13	3.10	0.82	6.13	29.48	2.98
sum			47.48	6.45	0.55	4.35	14.39	4.18	14.35	91.75	11.62
9	**HD1**	**1**	5.16	1.94	0.20	0.84	6.16	1.06	2.96	18.32	4.00
10		**2**	5.87	1.80	0.17	0.95	4.37	1.11	2.26	16.53	4.80
11		**3**	5.45	3.06	0.18	2.05	5.99	1.86	3.01	21.60	11.40
sum			16.48	6.80	0.55	3.84	16.52	4.03	8.23	56.45	20.20
16	**HG3**	**1**	4.43	6.08	0.09	1.24	3.76	2.35	3.57	21.52	0.90
17		**2**	8.15	5.80	0.15	1.13	4.20	1.28	2.20	22.91	1.08
18		**3**	14.58	5.91	0.18	0.99	4.62	1.70	2.68	30.66	2.65
19		**4**	13.11	7.42	0.16	1.45	5.98	1.58	3.09	32.79	4.90
sum			40.27	25.21	0.58	4.81	18.56	6.91	11.54	107.88	9.53
13	**HG1**	**1**	12.04	9.10	0.19	1.94	7.95	2.14	4.26	37.62	1.00
14		**2**	15.19	6.46	0.27	1.56	4.76	2.19	8.36	38.79	2.10
15		**3**	6.81	1.86	0.15	1.17	3.88	1.73	9.62	25.22	1.70
sum			34.04	17.42	0.61	4.67	16.59	6.06	22.24	101.63	4.80
12	**MA3**	**1**	13.85	10.09	0.75	1.20	7.84	3.53	4.37	41.63	4.33
1		**2**	12.35	15.95	4.47	2.52	28.98	13.75	10.16	88.18	92.84
2		**3**	11.60	12.01	3.19	1.92	21.33	9.85	10.18	70.08	79.92
3		**4**	13.98	20.91	3.39	3.21	36.57	0.00	3.32	81.38	71.20
sum			51.78	58.96	11.80	8.85	94.72	27.13	28.03	281.27	248.29

AUGUST 2002

No	R	D	Ca	Na	Mg	K	Cl	NO_3	SO_4	total	Ws
1	**MD1**	**1**	1.44	0.38	0.13	0.40	1.24	3.88	1.25	8.72	1.00
2		**2**	4.61	0.43	0.35	0.28	1.33	0.47	1.04	8.51	1.00
3		**3**	7.52	0.69	0.55	0.59	1.61	0.21	1.74	12.91	5.00
4		**4**	7.22	0.09	0.48	0.01	0.41	0.20	0.84	9.26	7.00
5		**5**	6.91	0.17	0.40	0.12	0.64	0.29	1.13	9.65	2.00
sum			27.70	1.76	1.91	1.40	5.23	5.04	6.00	49.04	16.00

6	**MD2**	**1**	6.46	0.06	0.24	0.03	0.52	0.20	11.87	19.37	1.00
7		**2**	6.94	0.12	0.16	0.04	0.70	0.19	4.82	12.97	3.00
8		**3**	9.17	0.13	0.26	0.00	0.77	0.20	6.76	17.29	14.00
9		**4**	7.50	0.12	0.15	0.02	0.69	0.21	3.17	11.85	1.00
10		**5**	6.58	0.15	0.14	0.07	0.78	0.45	0.83	9.00	4.00
sum			36.65	0.58	0.95	0.16	3.46	1.24	27.45	70.49	23.00
11	**MD3**	**1**	0.23	1.98	0.01	0.21	3.17	0.65	0.81	7.06	1.00
12		**2**	1.77	4.21	0.09	0.00	6.63	0.33	0.82	13.85	1.00
13		**3**	6.06	2.09	0.29	0.05	4.22	0.48	0.91	14.10	1.00
14		**4**	5.74	0.25	0.29	0.07	1.71	0.25	0.81	9.12	1.00
15		**5**	7.23	0.67	0.55	0.10	3.35	0.41	0.83	13.13	7.00
sum			21.03	9.20	1.23	0.43	19.06	2.12	4.18	57.25	11.00
16	**MA1**	**1**	6.17	0.70	0.12	0.50	1.97	0.23	1.96	11.66	69.00
17		**2**	6.55	0.38	0.17	0.14	1.26	0.79	2.11	11.40	132.00
18		**3**	6.88	1.24	0.26	0.45	2.05	0.90	3.39	15.17	245.00
19		**4**	5.70	0.43	0.13	0.21	1.39	0.68	1.51	10.05	102.00
20		**5**	10.12	1.25	0.30	0.45	2.56	1.31	2.60	18.59	218.00
sum			35.42	4.00	0.98	1.75	9.23	3.91	11.57	66.86	766.00
21	**MA2**	**1**	1.29	0.06	0.06	0.08	0.50	1.94	0.81	4.74	1.00
22		**2**	5.30	0.11	0.11	0.03	0.92	0.21	0.82	7.50	1.00
23		**3**	7.62	0.07	0.15	0.02	0.46	0.24	0.84	9.39	17.00
24		**4**	10.63	0.09	0.20	0.01	0.63	0.19	0.81	12.55	59.00
25		**5**	8.51	0.26	0.18	0.10	1.17	0.50	0.97	11.69	53.00
26		**6**	7.33	0.14	0.17	0.12	0.96	0.26	0.91	9.89	22.00
sum			40.68	0.73	0.87	0.36	4.64	3.34	5.15	55.77	153.00
27	**MA3**	**1**	5.54	0.23	0.18	0.13	1.39	0.66	1.24	9.36	8.00
28		**2**	7.72	0.47	0.39	0.09	1.75	1.41	2.43	14.25	130.00
29		**3**	6.58	0.35	0.35	0.07	1.33	0.85	1.42	10.95	41.00
30		**4**	5.31	0.38	0.46	0.16	1.53	1.44	1.10	10.37	24.00
31		**5**	6.24	0.62	0.53	0.15	1.79	3.35	1.37	14.05	28.00
sum			31.39	2.05	1.91	0.60	7.77	7.70	7.54	58.97	231.00
32	**HD1**	**1**	6.88	0.15	0.14	0.08	1.06	0.22	1.00	9.53	18.00
33		**2**	7.19	0.19	0.19	0.03	1.13	0.24	1.47	10.44	29.00
34		**3**	7.54	1.13	0.48	0.38	2.14	0.21	1.29	13.17	224.00
sum			21.61	1.47	0.81	0.49	4.32	0.67	3.76	33.13	271.00
35	**HD2**	**1**	6.23	0.29	0.27	0.06	3.33	0.00	1.28	11.45	22.00
36		**2**	6.52	0.86	0.21	0.03	2.17	0.20	0.83	10.81	37.00
37		**3**	6.34	1.00	0.27	0.06	3.42	0.23	0.88	12.20	50.00
38		**4**	5.82	0.72	0.20	0.10	3.02	0.19	0.88	10.93	30.00
39		**5**	7.31	0.60	0.19	0.15	2.01	0.23	0.84	11.33	19.00
sum			32.22	3.47	1.14	0.40	13.95	0.85	4.70	56.72	158.00
40	**HD3**	**1**	4.26	0.03	0.05	0.06	0.67	0.32	0.88	6.27	1.00
41		**2**	6.58	0.10	0.09	0.00	1.23	1.14	0.95	10.09	4.00

42		**3**	7.99	0.09	0.12	0.03	3.67	0.53	0.90	13.32	22.00
43		**4**	8.28	0.10	0.14	0.04	0.86	0.39	1.00	10.81	29.00
44		**5**	8.42	0.15	0.14	0.12	0.98	0.22	0.91	10.94	53.00
sum			35.53	0.47	0.54	0.25	7.41	2.59	4.64	51.43	109.00
45	**HG1**	**1**	2.15	0.00	0.20	0.01	0.80	0.25	0.90	4.31	1.00
46		**2**	6.40	0.01	0.34	0.04	1.49	0.49	1.02	9.79	1.00
47		**3**	6.94	0.12	0.44	0.07	0.83	0.25	1.01	9.66	5.00
48		**4**	7.86	0.09	0.80	0.11	1.22	0.22	1.00	11.30	85.00
49		**5**	7.41	0.13	0.28	0.17	0.75	0.20	0.82	9.75	59.00
sum			30.76	0.35	2.06	0.40	5.08	1.42	4.74	44.81	151.00
50	**HG2**	**1**	2.10	85.55	0.04	0.03	137.13	1.93	8.10	234.88	39.00
51		**2**	8.31	5.70	1.25	0.34	11.90	4.77	10.83	43.11	146.00
52		**3**	8.64	8.93	0.72	0.15	14.90	1.01	2.08	36.43	119.00
53		**4**	11.84	27.61	4.26	1.34	57.46	6.51	6.49	115.51	1561.00
54		**5**	9.86	12.01	2.02	0.69	23.44	2.82	2.85	53.69	353.00
sum			40.75	139.80	8.29	2.55	244.83	17.05	30.34	483.61	2218.00
55	**HG3**	**1**	6.19	-0.04	0.08	0.05	0.47	0.30	0.86	7.90	1.00
56		**2**	6.73	0.03	0.12	0.05	0.57	0.54	0.86	8.90	1.00
57		**3**	7.70	0.01	0.10	0.00	0.73	0.25	0.86	9.64	32.00
58		**4**	7.89	0.09	0.11	0.03	1.82	0.34	0.99	11.28	74.00
59		**5**	7.24	0.09	0.08	0.06	0.83	0.38	1.29	9.97	31.00
sum			35.75	0.18	0.49	0.19	4.41	1.81	4.85	47.68	139.00

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No	**R**	**D**	**Ca**	**Na**	**Mg**	**K**	**Cl**	**NO_3**	**SO_4**	**total**	**W(mg)**
1	**HG3**	**1**	3.45	0.12	0.08	0.05	1.16	1.98	7.13	13.97	0.60
2		**2**	3.96	0.16	0.17	0.12	0.63	0.64	5.82	11.50	1.90
3		**3**	4.09	0.08	0.15	0.09	0.75	0.33	3.82	9.30	2.04
4		**4**	3.13	0.13	0.11	0.14	3.26	0.33	1.12	8.22	1.93
sum			14.63	0.49	0.51	0.40	5.80	3.28	17.89	43.00	6.47
5	**HG2**	**1**	3.68	0.58	0.23	0.21	2.08	0.57	2.95	10.30	0.57
6		**2**	5.44	2.08	0.62	0.28	4.84	1.66	1.76	16.68	1.42
7		**3**	5.32	3.58	0.81	0.53	7.55	2.51	1.05	21.36	2.96
8		**4**	3.49	2.43	0.36	0.21	4.90	1.35	0.65	13.38	1.00
sum			17.93	8.67	2.02	1.23	19.37	6.08	6.41	61.71	5.95
9	**HG21**	**1**	2.51	0.06	0.41	0.17	0.36	0.07	5.92	9.51	2.34
10		**2**	4.21	0.03	0.54	0.11	0.44	0.00	1.29	6.62	5.24
11		**3**	3.71	0.00	0.30	0.19	0.46	2.59	0.63	7.87	5.48
sum			10.43	0.09	1.25	0.47	1.26	2.66	7.84	24.00	13.06
12	**HD3**	**1**	1.57	0.02	0.03	0.04	0.07	0.37	0.04	2.13	0.27
13		**2**	6.15	0.00	0.11	0.03	0.02	0.35	0.00	6.66	2.53

14		**3**	4.71	0.00	0.14	0.07	0.43	0.06	0.26	5.66	6.56
15		**4**	3.23	0.00	0.11	0.07	0.23	0.03	0.00	3.67	5.13
16		**5**	3.37	0.00	0.09	0.04	0.29	0.01	0.09	3.88	3.63
sum			19.03	0.02	0.48	0.25	1.03	0.81	0.38	22.00	18.12
17	**HD2**	**1**	3.84	0.00	0.13	0.02	0.61	0.03	0.13	4.77	1.00
18		**2**	4.08	1.00	0.33	0.06	2.65	0.15	1.38	9.65	5.66
19		**3**	6.26	1.70	0.68	0.11	4.04	0.05	0.05	12.88	8.68
20		**4**	2.91	0.29	0.34	0.01	1.71	0.05	0.16	5.47	2.48
sum			17.09	2.99	1.48	0.20	9.01	0.28	1.73	32.77	17.82
21	**HD1**	**1**	3.51	0.32	0.25	0.09	1.45	2.55	1.91	10.08	4.82
22		**2**	6.42	0.12	0.27	0.10	1.21	0.21	0.89	9.22	2.67
23		**3**	7.61	0.62	0.39	0.13	2.21	0.06	8.50	19.51	6.61
sum			17.54	1.06	0.91	0.32	4.87	2.81	11.30	38.81	14.10
24	**MA3**	**1**	0.85	0.17	0.09	0.03	1.34	0.27	2.34	5.09	3.01
25		**2**	0.61	0.27	0.08	0.04	1.49	1.10	0.00	3.59	4.23
26		**3**	7.40	3.41	0.60	0.32	6.83	4.33	2.76	25.65	7.50
sum			8.86	3.85	0.77	0.39	9.66	5.70	5.10	34.33	14.74
27	**MA2**	**1**	3.40	0.71	0.14	0.13	1.09	0.77	2.78	9.01	14.57
28		**2**	3.56	1.63	0.17	0.27	2.09	0.77	1.99	10.48	16.74
29		**3**	6.48	2.43	0.30	0.57	2.32	0.24	1.45	13.79	23.61
sum			13.44	4.77	0.61	0.97	5.50	1.77	6.21	33.28	54.92
30	**MA1**	**1**	7.69	3.75	0.51	0.45	5.17	2.06	6.14	25.77	18.37
31		**2**	9.27	9.50	0.84	0.81	12.96	8.20	8.85	50.43	59.46
32		**3**	4.49	0.61	0.14	0.15	1.38	0.60	0.19	7.55	12.02
sum			21.45	13.86	1.49	1.41	19.50	10.86	15.17	83.75	89.85
33	**MD3**	**1**	1.57	1.17	0.07	0.08	2.48	0.48	4.95	10.80	5.56
34		**2**	9.64	5.01	0.43	0.28	9.02	1.24	27.83	53.46	14.27
35		**3**	14.14	30.83	4.51	2.73	74.32	17.28	2.77	146.57	45.00
sum			25.35	37.01	5.01	3.09	85.81	19.01	35.55	210.83	64.83
36	**MA2**	**1**	12.34	0.50	0.46	0.23	2.22	0.07	111.50	127.32	2.88
37		**2**	33.71	3.94	2.83	0.69	9.03	2.46	197.20	249.85	36.63
sum			46.05	4.44	3.29	0.92	11.25	2.53	308.70	377.17	39.51
38	**MA1**	**1**	7.10	1.16	13.05	0.23	4.76	1.75	62.71	90.75	6.38
39		**2**	5.97	0.04	1.38	0.08	2.22	0.55	3.63	13.87	1.86
40		**3**	3.45	0.00	0.82	0.08	1.51	0.67	1.37	7.90	2.05
sum			16.52	1.20	15.25	0.39	8.49	2.97	67.71	112.53	10.29

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No	R	D	Ca	Na	Mg	K	Cl	NO_3	SO_4	total	w (mg)
1	MD3	1	7.84	41.10	0.49	0.00	63.45	22.86	0.40	136.14	2.38
2		2	7.43	6.27	0.71	0.06	10.97	18.85	0.90	45.20	3.71
3		3	8.84	28.58	1.27	0.23	55.14	18.26	2.02	114.34	7.05
4		4	11.12	9.27	2.07	0.44	23.10	21.43	0.89	68.33	11.67
5		5	10.04	16.14	3.12	1.34	41.41	28.13	1.44	101.61	15.69
sum			45.27	101.36	7.66	2.07	194.07	109.54	5.65	465.62	40.50
6	MD2	1	13.36	0.03	0.52	0.09	0.60	21.07	31.23	66.90	5.13
7		2	61.89	1.38	1.07	0.09	2.70	19.39	82.77	169.29	6.27
8		3	58.01	1.67	1.07	0.20	2.54	19.42	65.64	148.55	8.00
9		4	9.46	1.33	0.54	0.13	2.24	14.08	13.99	41.76	8.06
10		5	6.95	0.80	0.40	0.11	1.38	14.76	7.54	31.94	7.09
sum			149.67	5.21	3.60	0.62	9.47	88.72	201.17	458.45	34.55
11	MD1	1	5.75	0.96	0.70	0.05	1.75	20.76	4.74	34.72	1.50
12		2	5.29	3.33	1.36	0.20	10.87	19.99	4.49	45.52	4.43
13		3	7.55	5.74	2.17	0.30	27.88	62.19	4.41	110.24	7.34
14		4	5.76	3.56	1.34	0.23	6.32	17.81	1.34	36.35	5.31
sum			24.35	13.59	5.57	0.78	46.82	120.75	14.97	226.83	18.58
15	MA3	1	6.90	0.03	0.44	0.04	0.17	13.18	4.74	25.50	1.33
16		2	4.97	0.03	0.31	0.02	0.10	17.04	0.99	23.46	1.48
17		3	6.11	0.15	0.33	0.01	0.47	16.66	1.68	25.41	4.44
18		4	5.05	0.51	0.36	0.11	1.38	18.19	0.85	26.45	7.50
19		5	11.13	0.28	0.37	0.04	0.99	16.84	0.62	30.26	11.08
sum			34.16	1.00	1.81	0.22	3.11	81.89	8.88	131.07	25.83
20	MA2	1	3.87	0.01	0.08	0.03	0.19	16.89	0.58	21.64	1.11
21		2	5.63	0.41	0.14	0.06	0.62	21.45	0.80	29.11	3.07
22		3	5.60	0.36	0.14	0.01	1.17	18.31	0.93	26.53	4.81
23		4	6.03	0.78	0.20	0.07	1.48	17.76	1.38	27.70	11.78
24		5	5.42	0.86	0.17	0.04	2.15	16.70	0.48	25.81	3.97
sum			26.55	2.42	0.73	0.21	5.60	91.11	4.17	130.78	24.74
25	MA1	1	5.97	0.64	0.12	0.00	0.96	15.97	3.04	26.70	2.21
26		2	5.85	0.55	0.14	0.05	1.85	15.60	1.86	25.89	4.17
27		3	5.41	0.94	0.19	0.04	1.70	15.84	1.18	25.31	6.27
28		4	5.70	1.29	0.26	0.06	1.73	15.52	0.97	25.53	8.31
sum			22.93	3.42	0.71	0.15	6.23	62.94	7.05	103.43	20.96
29	HD3	1	5.83	0.03	0.19	0.04	0.59	0.50	0.82	7.92	1.59
30		2	5.86	0.25	0.24	0.04	1.51	0.00	0.31	8.20	3.79
31		3	7.78	0.83	0.42	0.09	2.31	0.00	1.23	12.65	13.89
32		4	6.92	0.33	0.28	0.04	0.89	0.00	0.20	8.66	13.10
sum			26.39	1.44	1.13	0.13	5.29	0.50	2.55	37.43	32.37
33	HD2	1	7.57	12.32	0.36	0.12	17.39	0.00	2.20	39.96	5.39

34		**2**	7.82	7.00	0.51	0.05	10.72	0.00	2.76	28.85	12.63
35		**3**	7.26	2.53	0.45	0.07	4.98	0.03	1.77	17.09	8.84
sum			22.65	21.85	1.32	0.24	33.09	0.03	6.72	85.90	26.86
36	**HD1**	**1**	7.86	1.44	0.49	0.05	1.91	0.00	2.10	13.86	7.83
37		**2**	4.76	0.00	0.10	0.00	0.22	0.00	0.67	5.75	2.90
38		**3**	5.73	1.20	0.42	0.17	2.19	0.00	1.35	11.06	9.96
sum			18.35	2.64	1.01	0.22	4.32	0.00	4.12	30.66	20.69
39	**HG3**	**1**	7.58	0.05	0.19	0.00	0.51	28.73	8.60	45.67	2.21
40		**2**	6.34	0.08	0.19	0.06	0.44	29.93	3.97	41.02	3.26
41		**3**	6.32	0.49	0.20	0.09	0.65	28.33	3.13	39.21	6.62
42		**4**	10.14	0.15	0.19	0.10	0.96	27.87	2.00	41.41	8.90
sum			30.38	0.77	0.77	0.25	2.56	114.86	17.71	167.30	20.99
43	**HG2**	**1**	7.17	3.22	0.51	0.04	4.89	22.86	2.75	41.44	2.46
44		**2**	9.23	2.54	0.40	0.09	3.64	26.98	1.64	44.52	2.36
45		**3**	9.02	6.09	1.17	0.18	9.25	24.16	2.51	52.39	10.94
46		**4**	6.33	4.49	0.69	0.12	13.47	27.78	2.93	55.80	8.18
47		**5**	8.01	2.84	0.50	0.10	4.64	27.21	1.24	44.54	7.16
sum			39.76	19.18	3.27	0.53	35.88	128.99	11.07	238.68	31.10
48	**HG1**	**1**	6.28	2.19	1.37	0.09	5.76	25.64	5.83	47.15	2.92
49		**2**	5.44	3.22	1.40	0.11	6.37	24.78	2.04	43.35	2.98
50		**3**	6.89	6.62	2.29	0.33	12.34	24.07	3.97	56.51	7.07
51		**4**	6.65	6.56	1.59	0.34	11.02	25.22	1.44	52.81	7.38
sum			25.26	18.59	6.65	0.87	35.48	99.70	13.27	199.82	20.35

V.B % weight of sample

NOVEMBER 2002

No	R-H	D	Ca	Na	Mg	K	Cl	NO_3	SO_4	total
1	**MD1**	4	8.33	2.10	0.10	0.40	2.32	0.50	13.39	27.14
2		3	7.95	3.64	0.13	0.79	3.93	0.34	17.06	33.84
3		2	8.61	5.48	0.15	0.75	4.52	1.00	17.53	38.03
4		1	2.03	0.50	0.05	0.07	0.52	0.10	4.80	8.07
av			3.90	1.32	0.07	0.23	1.33	0.23	7.95	15.03
5	**MD2**	1	1.22	0.60	0.13	0.12	0.95	0.20	2.43	5.62
6		2	5.73	2.39	0.18	0.44	2.24	0.45	14.42	25.84
7		3	5.54	4.72	0.22	0.85	3.97	0.52	13.97	29.78
av			2.26	1.23	0.14	0.23	1.41	0.26	5.19	10.72
8	**MD3**	1	0.64	2.09	0.06	0.62	2.46	0.16	1.12	7.16
9		2	1.71	1.10	0.16	0.25	1.85	0.20	1.14	6.40
10		3	0.64	1.27	0.10	0.27	2.08	0.00	0.40	4.76

11		**4**	0.61	0.92	0.10	0.08	1.45	0.17	0.33	3.67
av			0.97	1.26	0.11	0.27	1.90	0.14	0.73	5.38
12	**MA3**	**1**	0.87	0.40	0.08	0.06	0.61	0.00	0.36	2.38
13		**2**	0.57	0.63	0.14	0.11	1.00	0.56	0.22	3.24
14		**3**	0.71	0.56	0.12	0.07	0.89	0.00	0.14	2.49
av			0.68	0.55	0.12	0.09	0.88	0.25	0.23	2.80
28	**HD3**	**1**	2.64	10.32	0.15	2.71	10.34	2.11	4.59	32.85
29		**6**	1.35	0.59	0.03	0.07	0.53	0.13	0.37	3.08
30		**5**	1.44	2.52	0.05	0.30	3.01	2.65	1.61	11.59
31		**4**	1.63	2.29	0.07	0.18	1.81	0.75	1.56	8.29
32		**3**	1.81	5.40	0.09	0.46	4.49	1.65	3.34	17.24
33		**2**	3.35	6.80	0.13	0.60	5.05	1.56	4.12	21.60
av			1.62	2.29	0.05	0.32	2.12	0.90	1.34	8.63
34	**HD1**	**1**	0.98	3.37	0.08	0.31	3.35	0.86	2.34	11.28
35		**2**	0.80	2.30	0.06	0.19	1.96	0.49	1.33	7.14
36		**3**	1.26	2.80	0.07	0.04	2.10	0.80	1.86	8.93
37		**4**	0.60	0.72	0.04	0.03	1.17	0.40	0.53	3.50
38		**5**	0.23	0.32	0.03	0.02	0.46	0.06	0.19	1.30
av			0.38	0.68	0.03	0.04	0.81	0.19	0.43	2.56
39	**HG3**	**1**	1.91	4.69	0.08	0.20	3.42	1.45	3.31	15.06
40		**2**	2.00	6.33	0.09	0.13	4.71	2.06	4.41	19.73
41		**3**	0.77	0.79	0.02	0.04	0.56	0.25	0.53	2.98
42		**4**	0.45	0.47	0.01	0.10	0.46	0.09	0.24	1.83
43		**5**	1.72	1.32	0.03	0.06	1.21	0.42	0.85	5.62
av			0.77	0.94	0.02	0.09	0.78	0.27	0.59	3.46
44	**HG1**	**1**	1.44	6.68	0.06	0.14	2.62	0.96	5.56	17.46
45		**2**	4.63	1.52	0.03	0.07	1.50	0.49	11.55	19.78
av			3.62	3.16	0.04	0.09	1.86	0.64	9.65	19.05

MARCH 2002

No	**RH**	**D**	**Ca**	**Na**	**Mg**	**K**	**Cl**	**NO_3**	**SO_4**	**total**
4	**HD3**	1	2.17	2.61	0.02	1.61	7.26	1.89	5.07	20.65
5		2	12.73	0.92	0.05	0.73	1.67	1.14	1.79	19.09
6		3	7.29	1.24	0.11	0.85	2.81	0.57	1.43	14.32
7		4	6.28	0.70	0.10	0.44	1.58	0.52	1.51	11.15
8		5	11.08	1.08	0.12	0.76	2.08	0.55	4.11	19.80
av			8.19	1.12	0.10	0.76	2.48	0.72	2.48	15.83
9	**HD1**	1	2.58	0.97	0.10	0.42	3.08	0.53	1.48	9.16
10		2	2.45	0.75	0.07	0.40	1.82	0.46	0.94	6.89
11		3	0.96	0.54	0.03	0.36	1.05	0.33	0.53	3.79
av			1.63	0.67	0.05	0.38	1.64	0.40	0.81	5.59
16	**HG3**	1	9.84	13.51	0.20	2.76	8.36	5.22	7.93	47.78
17		2	15.09	10.74	0.28	2.09	7.78	2.37	4.07	42.41

18		3	11.00	4.46	0.14	0.75	3.49	1.28	2.02	23.17
19		4	5.35	3.03	0.07	0.59	2.44	0.64	1.26	13.39
av			8.45	5.29	0.12	1.01	3.90	1.45	2.42	22.64
13	HG1	1	24.08	18.20	0.38	3.88	15.90	4.28	8.52	75.20
14		2	14.47	6.15	0.26	1.49	4.53	2.09	7.96	36.95
15		3	8.01	2.19	0.18	1.38	4.56	2.04	11.32	29.65
av			20.82	10.65	0.37	2.86	10.15	3.71	13.60	62.14
12	MA3	1	6.40	4.66	0.35	0.55	3.62	1.63	2.02	19.22
1		2	0.27	0.34	0.10	0.05	0.62	0.30	0.22	1.90
2		3	0.29	0.30	0.08	0.05	0.53	0.25	0.26	1.75
3		4	0.39	0.59	0.10	0.09	1.03	0.00	0.09	2.29
av			0.42	0.47	0.10	0.07	0.76	0.22	0.23	2.27

AUGUST 2002

No	R-H	D	Ca	Na	Mg	K	Cl	NO_3	SO_4	total
1	MD1	1	2.88	0.76	0.26	0.80	2.48	7.75	2.50	17.43
2		2	9.22	0.86	0.70	0.56	2.65	0.94	2.09	17.02
3		3	3.01	0.28	0.22	0.24	0.64	0.09	0.69	5.16
4		4	2.06	0.03	0.14	0.00	0.12	0.06	0.24	2.64
5		5	6.91	0.17	0.40	0.12	0.64	0.29	1.13	9.65
av			3.46	0.22	0.24	0.18	0.65	0.63	0.75	6.13
6	MD2	1	12.92	0.12	0.48	0.06	1.03	0.40	23.73	38.75
7		2	4.63	0.08	0.11	0.03	0.46	0.13	3.22	8.64
8		3	1.31	0.02	0.04	0.00	0.11	0.03	0.97	2.47
9		4	15.00	0.24	0.30	0.04	1.38	0.42	6.33	23.70
10		5	3.29	0.08	0.07	0.04	0.39	0.22	0.42	4.50
av			3.19	0.05	0.08	0.01	0.30	0.11	2.39	6.13
11	MD3	1	0.46	3.96	0.02	0.42	6.33	1.31	1.62	14.11
12		2	3.54	8.42	0.18	0.00	13.25	0.66	1.65	27.70
13		3	12.12	4.18	0.58	0.10	8.44	0.96	1.81	28.19
14		4	11.48	0.50	0.58	0.14	3.41	0.50	1.63	18.24
15		5	2.07	0.19	0.16	0.03	0.96	0.12	0.24	3.75
av			3.82	1.67	0.22	0.08	3.47	0.39	0.76	10.41
16	MA1	1	0.18	0.02	0.00	0.01	0.06	0.01	0.06	0.34
17		2	0.10	0.01	0.00	0.00	0.02	0.01	0.03	0.17
18		3	0.06	0.01	0.00	0.00	0.02	0.01	0.03	0.12
19		4	0.11	0.01	0.00	0.00	0.03	0.01	0.03	0.20
20		5	0.09	0.01	0.00	0.00	0.02	0.01	0.02	0.17
av			0.09	0.01	0.00	0.00	0.02	0.01	0.03	0.17
21	MA2	1	2.58	0.12	0.12	0.16	0.99	3.89	1.62	9.48
22		2	10.60	0.22	0.22	0.06	1.84	0.42	1.64	15.00
23		3	0.90	0.01	0.02	0.00	0.05	0.03	0.10	1.11
24		4	0.36	0.00	0.01	0.00	0.02	0.01	0.03	0.43

25		**5**	0.32	0.01	0.01	0.00	0.04	0.02	0.04	0.44
26		**6**	0.67	0.01	0.02	0.01	0.09	0.02	0.08	0.90
av			0.53	0.01	0.01	0.00	0.06	0.04	0.07	0.73
27	**MA3**	**1**	1.39	0.06	0.05	0.03	0.35	0.16	0.31	2.34
28		**2**	0.12	0.01	0.01	0.00	0.03	0.02	0.04	0.22
29		**3**	0.32	0.02	0.02	0.00	0.06	0.04	0.07	0.53
30		**4**	0.44	0.03	0.04	0.01	0.13	0.12	0.09	0.86
31		**5**	0.45	0.04	0.04	0.01	0.13	0.24	0.10	1.00
av			0.27	0.02	0.02	0.01	0.07	0.07	0.07	0.51
32	**HD1**	**1**	0.76	0.02	0.02	0.01	0.12	0.02	0.11	1.06
33		**2**	0.50	0.01	0.01	0.00	0.08	0.02	0.10	0.72
34		**3**	0.07	0.01	0.00	0.00	0.02	0.00	0.01	0.12
av			0.16	0.01	0.01	0.00	0.03	0.00	0.03	0.24
35	**HD2**	**1**	0.57	0.03	0.02	0.01	0.30	0.00	0.12	1.04
36		**2**	0.35	0.05	0.01	0.00	0.12	0.01	0.04	0.58
37		**3**	0.25	0.04	0.01	0.00	0.14	0.01	0.04	0.49
38		**4**	0.39	0.05	0.01	0.01	0.20	0.01	0.06	0.73
39		**5**	0.77	0.06	0.02	0.02	0.21	0.02	0.09	1.19
av			0.41	0.04	0.01	0.01	0.18	0.01	0.06	0.72
40	**HD3**	**1**	8.52	0.06	0.10	0.12	1.35	0.63	1.76	12.54
41		**2**	3.29	0.05	0.05	0.00	0.61	0.57	0.48	5.04
42		**3**	0.73	0.01	0.01	0.00	0.33	0.05	0.08	1.21
43		**4**	0.57	0.01	0.01	0.00	0.06	0.03	0.07	0.75
44		**5**	0.32	0.01	0.01	0.00	0.04	0.01	0.03	0.41
av			0.65	0.01	0.01	0.00	0.14	0.05	0.09	0.94
45	**HG1**	**1**	4.30	0.00	0.40	0.02	1.60	0.51	1.79	8.61
46		**2**	12.80	0.02	0.68	0.08	2.98	0.98	2.05	19.59
47		**3**	2.78	0.05	0.18	0.03	0.33	0.10	0.40	3.86
48		**4**	0.18	0.00	0.02	0.00	0.03	0.01	0.02	0.27
49		**5**	0.25	0.00	0.01	0.01	0.03	0.01	0.03	0.33
av			0.41	0.00	0.03	0.01	0.07	0.02	0.06	0.59
50	**HG2**	**1**	0.11	4.39	0.00	0.00	7.03	0.10	0.42	12.05
51		**2**	0.11	0.08	0.02	0.00	0.16	0.07	0.15	0.59
52		**3**	0.15	0.15	0.01	0.00	0.25	0.02	0.03	0.61
53		**4**	0.02	0.04	0.01	0.00	0.07	0.01	0.01	0.15
54		**5**	0.06	0.07	0.01	0.00	0.13	0.02	0.02	0.30
av			0.04	0.13	0.01	0.00	0.22	0.02	0.03	0.44
55	**HG3**	**1**	12.38	0.08	0.16	0.10	0.93	0.60	1.72	15.81
56		**2**	13.46	0.06	0.24	0.10	1.13	1.08	1.72	17.79
57		**3**	0.48	0.00	0.01	0.00	0.05	0.02	0.05	0.60
58		**4**	0.21	0.00	0.00	0.00	0.05	0.01	0.03	0.30
59		**5**	0.47	0.01	0.01	0.00	0.05	0.02	0.08	0.64
av			0.51	0.00	0.01	0.00	0.06	0.03	0.07	0.69

JANUARY 2003

No	R	D	Ca	Na	Mg	K	Cl	NO_3	SO_4	total
1	HG3	1	11.50	0.40	0.27	0.17	3.88	6.59	23.77	46.57
2		2	4.17	0.17	0.18	0.13	0.67	0.68	6.12	12.11
3		3	4.01	0.08	0.15	0.09	0.73	0.32	3.74	9.12
4		4	3.24	0.13	0.11	0.15	3.38	0.34	1.16	8.52
av			4.52	0.15	0.16	0.12	1.79	1.01	5.53	13.29
5	HG2	1	12.91	2.04	0.81	0.74	7.29	1.99	10.36	36.13
6		2	7.66	2.93	0.87	0.39	6.82	2.33	2.48	23.49
7		3	3.60	2.42	0.55	0.36	5.10	1.70	0.71	14.43
8		4	6.98	4.86	0.72	0.42	9.80	2.69	1.29	26.76
av			6.03	2.91	0.68	0.41	6.51	2.04	2.16	20.74
9	HG1	1	2.15	0.05	0.35	0.15	0.31	0.06	5.06	8.12
10		2	1.61	0.01	0.21	0.04	0.17	0.00	0.49	2.53
11		3	1.35	0.00	0.11	0.07	0.17	0.94	0.23	2.87
av			1.60	0.01	0.19	0.07	0.19	0.41	1.20	3.68
12	HD3	1	11.63	0.15	0.22	0.30	0.50	2.70	0.29	15.79
13		2	4.86	0.00	0.09	0.02	0.01	0.28	0.00	5.26
14		3	1.44	0.00	0.04	0.02	0.13	0.02	0.08	1.72
15		4	1.26	0.00	0.04	0.03	0.09	0.01	0.00	1.43
16		5	1.86	0.00	0.05	0.02	0.16	0.01	0.05	2.14
av			2.10	0.00	0.05	0.03	0.11	0.09	0.04	2.43
17	HD2	1	7.68	0.00	0.26	0.04	1.23	0.06	0.27	9.53
18		2	1.44	0.35	0.12	0.02	0.94	0.05	0.49	3.41
19		3	1.44	0.39	0.16	0.03	0.93	0.01	0.01	2.97
20		4	2.35	0.23	0.27	0.01	1.38	0.04	0.13	4.41
av			1.92	0.34	0.17	0.02	1.01	0.03	0.19	3.68
21	HD1	1	1.46	0.13	0.10	0.04	0.60	1.06	0.79	4.18
22		2	4.81	0.09	0.20	0.07	0.91	0.16	0.66	6.91
23		3	2.30	0.19	0.12	0.04	0.67	0.02	2.57	5.90
av			2.49	0.15	0.13	0.05	0.69	0.40	1.60	5.51
24	MA3	1	0.57	0.11	0.06	0.02	0.89	0.18	1.56	3.38
25		2	0.29	0.13	0.04	0.02	0.71	0.52	0.00	1.70
26		3	1.97	0.91	0.16	0.09	1.82	1.16	0.74	6.84
av			1.20	0.52	0.10	0.05	1.31	0.77	0.69	4.66
27	MA2	1	0.47	0.10	0.02	0.02	0.15	0.11	0.38	1.24
28		2	0.43	0.19	0.02	0.03	0.25	0.09	0.24	1.25
29		3	0.55	0.21	0.03	0.05	0.20	0.02	0.12	1.17
av			0.49	0.17	0.02	0.04	0.20	0.06	0.23	1.21
30	MA1	1	0.84	0.41	0.06	0.05	0.56	0.22	0.67	2.81
31		2	0.31	0.32	0.03	0.03	0.44	0.28	0.30	1.70

32		3	0.75	0.10	0.02	0.03	0.23	0.10	0.03	1.26
av			0.48	0.31	0.03	0.03	0.43	0.24	0.34	1.86
33	MD3	1	0.57	0.42	0.03	0.03	0.89	0.17	1.78	3.89
34		2	1.35	0.70	0.06	0.04	1.26	0.17	3.90	7.49
35		3	0.63	1.37	0.20	0.12	3.30	0.77	0.12	6.51
av			0.78	1.14	0.15	0.10	2.65	0.59	1.10	6.50
36	MD2	1	8.57	0.35	0.32	0.16	1.54	0.05	77.43	88.42
37		2	1.84	0.22	0.15	0.04	0.49	0.13	10.77	13.64
av			2.33	0.22	0.17	0.05	0.57	0.13	15.63	19.09
38	MD1	1	2.23	0.36	4.09	0.07	1.49	0.55	19.66	28.45
39		2	6.42	0.04	1.48	0.09	2.39	0.59	3.90	14.91
40		3	3.37	0.00	0.80	0.08	1.47	0.66	1.34	7.71
av			3.21	0.23	2.96	0.08	1.65	0.58	13.16	21.87

MAY 2003

No	R-H	D	Ca	Na	Mg	K	Cl	NO_3	SO_4	total
1	MD3	1	6.59	34.54	0.41	0.00	53.32	19.21	0.33	114.40
2		2	4.01	3.38	0.38	0.03	5.91	10.16	0.49	24.36
3		3	2.51	8.11	0.36	0.07	15.64	5.18	0.57	32.44
4		4	1.91	1.59	0.35	0.08	3.96	3.67	0.15	11.71
5		5	1.28	2.06	0.40	0.17	5.28	3.59	0.18	12.95
av			2.24	5.01	0.38	0.10	9.58	5.41	0.28	22.99
6	MD2	1	5.21	0.01	0.20	0.04	0.24	8.21	12.18	26.08
7		2	19.74	0.44	0.34	0.03	0.86	6.19	26.40	54.00
8		3	14.50	0.42	0.27	0.05	0.64	4.86	16.41	37.14
9		4	2.35	0.33	0.13	0.03	0.56	3.49	3.47	10.36
10		5	1.96	0.23	0.11	0.03	0.39	4.16	2.13	9.01
av			8.66	0.30	0.21	0.04	0.55	5.14	11.65	26.54
11	MD1	1	7.67	1.28	0.93	0.07	2.34	27.69	6.32	46.29
12		2	2.39	1.50	0.61	0.09	4.91	9.03	2.03	20.55
13		3	2.06	1.56	0.59	0.08	7.60	16.95	1.20	30.04
14		4	2.17	1.34	0.50	0.09	2.38	6.71	0.50	13.69
av			2.62	1.46	0.60	0.08	5.04	13.00	1.61	24.42
15	MA3	1	10.38	0.05	0.66	0.06	0.26	19.81	7.13	38.35
16		2	6.72	0.04	0.42	0.03	0.14	23.02	1.34	31.70
17		3	2.75	0.07	0.15	0.00	0.21	7.50	0.76	11.44
18		4	1.35	0.14	0.10	0.03	0.37	4.85	0.23	7.05
19		5	2.01	0.05	0.07	0.01	0.18	3.04	0.11	5.46
av			2.65	0.08	0.14	0.02	0.24	6.34	0.69	10.15
20	MA2	1	6.97	0.02	0.14	0.05	0.34	30.43	1.04	38.99

21		**2**	3.67	0.27	0.09	0.04	0.40	13.98	0.52	18.97
22		**3**	2.33	0.15	0.06	0.00	0.49	7.61	0.39	11.03
23		**4**	1.02	0.13	0.03	0.01	0.25	3.01	0.24	4.70
24		**5**	2.73	0.43	0.09	0.02	1.08	8.41	0.24	13.00
av			2.15	0.20	0.06	0.02	0.45	7.37	0.34	10.57
25	**MA1**	1	5.40	0.58	0.11	0.00	0.87	14.45	2.75	24.16
26		2	2.81	0.26	0.07	0.02	0.89	7.48	0.89	12.42
27		3	1.73	0.30	0.06	0.01	0.54	5.05	0.38	8.07
28		4	1.37	0.31	0.06	0.01	0.42	3.74	0.23	6.14
av			2.19	0.33	0.07	0.01	0.60	6.01	0.67	9.87
29	**HD3**	1	7.33	0.04	0.24	-0.05	0.74	0.63	1.03	9.96
30		2	3.09	0.13	0.13	0.02	0.79	0.00	0.16	4.33
31		3	1.12	0.12	0.06	0.01	0.33	0.00	0.18	1.82
32		4	1.06	0.05	0.04	0.01	0.14	0.00	0.03	1.32
av			1.63	0.09	0.07	0.01	0.33	0.03	0.16	2.31
33	**HD2**	1	2.81	4.57	0.13	0.04	6.45	0.00	0.82	14.83
34		2	1.24	1.11	0.08	0.01	1.70	0.00	0.44	4.57
35		3	1.64	0.57	0.10	0.02	1.13	0.01	0.40	3.87
av			1.69	1.63	0.10	0.02	2.46	0.00	0.50	6.40
36	**HD1**	1	2.01	0.37	0.13	0.01	0.49	0.00	0.54	3.54
37		2	3.28	0.00	0.07	0.00	0.15	0.00	0.46	3.96
38		3	1.15	0.24	0.08	0.03	0.44	0.00	0.27	2.22
av			1.77	0.26	0.10	0.02	0.42	0.00	0.40	2.96
39	**HG3**	1	6.86	0.05	0.17	0.00	0.46	26.00	7.78	41.33
40		2	3.89	0.05	0.12	0.04	0.27	18.36	2.44	25.16
41		3	1.91	0.15	0.06	0.03	0.20	8.56	0.95	11.85
42		4	2.28	0.03	0.04	0.02	0.22	6.26	0.45	9.31
av			2.90	0.07	0.07	0.02	0.24	10.94	1.69	15.94
43	**HG2**	1	5.83	2.62	0.41	0.03	3.98	18.58	2.24	33.69
44		2	7.82	2.15	0.34	0.08	3.09	22.87	1.39	37.73
45		3	1.65	1.11	0.21	0.03	1.69	4.42	0.46	9.58
46		4	1.55	1.10	0.17	0.03	3.29	6.79	0.72	13.64
47		5	2.24	0.79	0.14	0.03	1.30	7.60	0.35	12.44
av			2.56	1.23	0.21	0.03	2.31	8.30	0.71	15.35
48	**HG1**	1	4.30	1.50	0.94	0.06	3.94	17.56	3.99	32.30
49		2	3.65	2.16	0.94	0.07	4.27	16.63	1.37	29.09
50		3	1.95	1.87	0.65	0.09	3.49	6.81	1.12	15.99
51		4	1.80	1.78	0.43	0.09	2.99	6.83	0.39	14.31
av			2.48	1.83	0.65	0.09	3.49	9.80	1.30	19.64

Supplementary samples. % weight of sample								
	Ca	Na	Mg	K	Cl	NO_3	SO_4	total
HGcs	0.52	0.35	0.09	0.03	0.34	1.46	1.58	4.38
HGmosM	0.47	4.41	0.33	0.35	6.85	1.01	1.80	15.22
HGcon1	0.35	1.23	0.08	0.06	0.71	0.16	0.27	2.87
HGcon2	1.01	0.51	0.03	0.08	0.52	0.15	1.54	3.84
HGmos	3.34	2.98	0.33	0.43	2.94	0.93	5.38	16.34
HDcon	0.37	0.17	0.09	0.04	0.12	0.01	0.06	0.86
HDgr	0.45	0.12	0.05	0.06	0.04	0.01	0.05	0.79
MAcon1	1.26	0.24	0.02	0.05	0.17	0.12	0.98	2.84
MAgr	1.39	0.33	0.10	0.07	0.73	0.57	0.44	3.62
MAcon2	2.58	0.80	0.10	0.05	1.18	0.60	3.98	9.28
MDmos	1.93	0.23	0.05	0.10	0.41	0.07	2.22	5.01
MDgr	5.23	1.66	0.29	0.12	1.94	0.61	5.98	15.84
MDcs	0.01	0.07	0.00	0.00	0.21	0.00	0.00	0.30

V.C Molar concentrations (mM)

NOVEMBER 2001

No	R-H	D	Ca	Na	Mg	K	Cl	NO_3	SO_4	sum+	sum-	BAL
1	MD1	4	0.54	0.24	0.01	0.03	0.17	0.02	0.36	1.37	0.92	1.49
2		3	0.32	0.25	0.01	0.03	0.18	0.01	0.28	0.94	0.75	1.24
3		2	0.21	0.24	0.01	0.02	0.13	0.02	0.18	0.70	0.51	1.38
4		1	0.61	0.27	0.03	0.02	0.18	0.02	0.61	1.57	1.41	1.11
sum			1.69	0.99	0.05	0.10	0.65	0.06	1.44	4.57	3.59	1.27
5	MD2	1	0.33	0.28	0.06	0.03	0.29	0.03	0.27	1.08	0.87	1.24
6		2	0.29	0.21	0.01	0.02	0.13	0.01	0.30	0.83	0.74	1.12
7		3	0.18	0.27	0.01	0.03	0.15	0.01	0.19	0.68	0.53	1.27
sum			0.79	0.75	0.08	0.08	0.56	0.06	0.76	2.59	2.14	1.21
8	MD3	1	0.06	0.34	0.01	0.06	0.26	0.01	0.04	0.54	0.36	1.51
9		2	0.28	0.31	0.04	0.04	0.34	0.02	0.08	1.00	0.52	1.93
10		3	0.08	0.27	0.02	0.03	0.29	0.00	0.02	0.50	0.33	1.53
11		4	0.09	0.24	0.02	0.01	0.25	0.02	0.02	0.49	0.31	1.60
sum			0.51	1.17	0.10	0.15	1.14	0.05	0.16	2.53	1.51	1.68
12	MA3	1	0.35	0.28	0.05	0.03	0.28	0.00	0.06	1.13	0.41	2.78
13		2	0.47	0.89	0.19	0.09	0.92	0.30	0.08	2.30	1.37	1.68
14		3	0.45	0.62	0.13	0.05	0.63	0.00	0.04	1.82	0.71	2.57
sum			1.27	1.79	0.37	0.16	1.84	0.30	0.18	5.25	2.49	2.11

28	HD3	**1**	0.05	0.34	0.00	0.05	0.22	0.03	0.04	0.50	0.32	1.57
29		**6**	0.26	0.20	0.01	0.01	0.12	0.02	0.03	0.75	0.19	3.92
30		**5**	0.08	0.25	0.00	0.02	0.19	0.10	0.04	0.44	0.36	1.20
31		**4**	0.05	0.13	0.00	0.01	0.07	0.02	0.02	0.25	0.12	2.00
32		**3**	0.04	0.20	0.00	0.01	0.11	0.02	0.03	0.29	0.19	1.55
33		**2**	0.07	0.25	0.00	0.01	0.12	0.02	0.04	0.42	0.21	1.93
sum			0.55	1.36	0.03	0.11	0.82	0.20	0.19	2.64	1.40	1.89
34	HD1	**1**	0.03	0.18	0.00	0.01	0.11	0.02	0.03	0.25	0.19	1.34
35		**2**	0.04	0.22	0.01	0.01	0.12	0.02	0.03	0.33	0.20	1.65
36		**3**	0.04	0.16	0.00	0.00	0.08	0.02	0.03	0.25	0.14	1.73
37		**4**	0.09	0.19	0.01	0.01	0.20	0.04	0.03	0.40	0.31	1.30
38		**5**	0.15	0.38	0.03	0.01	0.36	0.03	0.05	0.75	0.49	1.53
sum			0.36	1.12	0.05	0.04	0.87	0.12	0.17	1.98	1.33	1.49
39	HG3	**1**	0.04	0.16	0.00	0.00	0.08	0.02	0.03	0.25	0.15	1.65
40		**2**	0.03	0.19	0.00	0.00	0.09	0.02	0.03	0.27	0.18	1.49
41		**3**	0.11	0.20	0.01	0.01	0.09	0.02	0.03	0.45	0.18	2.46
42		**4**	0.17	0.31	0.01	0.04	0.20	0.02	0.04	0.72	0.30	2.40
43		**5**	0.15	0.20	0.00	0.01	0.12	0.02	0.03	0.51	0.20	2.51
sum			0.51	1.07	0.03	0.06	0.58	0.11	0.16	2.19	1.01	2.16
44	HG1	**1**	0.04	0.29	0.00	0.00	0.07	0.02	0.06	0.37	0.20	1.81
45		**2**	0.25	0.14	0.00	0.00	0.09	0.02	0.26	0.65	0.62	1.04
sum			0.28	0.43	0.01	0.01	0.16	0.03	0.32	1.02	0.83	1.23

MARCH 2002

No	RH	D	Ca	Na	Mg	K	Cl	NO$_3$	SO$_4$	sum+	sum-	ratio
4	HD3	1	0.02	0.05	0.00	0.02	0.09	0.01	0.02	0.12	0.17	0.71
5		2	0.21	0.03	0.00	0.01	0.03	0.01	0.01	0.46	0.08	5.77
6		3	0.27	0.08	0.01	0.03	0.12	0.01	0.02	0.65	0.19	3.53
7		4	0.27	0.05	0.01	0.02	0.08	0.01	0.03	0.63	0.16	3.91
8		5	0.41	0.07	0.01	0.03	0.09	0.01	0.06	0.94	0.24	3.88
sum			1.18	0.28	0.02	0.11	0.41	0.07	0.15	2.81	0.84	3.34
9	HD1	1	0.13	0.08	0.01	0.02	0.17	0.02	0.03	0.38	0.27	1.41
10		2	0.15	0.08	0.01	0.02	0.12	0.02	0.02	0.41	0.21	1.99
11		3	0.14	0.13	0.01	0.05	0.17	0.03	0.03	0.47	0.29	1.62
sum			0.41	0.30	0.02	0.10	0.47	0.07	0.09	1.26	0.77	1.64
16	HG3	1	0.11	0.26	0.00	0.03	0.11	0.04	0.04	0.52	0.26	2.05
17		2	0.20	0.25	0.01	0.03	0.12	0.02	0.02	0.70	0.21	3.41
18		3	0.36	0.26	0.01	0.03	0.13	0.03	0.03	1.02	0.24	4.25
19		4	0.33	0.32	0.01	0.04	0.17	0.03	0.03	1.03	0.28	3.62

sum			1.00	1.10	0.02	0.12	0.52	0.11	0.12	3.28	0.99	3.32
13	**HG1**	1	0.17	0.08	0.01	0.03	0.11	0.03	0.10	0.46	0.37	1.27
14		2	0.38	0.28	0.01	0.04	0.13	0.04	0.09	1.10	0.38	2.91
15		3	0.30	0.40	0.01	0.05	0.22	0.03	0.04	1.06	0.38	2.78
sum			0.85	0.76	0.03	0.12	0.47	0.10	0.23	2.62	1.13	2.33
12	**MA3**	1	0.35	0.44	0.03	0.03	0.22	0.06	0.05	1.22	0.43	2.87
1		2	0.31	0.69	0.18	0.06	0.82	0.22	0.11	1.74	1.47	1.18
2		3	0.29	0.52	0.13	0.05	0.60	0.16	0.11	1.41	1.13	1.25
3		4	0.35	0.91	0.14	0.08	1.03	0.00	0.03	1.97	1.10	1.79
sum			1.29	2.56	0.49	0.23	2.67	0.44	0.29	6.34	4.13	1.54

AUGUST 2002

No	R	D	Ca	Na	Mg	K	Cl	NO_3	SO_4	sum+	sum-	ratio
1	**MD1**	1	0.07	0.03	0.01	0.02	0.07	0.13	0.03	0.22	0.25	0.89
2		2	0.23	0.04	0.03	0.01	0.07	0.02	0.02	0.57	0.13	4.27
3		3	0.38	0.06	0.05	0.03	0.09	0.01	0.04	0.93	0.17	5.48
4		4	0.36	0.01	0.04	0.00	0.02	0.01	0.02	0.81	0.06	12.46
5		5	0.34	0.01	0.03	0.01	0.04	0.01	0.02	0.78	0.09	8.41
sum			1.38	0.15	0.16	0.07	0.29	0.16	0.12	3.30	0.71	4.67
6	**MD2**	1	0.32	0.01	0.02	0.00	0.03	0.01	0.25	0.69	0.53	1.30
7		2	0.35	0.01	0.01	0.00	0.04	0.01	0.10	0.73	0.25	2.97
8		3	0.46	0.01	0.02	0.00	0.04	0.01	0.14	0.97	0.33	2.92
9		4	0.37	0.01	0.01	0.00	0.04	0.01	0.07	0.78	0.18	4.42
10		5	0.33	0.01	0.01	0.00	0.04	0.01	0.02	0.70	0.09	7.47
sum			1.83	0.05	0.08	0.01	0.19	0.04	0.57	3.87	1.38	2.81
11	**MD3**	1	0.01	0.17	0.00	0.01	0.18	0.02	0.02	0.21	0.23	0.89
12		2	0.09	0.37	0.01	0.00	0.37	0.01	0.02	0.56	0.42	1.33
13		3	0.30	0.18	0.02	0.00	0.24	0.02	0.02	0.84	0.29	2.88
14		4	0.29	0.02	0.02	0.00	0.10	0.01	0.02	0.64	0.14	4.62
15		5	0.36	0.06	0.05	0.01	0.19	0.01	0.02	0.88	0.24	3.71
sum			1.05	0.80	0.10	0.01	1.07	0.07	0.09	3.12	1.32	2.37
16	**MA1**	1	0.31	0.06	0.01	0.03	0.11	0.01	0.04	0.72	0.20	3.60
17		2	0.33	0.03	0.01	0.01	0.07	0.03	0.04	0.72	0.18	3.91
18		3	0.34	0.11	0.02	0.02	0.12	0.03	0.07	0.86	0.29	3.01
19		4	0.28	0.04	0.01	0.01	0.08	0.02	0.03	0.64	0.16	3.92
20		5	0.50	0.11	0.02	0.02	0.14	0.04	0.05	1.19	0.29	4.04
sum			1.77	0.35	0.08	0.09	0.52	0.13	0.24	4.13	1.13	3.66
21	**MA2**	1	0.06	0.01	0.00	0.00	0.03	0.06	0.02	0.14	0.12	1.12
22		2	0.26	0.01	0.01	0.00	0.05	0.01	0.02	0.56	0.09	6.01
23		3	0.38	0.01	0.01	0.00	0.03	0.01	0.02	0.79	0.07	11.56
24		4	0.53	0.01	0.02	0.00	0.04	0.01	0.02	1.10	0.08	14.66
25		5	0.42	0.02	0.01	0.01	0.07	0.02	0.02	0.91	0.12	7.41

26		6	0.37	0.01	0.01	0.01	0.05	0.01	0.02	0.78	0.10	7.74
sum			2.03	0.06	0.07	0.01	0.26	0.11	0.11	4.27	0.58	7.32
27	**MA3**	1	0.28	0.02	0.01	0.01	0.08	0.02	0.03	0.61	0.15	4.04
28		2	0.39	0.04	0.03	0.00	0.10	0.05	0.05	0.88	0.24	3.59
29		3	0.33	0.03	0.03	0.00	0.07	0.03	0.03	0.75	0.16	4.64
30		4	0.26	0.03	0.04	0.01	0.09	0.05	0.02	0.65	0.18	3.63
31		5	0.31	0.05	0.04	0.01	0.10	0.11	0.03	0.77	0.27	2.90
sum			1.57	0.18	0.16	0.03	0.44	0.25	0.16	3.65	1.00	3.65
32	**HD1**	1	0.34	0.01	0.01	0.00	0.06	0.01	0.02	0.73	0.11	6.72
33		2	0.36	0.02	0.02	0.00	0.06	0.01	0.03	0.77	0.13	5.80
34		3	0.38	0.10	0.04	0.02	0.12	0.01	0.03	0.95	0.18	5.24
sum			1.08	0.13	0.07	0.03	0.24	0.02	0.08	2.44	0.42	5.79
35	**HD2**	1	0.31	0.03	0.02	0.00	0.19	0.00	0.03	0.69	0.24	2.89
36		2	0.33	0.07	0.02	0.00	0.12	0.01	0.02	0.76	0.16	4.66
37		3	0.32	0.09	0.02	0.00	0.19	0.01	0.02	0.77	0.24	3.24
38		4	0.29	0.06	0.02	0.01	0.17	0.01	0.02	0.68	0.21	3.20
39		5	0.36	0.05	0.02	0.01	0.11	0.01	0.02	0.82	0.16	5.26
sum			1.61	0.30	0.09	0.02	0.79	0.03	0.10	3.72	1.01	3.69
40	**HD3**	1	0.21	0.00	0.00	0.00	0.04	0.01	0.02	0.43	0.08	5.10
41		2	0.33	0.01	0.01	0.00	0.07	0.04	0.02	0.68	0.15	4.68
42		3	0.40	0.01	0.01	0.00	0.21	0.02	0.02	0.82	0.26	3.15
43		4	0.41	0.01	0.01	0.00	0.05	0.01	0.02	0.86	0.10	8.37
44		5	0.42	0.01	0.01	0.01	0.06	0.01	0.02	0.88	0.10	8.79
sum			1.77	0.04	0.04	0.00	0.42	0.08	0.10	3.68	0.69	5.30
45	**HG1**	1	0.11	0.00	0.02	0.00	0.04	0.01	0.02	0.25	0.09	2.73
46		2	0.32	0.00	0.03	0.00	0.08	0.02	0.02	0.69	0.14	4.87
47		3	0.35	0.01	0.04	0.00	0.05	0.01	0.02	0.78	0.10	8.03
48		4	0.39	0.01	0.07	0.01	0.07	0.01	0.02	0.93	0.12	7.92
49		5	0.37	0.01	0.02	0.01	0.04	0.01	0.02	0.81	0.08	9.77
sum			1.53	0.03	0.17	0.02	0.29	0.05	0.10	3.45	0.53	6.52
50	**HG2**	1	0.10	7.44	0.00	0.00	7.73	0.06	0.17	7.66	8.13	0.94
51		2	0.41	0.50	0.10	0.02	0.67	0.15	0.23	1.55	1.28	1.21
52		3	0.43	0.78	0.06	0.01	0.84	0.03	0.04	1.76	0.96	1.84
53		4	0.59	2.40	0.35	0.07	3.24	0.21	0.13	4.35	3.72	1.17
54		5	0.49	1.04	0.17	0.04	1.32	0.09	0.06	2.40	1.53	1.57
sum			2.03	12.16	0.68	0.13	13.79	0.55	0.63	17.72	15.61	1.14
55	**HG3**	1	0.31	0.00	0.01	0.00	0.03	0.01	0.02	0.62	0.07	8.72
56		2	0.34	0.00	0.01	0.00	0.03	0.02	0.02	0.69	0.09	8.13
57		3	0.38	0.00	0.01	0.00	0.04	0.01	0.02	0.79	0.08	9.29
58		4	0.39	0.01	0.01	0.00	0.10	0.01	0.02	0.81	0.15	5.26
59		5	0.36	0.01	0.01	0.00	0.05	0.01	0.03	0.75	0.11	6.63
sum			1.78	0.02	0.04	0.01	0.25	0.06	0.10	3.66	0.51	7.20

JANUARY 2003

No	R	D	Ca	Na	Mg	K	Cl	NO_3	SO_4	sum+	sum-	ratio
1	HG3	1	0.09	0.01	0.00	0.00	0.03	0.03	0.07	0.19	0.21	0.87
2		2	0.10	0.01	0.01	0.00	0.02	0.01	0.06	0.22	0.15	1.48
3		3	0.10	0.00	0.01	0.00	0.02	0.01	0.04	0.22	0.11	2.10
4		4	0.08	0.01	0.00	0.00	0.09	0.01	0.01	0.17	0.12	1.45
sum			0.36	0.02	0.02	0.01	0.16	0.05	0.19	0.80	0.59	1.36
5	HG2	1	0.09	0.03	0.01	0.01	0.06	0.01	0.03	0.23	0.13	1.81
6		2	0.14	0.09	0.03	0.01	0.14	0.03	0.02	0.42	0.20	2.10
7		3	0.13	0.16	0.03	0.01	0.21	0.04	0.01	0.50	0.28	1.82
8		4	0.09	0.11	0.01	0.01	0.14	0.02	0.01	0.31	0.17	1.82
sum			0.45	0.38	0.08	0.03	0.55	0.10	0.07	1.47	0.78	1.89
9	HG1	1	0.06	0.00	0.02	0.00	0.01	0.00	0.06	0.17	0.13	1.23
10		2	0.10	0.00	0.02	0.00	0.01	0.00	0.01	0.26	0.04	6.58
11		3	0.09	0.00	0.01	0.00	0.01	0.04	0.01	0.21	0.07	3.17
sum			0.26	0.00	0.05	0.01	0.04	0.04	0.08	0.64	0.24	2.65
12	HD3	1	0.04	0.00	0.00	0.00	0.00	0.01	0.00	0.08	0.01	9.60
13		2	0.15	0.00	0.00	0.00	0.00	0.01	0.00	0.32	0.01	52.06
14		3	0.12	0.00	0.01	0.00	0.01	0.00	0.00	0.25	0.02	13.65
15		4	0.08	0.00	0.00	0.00	0.01	0.00	0.00	0.17	0.01	24.60
16		5	0.08	0.00	0.00	0.00	0.01	0.00	0.00	0.18	0.01	17.58
sum			0.47	0.00	0.02	0.01	0.03	0.01	0.00	1.00	0.05	19.95
17	HD2	1	0.10	0.00	0.01	0.00	0.02	0.00	0.00	0.20	0.02	9.87
18		2	0.10	0.04	0.01	0.00	0.07	0.00	0.01	0.28	0.11	2.60
19		3	0.16	0.07	0.03	0.00	0.11	0.00	0.00	0.44	0.12	3.85
20		4	0.07	0.01	0.01	0.00	0.05	0.00	0.00	0.19	0.05	3.56
sum			0.43	0.13	0.06	0.01	0.25	0.00	0.02	1.11	0.29	3.77
21	HD1	1	0.09	0.01	0.01	0.00	0.04	0.04	0.02	0.21	0.12	1.74
22		2	0.16	0.01	0.01	0.00	0.03	0.00	0.01	0.35	0.06	6.26
23		3	0.19	0.03	0.02	0.00	0.06	0.00	0.09	0.44	0.24	1.84
sum			0.44	0.05	0.04	0.01	0.14	0.05	0.12	1.00	0.42	2.40
24	MA3	1	0.02	0.01	0.00	0.00	0.04	0.00	0.02	0.06	0.09	0.64
25		2	0.02	0.01	0.00	0.00	0.04	0.02	0.00	0.05	0.06	0.83
26		3	0.18	0.15	0.02	0.01	0.19	0.07	0.03	0.57	0.32	1.80
sum			0.22	0.17	0.03	0.01	0.27	0.09	0.05	0.68	0.47	1.45
27	MA2	1	0.08	0.03	0.01	0.00	0.03	0.01	0.03	0.22	0.10	2.13
28		2	0.09	0.07	0.01	0.01	0.06	0.01	0.02	0.27	0.11	2.39
29		3	0.16	0.11	0.01	0.01	0.07	0.00	0.02	0.47	0.10	4.71
sum			0.34	0.21	0.03	0.02	0.16	0.03	0.06	0.95	0.31	3.04
30	MA1	1	0.19	0.16	0.02	0.01	0.15	0.03	0.06	0.60	0.31	1.96
31		2	0.23	0.41	0.03	0.02	0.37	0.13	0.09	0.97	0.68	1.42
32		3	0.11	0.03	0.01	0.00	0.04	0.01	0.00	0.27	0.05	5.08
sum			0.53	0.60	0.06	0.04	0.55	0.18	0.16	1.83	1.04	1.76
33	MD3	1	0.04	0.05	0.00	0.00	0.07	0.01	0.05	0.14	0.18	0.76
34		2	0.24	0.22	0.02	0.01	0.25	0.02	0.29	0.74	0.85	0.87

35		**3**	0.35	1.34	0.19	0.07	2.09	0.28	0.03	2.49	2.43	1.02
sum			0.63	1.61	0.21	0.08	2.42	0.31	0.37	3.36	3.46	0.97
36	**MD2**	**1**	0.31	0.02	0.02	0.01	0.06	0.00	1.16	0.68	2.38	0.29
37		**2**	0.84	0.17	0.12	0.02	0.25	0.04	2.05	2.10	4.40	0.48
sum			1.15	0.19	0.14	0.02	0.32	0.04	3.21	2.78	6.78	0.41
38	**MD1**	**1**	0.18	0.05	0.54	0.01	0.13	0.03	0.65	1.48	1.47	1.01
39		**2**	0.15	0.00	0.06	0.00	0.06	0.01	0.04	0.42	0.15	2.83
40		**3**	0.09	0.00	0.03	0.00	0.04	0.01	0.01	0.24	0.08	2.95
sum			0.41	0.05	0.63	0.01	0.24	0.05	0.70	2.14	1.70	1.26

MAY 2003

No	**R**	**D**	**Ca**	**Na**	**Mg**	**K**	**Cl**	**NO_3**	**SO_4**	**sum+**	**sum-**	**ratio**
1	**MD3**	**1**	0.20	1.79	0.02	0.00	1.79	0.37	0.00	2.22	2.16	1.02
2		**2**	0.19	0.27	0.03	0.00	0.31	0.30	0.01	0.70	0.63	1.11
3		**3**	0.22	1.24	0.05	0.01	1.55	0.29	0.02	1.79	1.89	0.95
4		**4**	0.28	0.40	0.09	0.01	0.65	0.35	0.01	1.14	1.02	1.12
5		**5**	0.25	0.70	0.13	0.03	1.17	0.45	0.01	1.49	1.65	0.91
sum			1.13	4.41	0.32	0.05	5.47	1.77	0.06	7.35	7.35	1.00
6	**MD2**	**1**	0.33	0.00	0.02	0.00	0.02	0.34	0.32	0.71	1.01	0.71
7		**2**	1.54	0.06	0.04	0.00	0.08	0.31	0.86	3.24	2.11	1.53
8		**3**	1.45	0.07	0.04	0.01	0.07	0.31	0.68	3.06	1.75	1.75
9		**4**	0.24	0.06	0.02	0.00	0.06	0.23	0.15	0.58	0.58	0.99
10		**5**	0.17	0.03	0.02	0.00	0.04	0.24	0.08	0.42	0.43	0.96
sum			3.73	0.23	0.15	0.02	0.27	1.43	2.09	8.00	5.88	1.36
11	**MD1**	**1**	0.14	0.04	0.03	0.00	0.05	0.33	0.05	0.39	0.48	0.80
12		**2**	0.13	0.14	0.06	0.01	0.31	0.32	0.05	0.53	0.72	0.73
13		**3**	0.19	0.25	0.09	0.01	0.79	1.00	0.05	0.81	1.88	0.43
14		**4**	0.14	0.15	0.06	0.01	0.18	0.29	0.01	0.56	0.49	1.13
sum			0.61	0.59	0.23	0.02	1.32	1.95	0.16	2.28	3.58	0.64
15	**MA3**	**1**	0.17	0.00	0.02	0.00	0.00	0.21	0.05	0.38	0.32	1.21
16		**2**	0.12	0.00	0.01	0.00	0.00	0.27	0.01	0.28	0.30	0.92
17		**3**	0.15	0.01	0.01	0.00	0.01	0.27	0.02	0.34	0.32	1.07
18		**4**	0.13	0.02	0.01	0.00	0.04	0.29	0.01	0.31	0.35	0.88
19		**5**	0.28	0.01	0.02	0.00	0.03	0.27	0.01	0.60	0.31	1.92
sum			0.85	0.04	0.07	0.01	0.09	1.32	0.09	1.90	1.59	1.19
20	**MA2**	**1**	0.10	0.00	0.00	0.00	0.01	0.27	0.01	0.20	0.29	0.69
21		**2**	0.14	0.02	0.01	0.00	0.02	0.35	0.01	0.31	0.38	0.82
22		**3**	0.14	0.02	0.01	0.00	0.03	0.30	0.01	0.31	0.35	0.88
23		**4**	0.15	0.03	0.01	0.00	0.04	0.29	0.01	0.35	0.36	0.99
24		**5**	0.14	0.04	0.01	0.00	0.06	0.27	0.00	0.32	0.34	0.95
sum			0.66	0.11	0.03	0.01	0.16	1.47	0.04	1.49	1.71	0.87

25	**MA1**	**1**	0.15	0.03	0.00	0.00	0.03	0.26	0.03	0.34	0.35	0.96
26		**2**	0.15	0.02	0.01	0.00	0.05	0.25	0.02	0.33	0.34	0.96
27		**3**	0.13	0.04	0.01	0.00	0.05	0.26	0.01	0.33	0.33	1.00
28		**4**	0.14	0.06	0.01	0.00	0.05	0.25	0.01	0.36	0.32	1.14
sum			0.57	0.15	0.03	0.00	0.18	1.02	0.07	1.35	1.34	1.01
29	**HD3**	**1**	0.15	0.00	0.01	0.00	0.02	0.01	0.01	0.31	0.04	7.37
30		**2**	0.15	0.01	0.01	0.00	0.04	0.00	0.00	0.32	0.05	6.64
31		**3**	0.19	0.04	0.02	0.00	0.06	0.00	0.01	0.46	0.09	5.09
32		**4**	0.17	0.01	0.01	0.00	0.02	0.00	0.00	0.38	0.03	13.18
sum			0.66	0.06	0.05	0.00	0.15	0.01	0.03	1.48	0.21	7.02
33	**HD2**	**1**	0.19	0.54	0.01	0.00	0.49	0.00	0.02	0.95	0.54	1.77
34		**2**	0.20	0.30	0.02	0.00	0.30	0.00	0.03	0.74	0.36	2.05
35		**3**	0.18	0.11	0.02	0.00	0.14	0.00	0.02	0.51	0.18	2.88
sum			0.56	0.95	0.05	0.01	0.93	0.00	0.07	2.19	1.07	2.05
36	**HD1**	**1**	0.20	0.06	0.02	0.00	0.05	0.00	0.02	0.50	0.10	5.08
37		**2**	0.12	0.00	0.00	0.00	0.01	0.00	0.01	0.25	0.02	12.23
38		**3**	0.14	0.05	0.02	0.00	0.06	0.00	0.01	0.38	0.09	4.20
sum			0.46	0.11	0.04	0.01	0.12	0.00	0.04	1.12	0.21	5.39
39	**HG3**	**1**	0.19	0.00	0.01	0.00	0.01	0.46	0.09	0.40	0.66	0.60
40		**2**	0.16	0.00	0.01	0.00	0.01	0.48	0.04	0.34	0.58	0.58
41		**3**	0.16	0.02	0.01	0.00	0.02	0.46	0.03	0.36	0.54	0.66
42		**4**	0.25	0.01	0.01	0.00	0.03	0.45	0.02	0.53	0.52	1.02
sum			0.76	0.03	0.03	0.01	0.07	1.85	0.18	1.62	2.29	0.71
43	**HG2**	**1**	0.18	0.14	0.02	0.00	0.14	0.37	0.03	0.54	0.56	0.96
44		**2**	0.23	0.11	0.02	0.00	0.10	0.44	0.02	0.61	0.57	1.06
45		**3**	0.22	0.26	0.05	0.00	0.26	0.39	0.03	0.82	0.70	1.16
46		**4**	0.16	0.20	0.03	0.00	0.38	0.45	0.03	0.57	0.89	0.64
47		**5**	0.20	0.12	0.02	0.00	0.13	0.44	0.01	0.57	0.60	0.95
sum			0.99	0.83	0.13	0.01	1.01	2.08	0.12	3.10	3.32	0.93
48	**HG1**	**1**	0.16	0.10	0.06	0.00	0.16	0.41	0.06	0.52	0.70	0.75
49		**2**	0.14	0.14	0.06	0.00	0.18	0.40	0.02	0.53	0.62	0.85
50		**3**	0.17	0.29	0.09	0.01	0.35	0.39	0.04	0.83	0.82	1.01
51		**4**	0.17	0.29	0.07	0.01	0.31	0.41	0.01	0.76	0.75	1.01
sum			0.63	0.81	0.27	0.02	1.00	1.61	0.14	2.64	2.88	0.91

V.D Charts

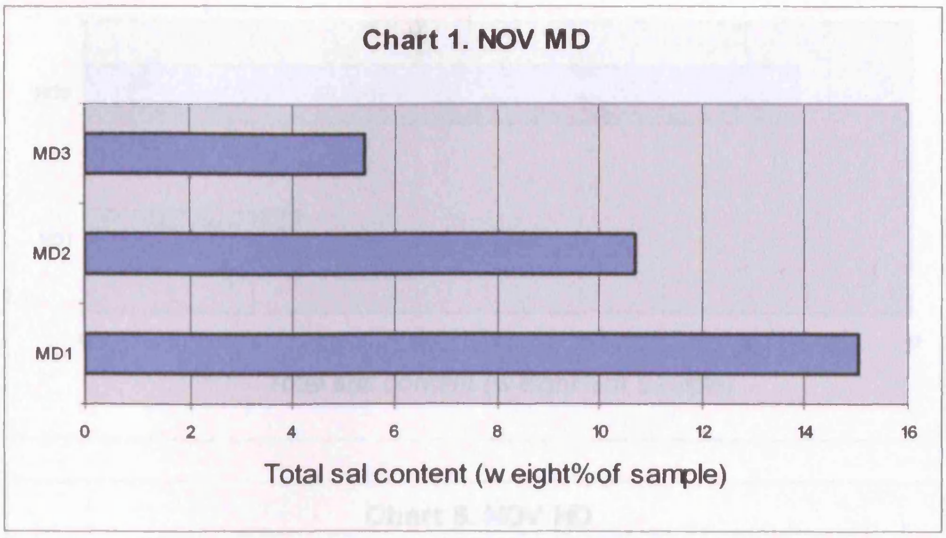


Chart 1. NOV MD
MD3
MD2
MD1
0
2
4
6
8
10
12
14
16
Total sal content (w eight%of sample)

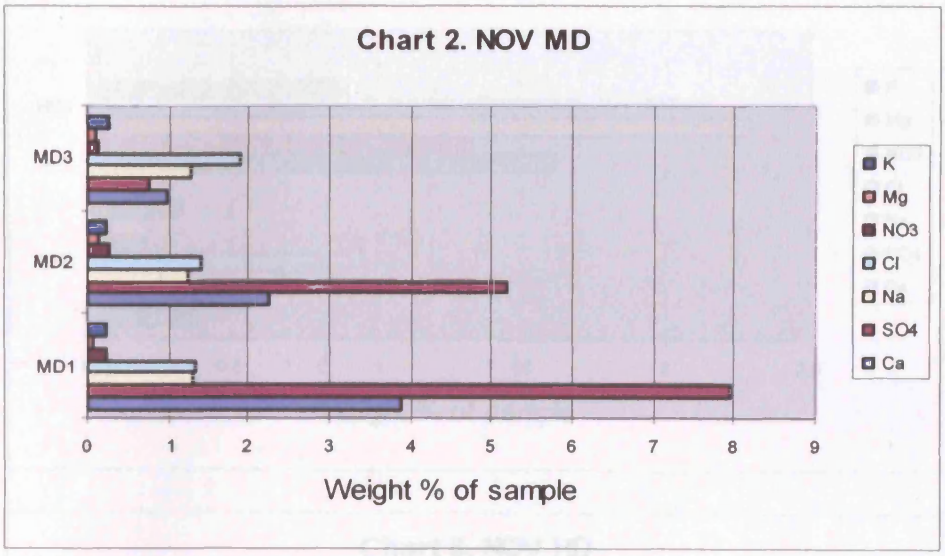


Chart 2. NOV MD
MD3
MD2
MD1
0
1
2
3
4
5
6
7
8
9
Weight % of sample
K
Mg
NO3
Cl
Na
SO4
Ca

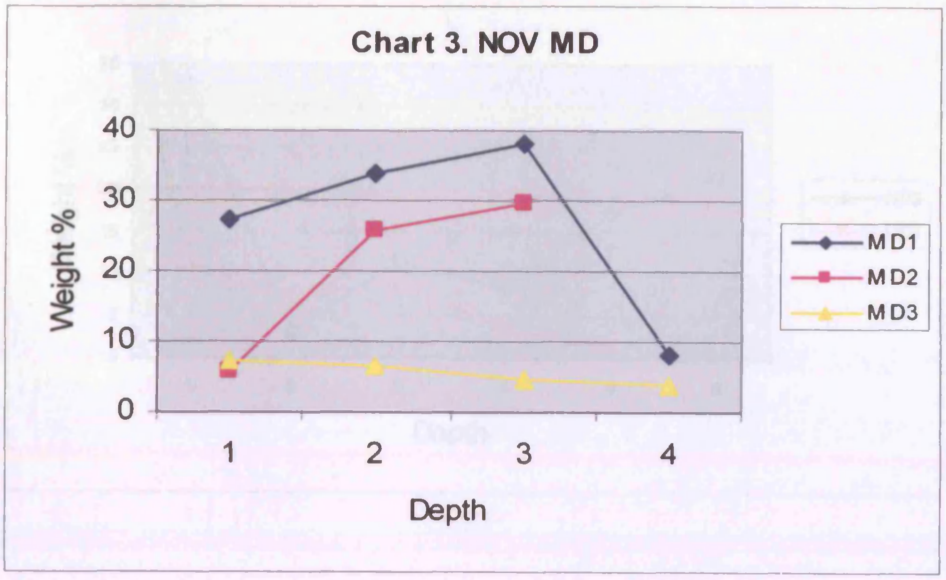


Chart 3. NOV MD
Weight %
40
30
20
10
0
1
2
3
4
Depth
MD1
MD2
MD3

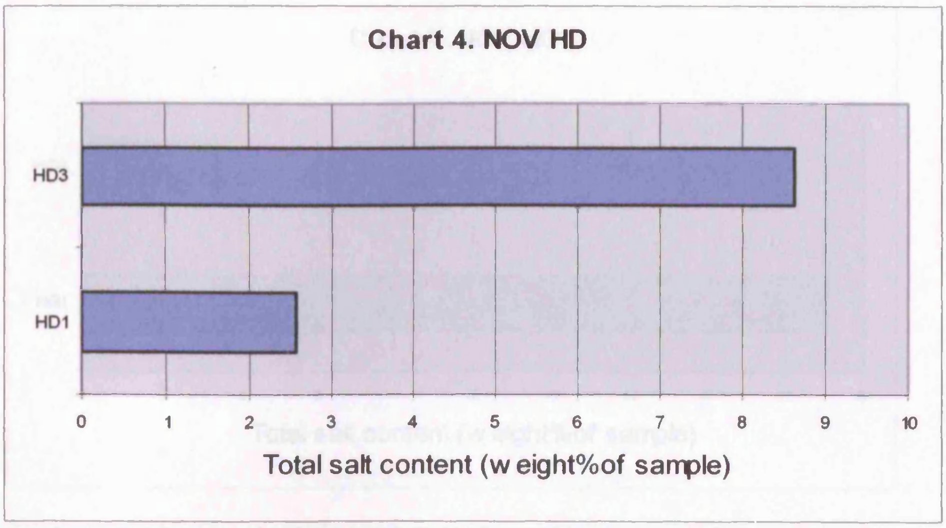


Chart 4. NOV HD
HD3
HD1
0
1
2
3
4
5
6
7
8
9
10
Total salt content (w eight%of sample)

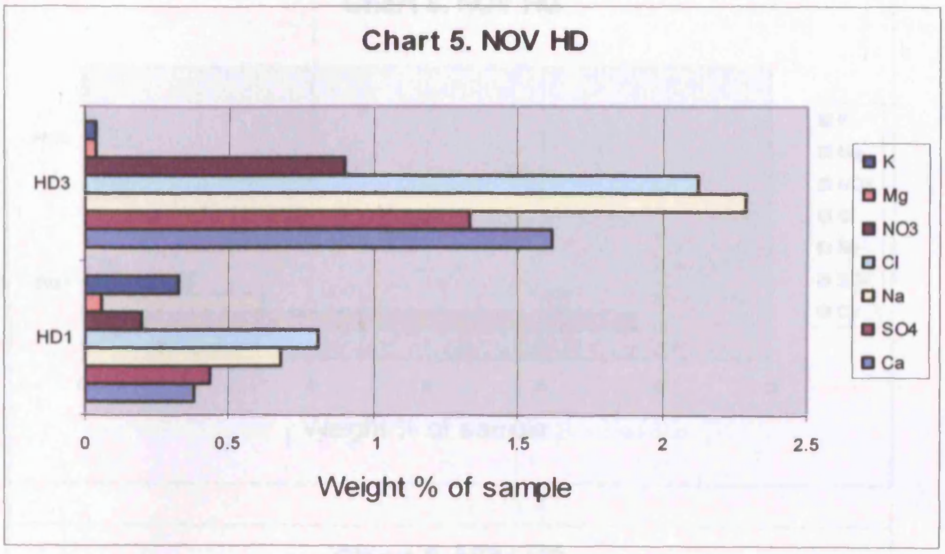


Chart 5. NOV HD
HD3
HD1
K
Mg
NO3
Cl
Na
SO4
Ca
0
0.5
1
1.5
2
2.5
Weight % of sample

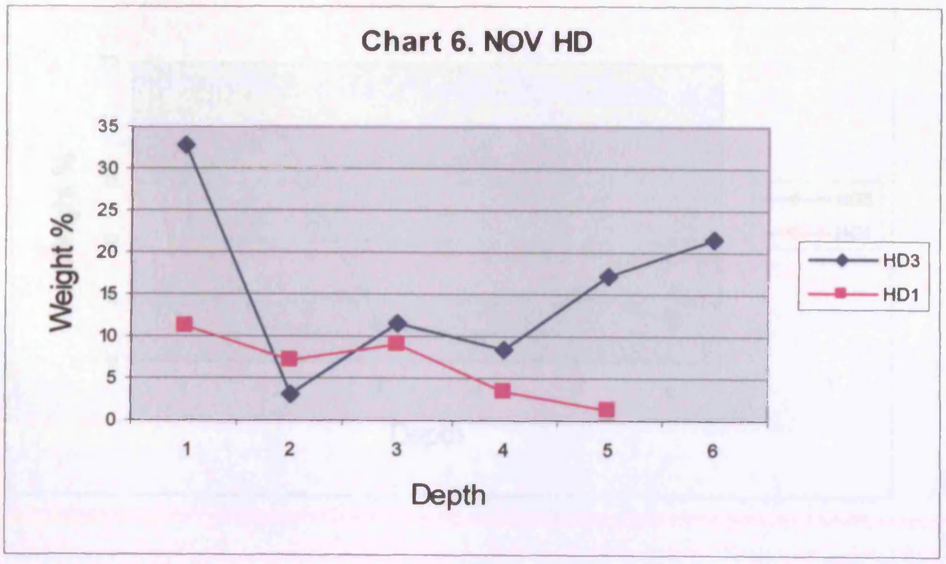


Chart 6. NOV HD
Weight %
35
30
25
20
15
10
5
0
1
2
3
4
5
6
Depth
HD3
HD1

Chart 7. NOV HG

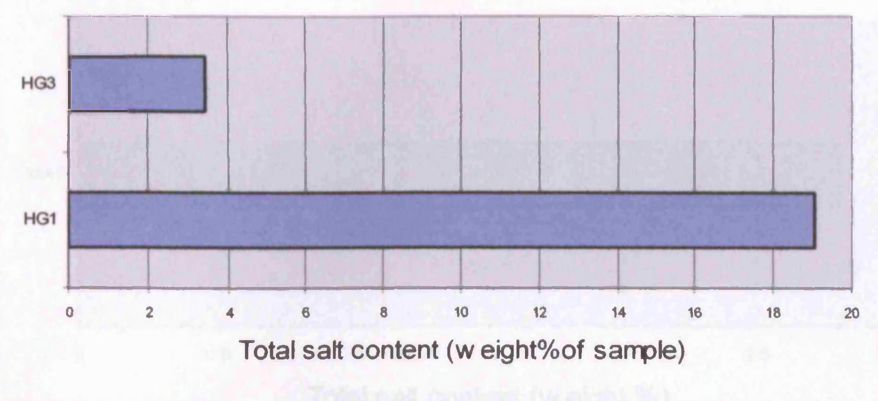


Chart 8. NOV HG

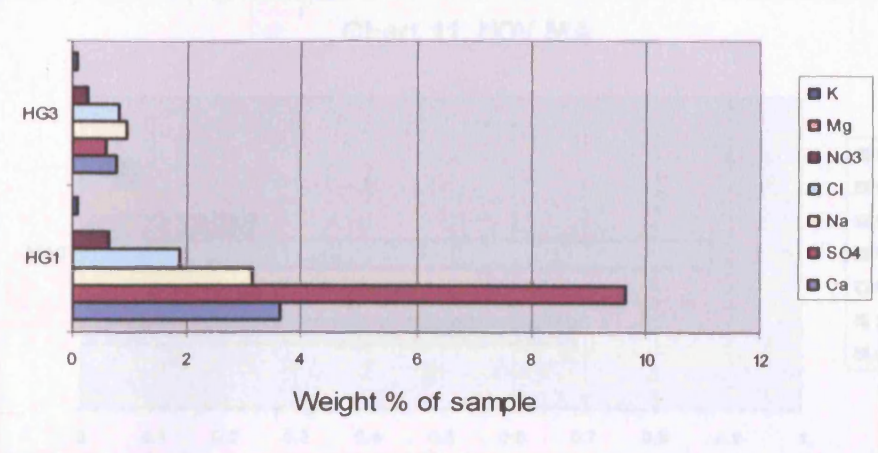
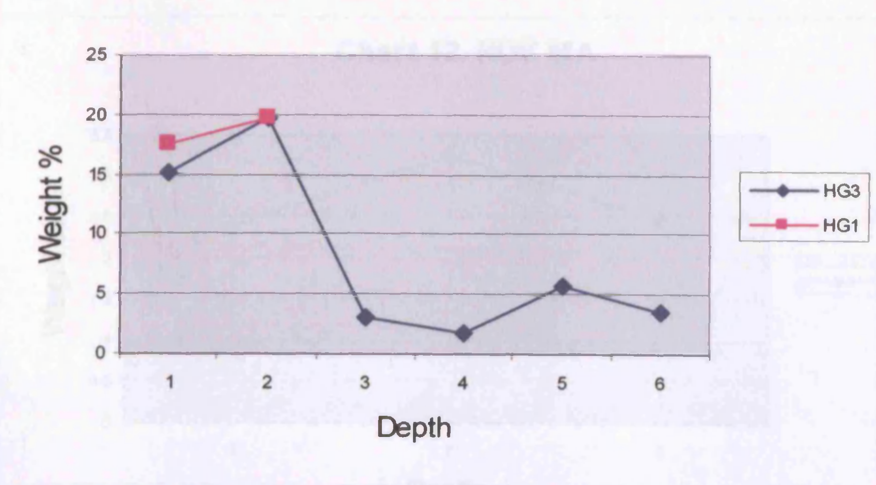


Chart 9. NOV HG



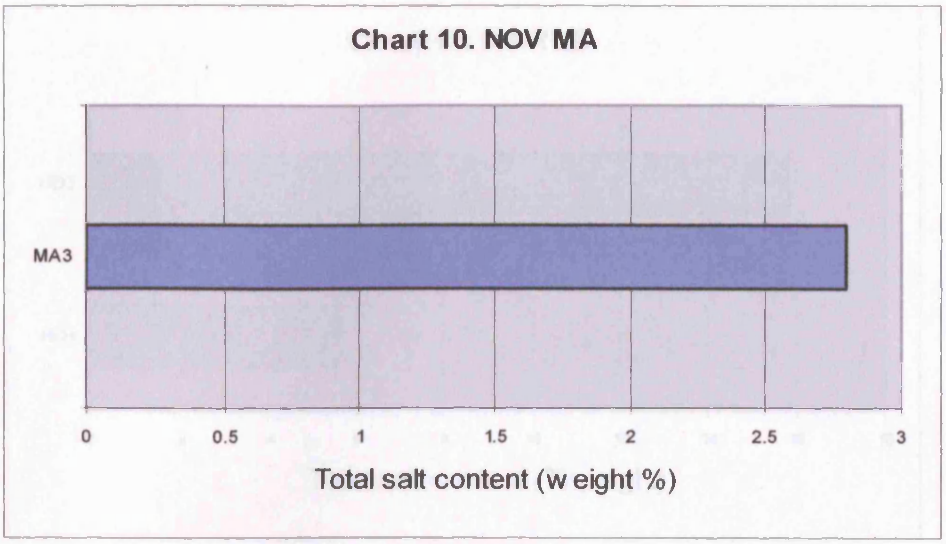


Chart 10. NOV MA
MA3
0
0.5
1
1.5
2
2.5
3
Total salt content (w eight %)

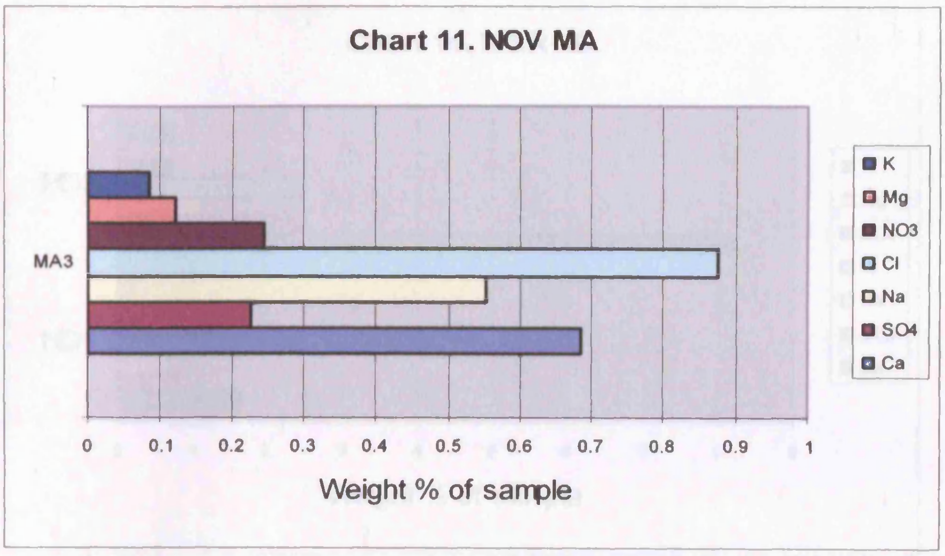


Chart 11. NOV MA
MA3
K
Mg
NO3
Cl
Na
SO4
Ca
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Weight % of sample

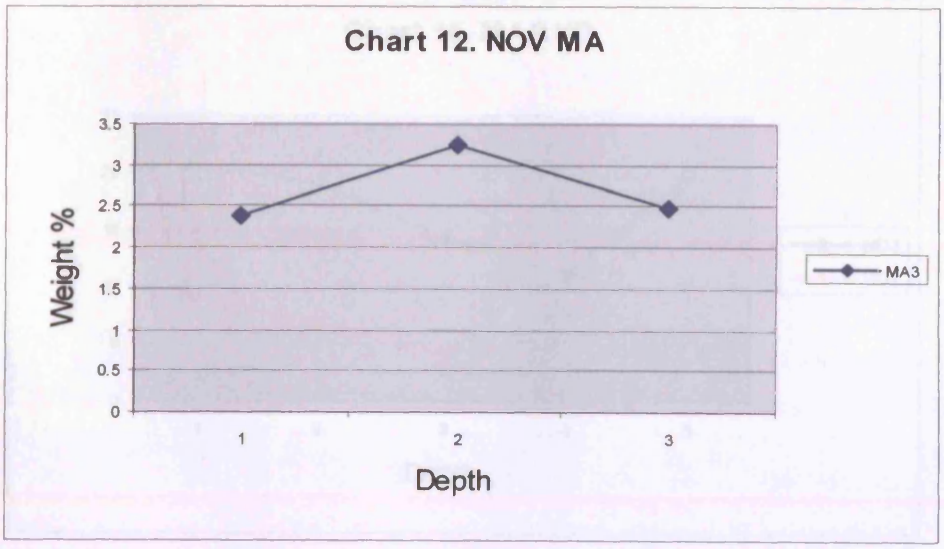


Chart 12. NOV MA
Weight %
3.5
3
2.5
2
1.5
1
0.5
0
1
2
3
Depth
MA3

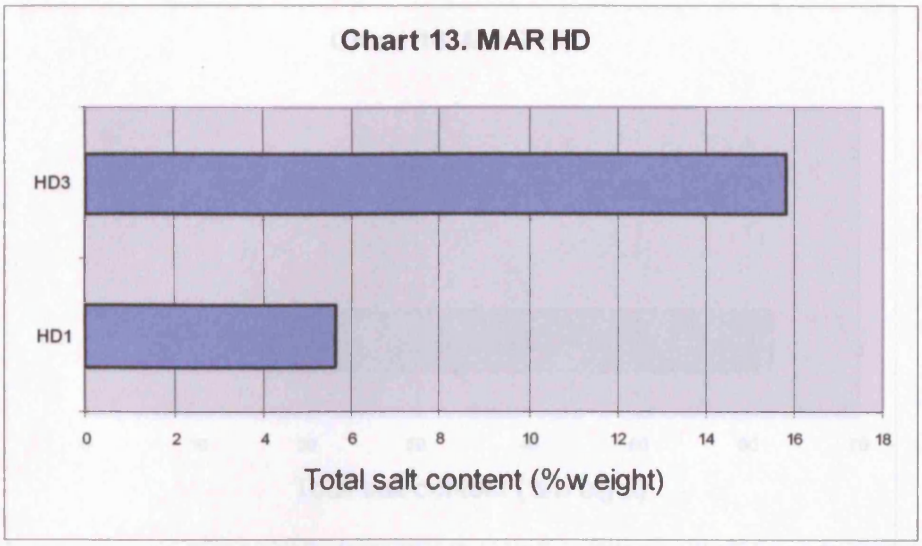


Chart 13. MAR HD

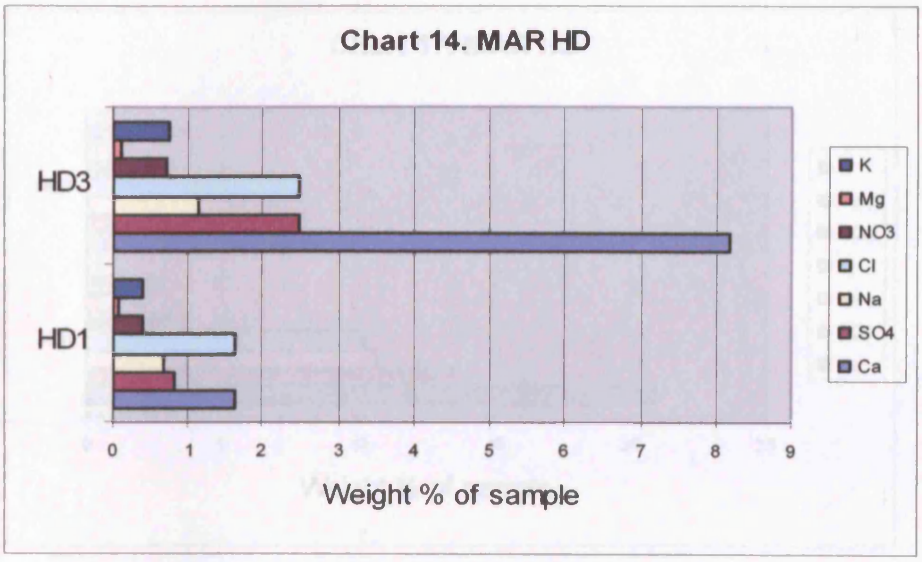


Chart 14. MAR HD

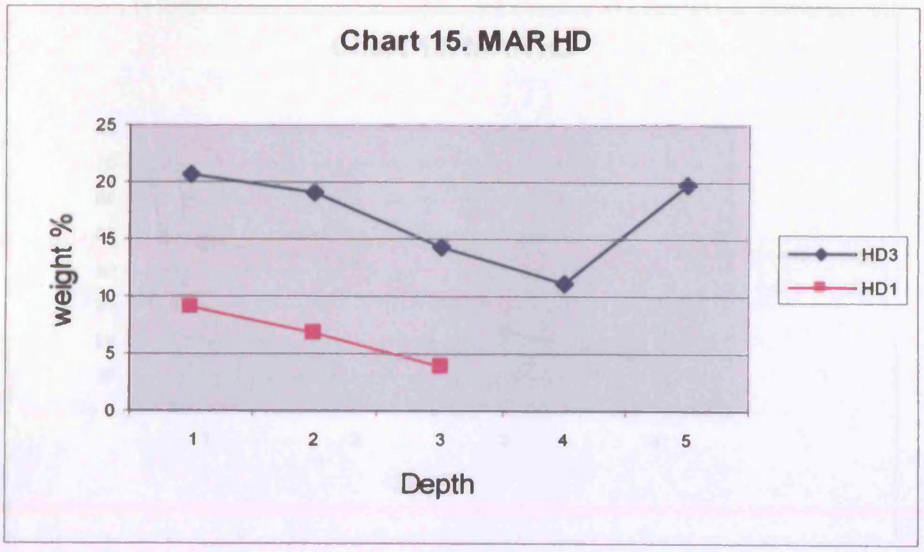


Chart 15. MAR HD

Chart 16. MAR HG

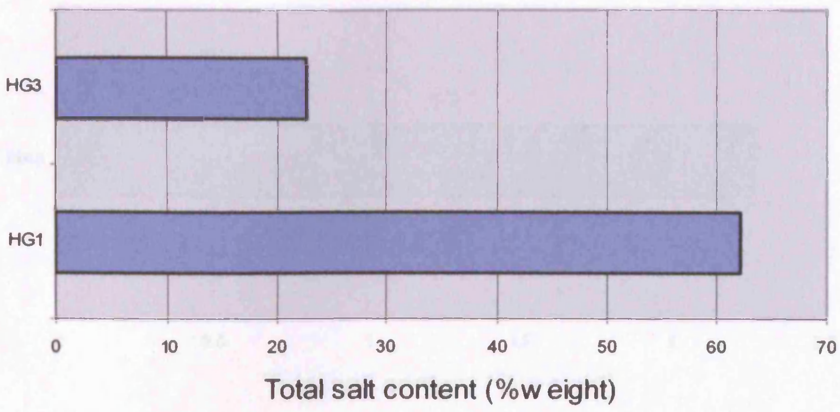


Chart 17. MAR HG

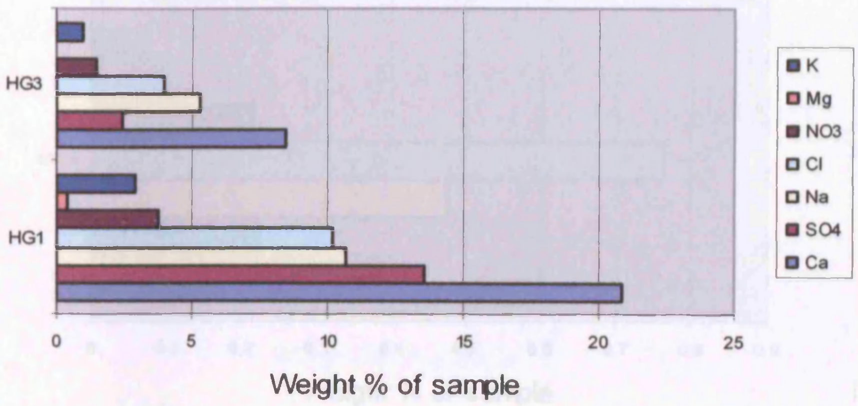
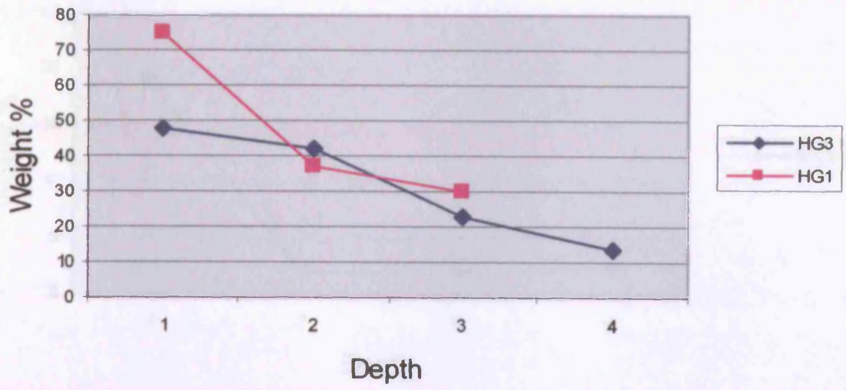


Chart 18. MAR HG



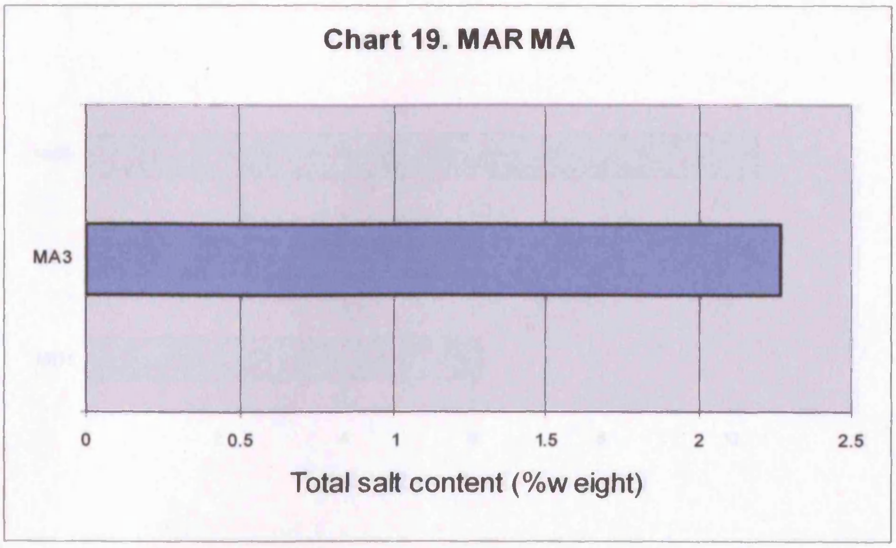


Chart 19. MAR MA
MA3
0
0.5
1
1.5
2
2.5
Total salt content (%w eight)

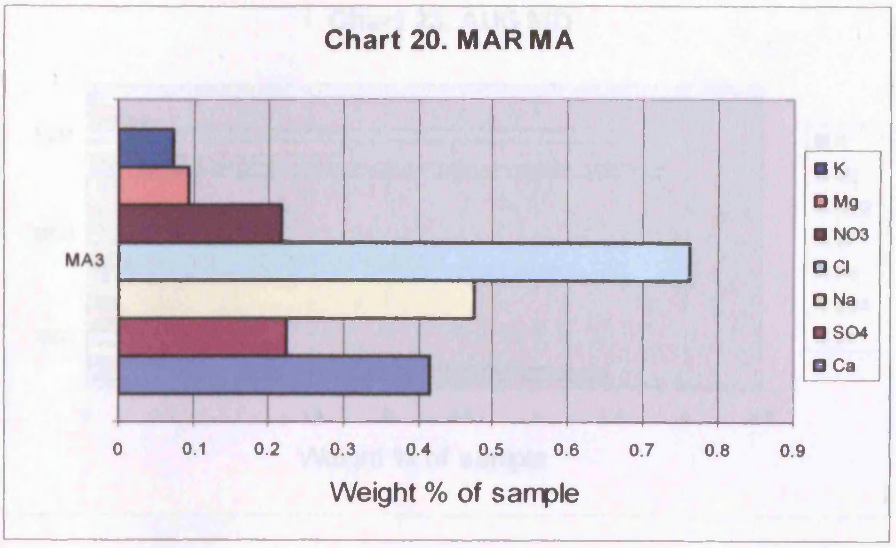


Chart 20. MAR MA
MA3
K
Mg
NO3
Cl
Na
SO4
Ca
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Weight % of sample

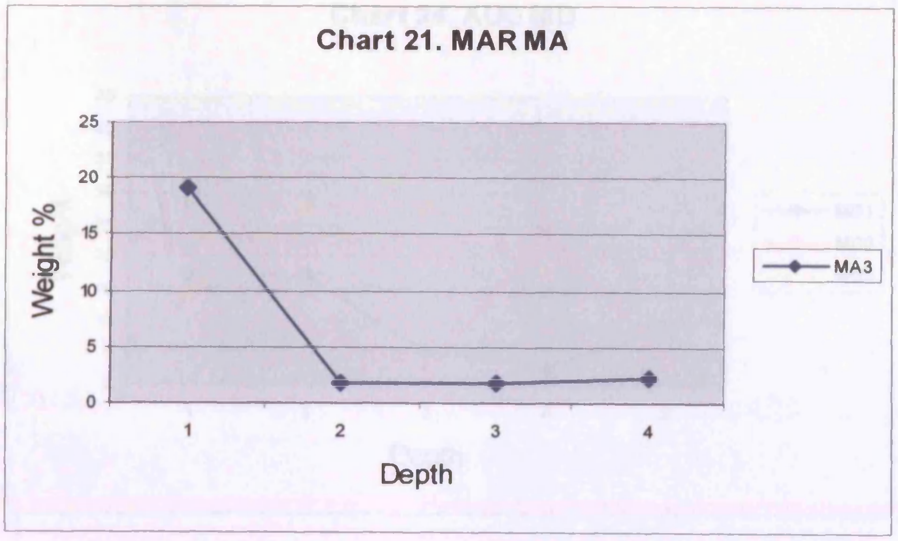


Chart 21. MAR MA
Weight %
25
20
15
10
5
0
1
2
3
4
Depth
MA3

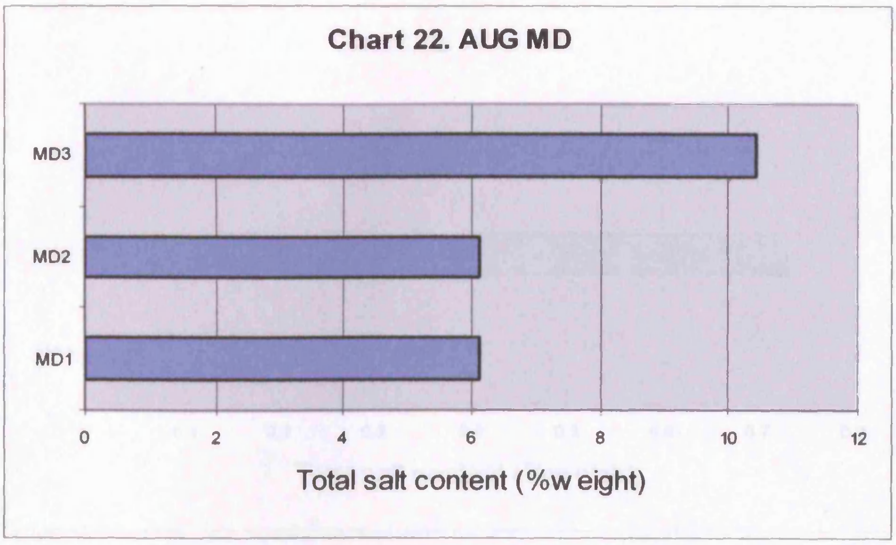


Chart 22. AUG MD

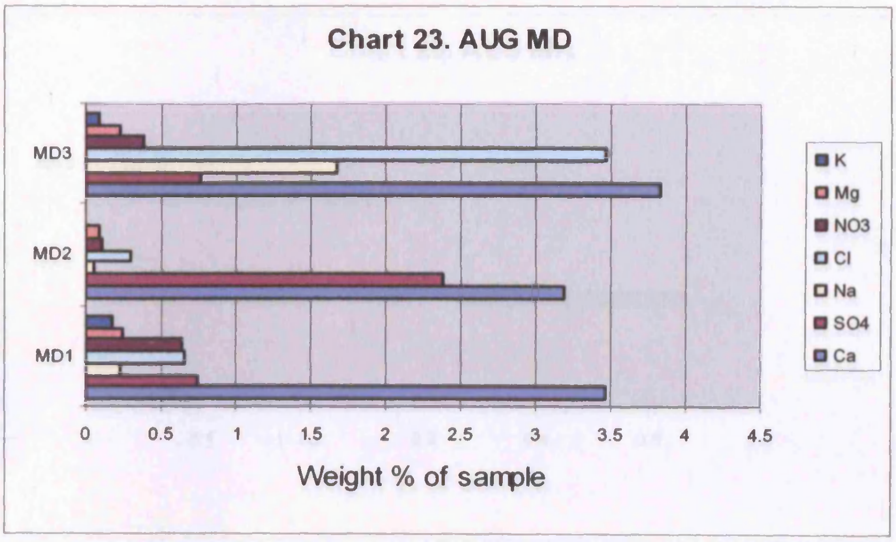


Chart 23. AUG MD

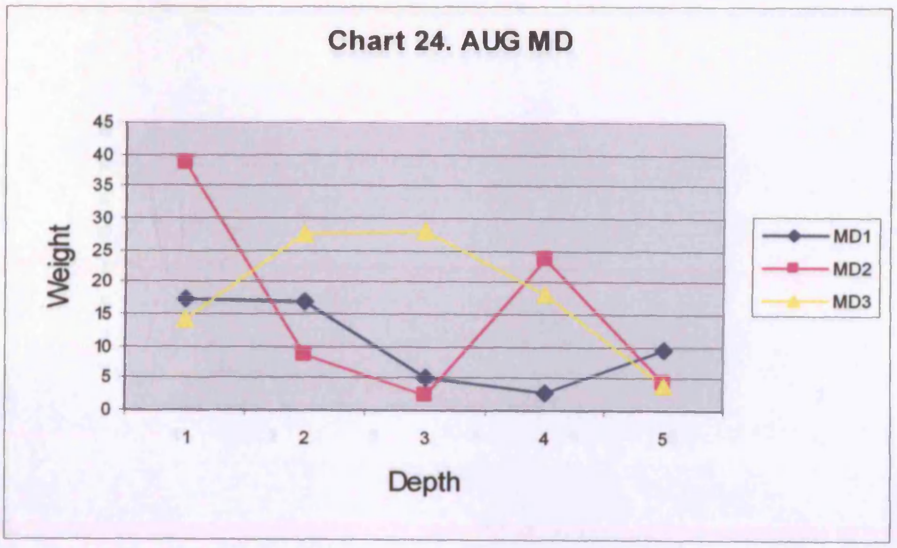


Chart 24. AUG MD

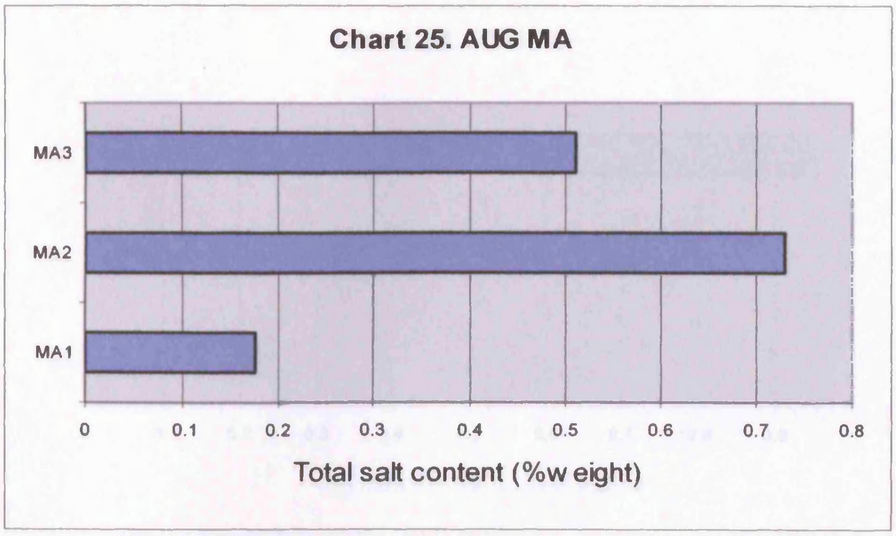


Chart 25. AUG MA

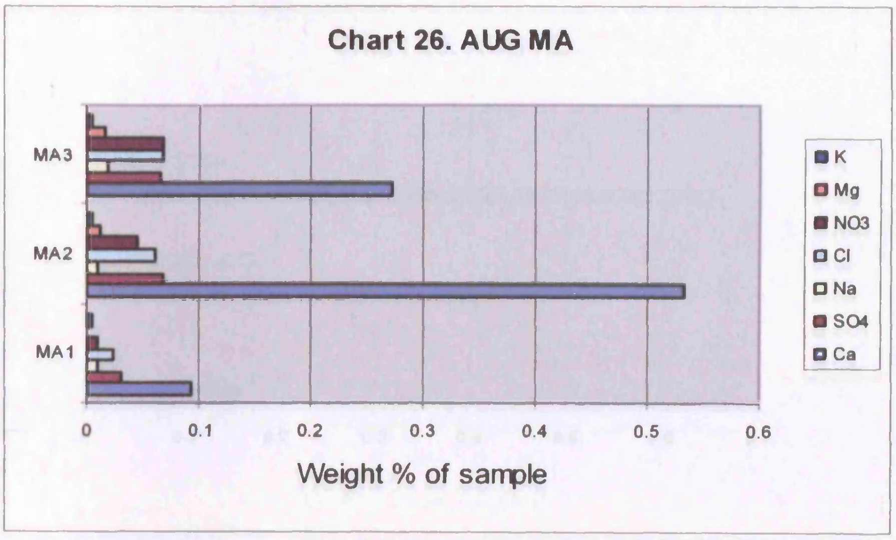


Chart 26. AUG MA

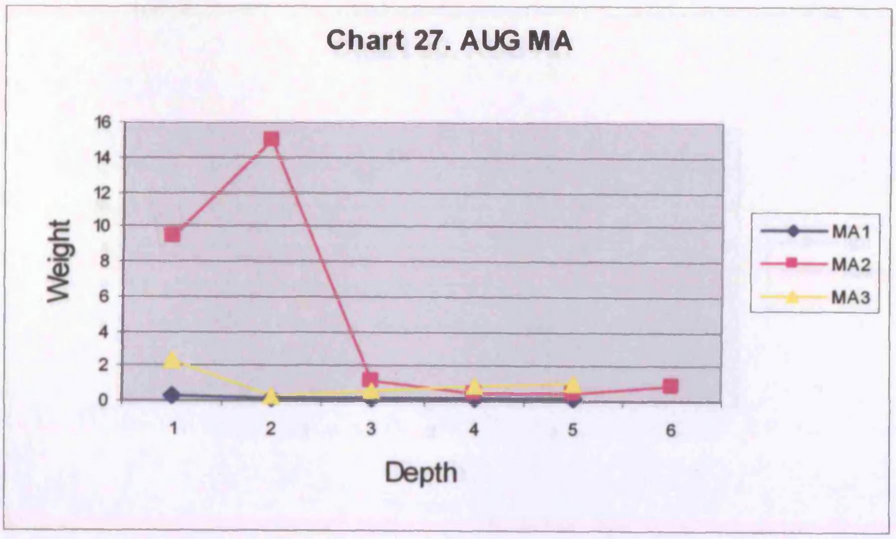


Chart 27. AUG MA

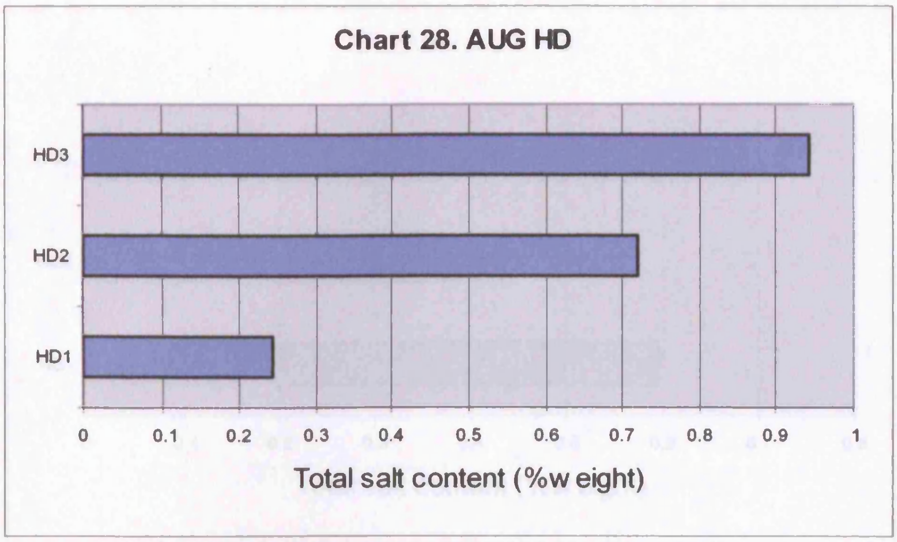


Chart 28. AUG HD
HD3
HD2
HD1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Total salt content (%w eight)

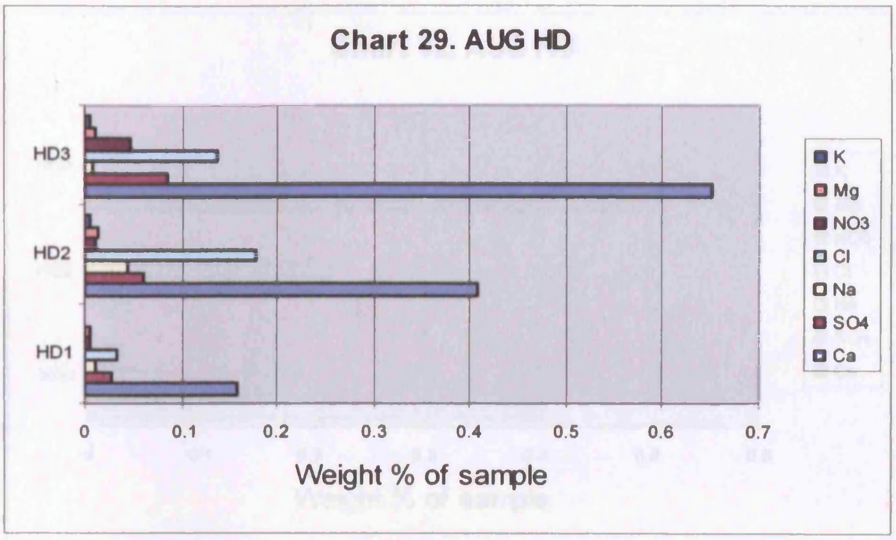


Chart 29. AUG HD
HD3
HD2
HD1
K
Mg
NO3
Cl
Na
SO4
Ca
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Weight % of sample

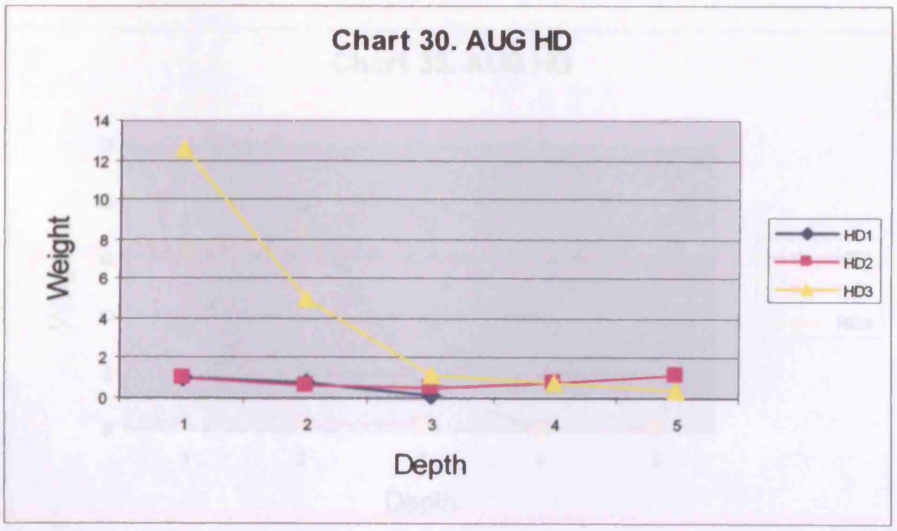


Chart 30. AUG HD
Weight
14
12
10
8
6
4
2
0
1
2
3
4
5
Depth
HD1
HD2
HD3

Chart 31. AUG HG

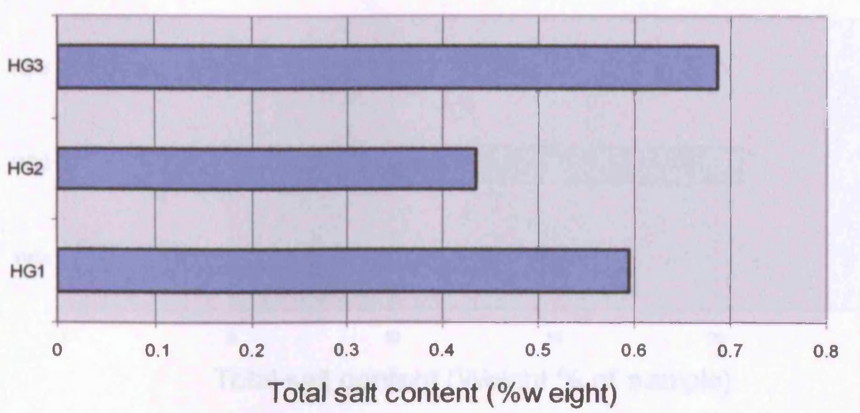


Chart 32. AUG HG

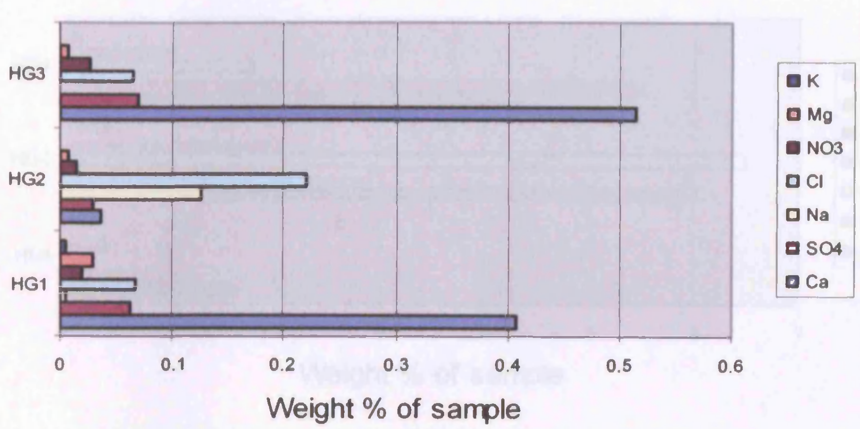


Chart 33. AUG HG

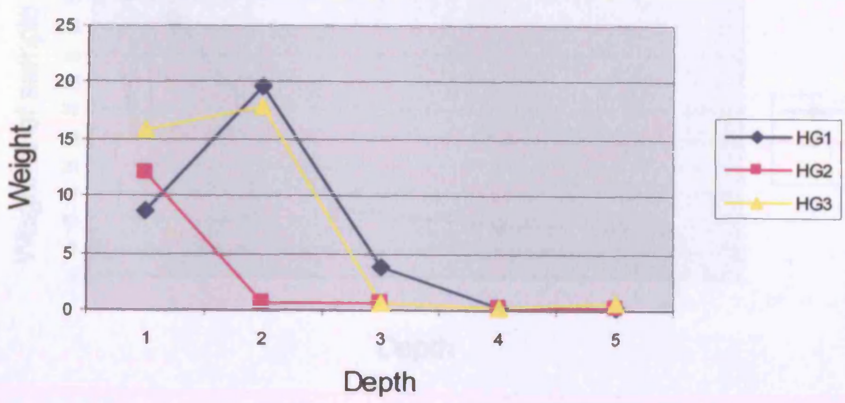


Table 34. JAN HG

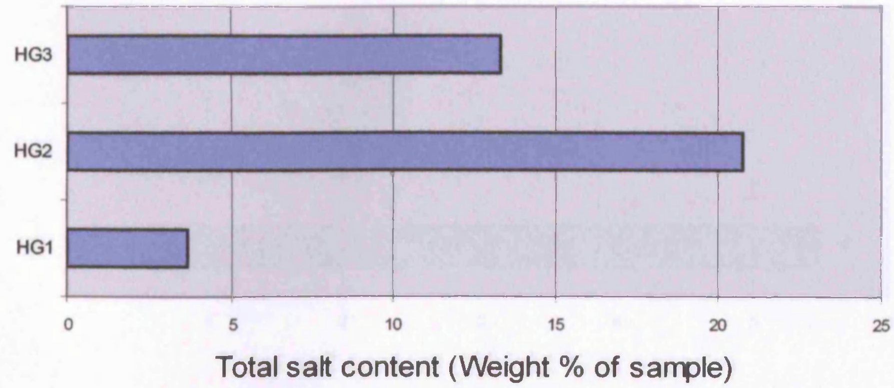
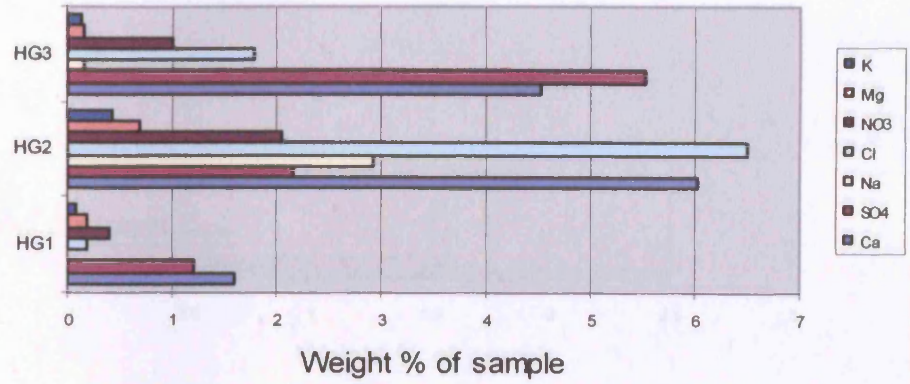


Table 35. JAN HG



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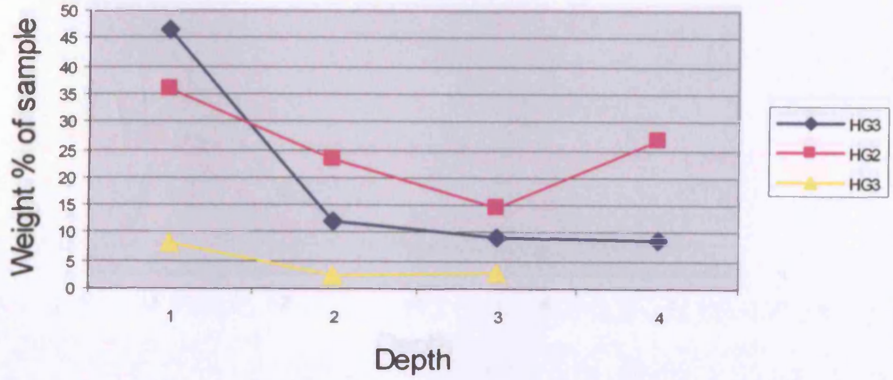
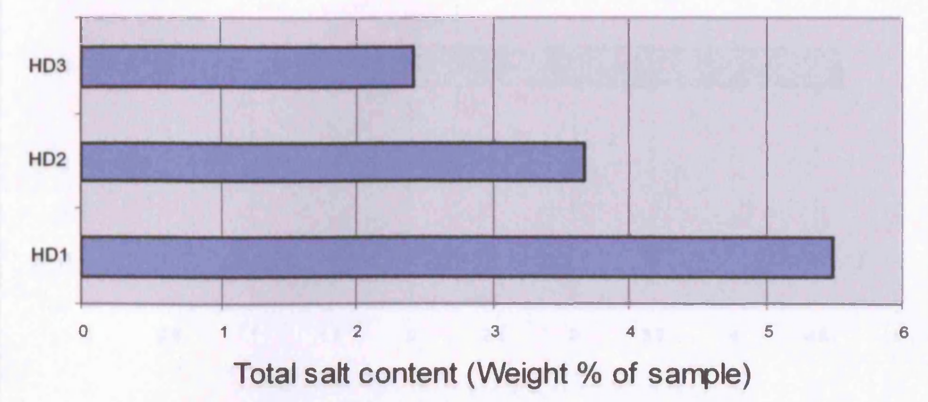


Table 37. JAN HD



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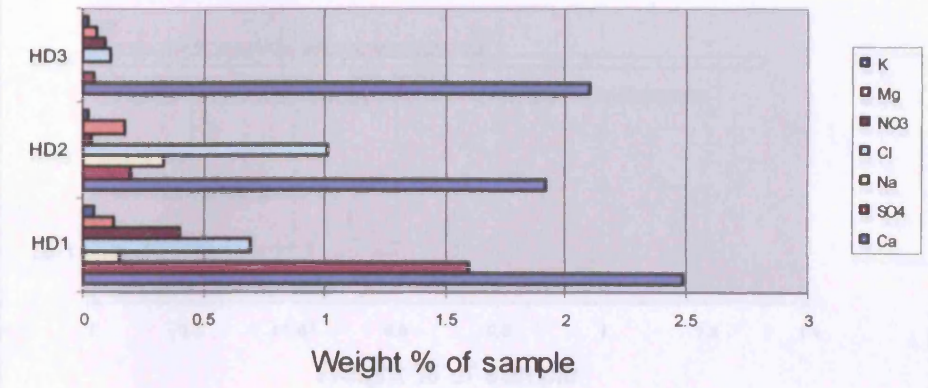


Table 39. JAN HD

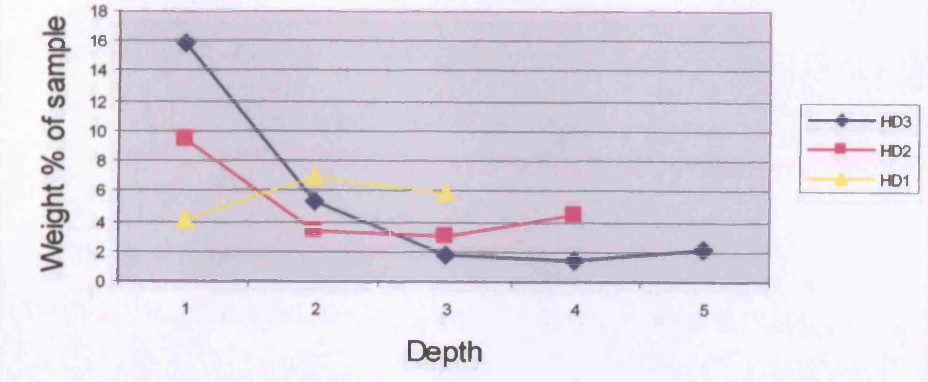
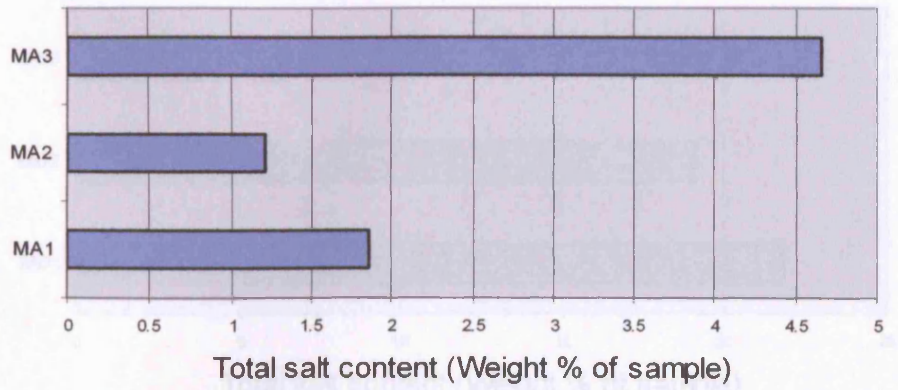


Table 40. JAN MA



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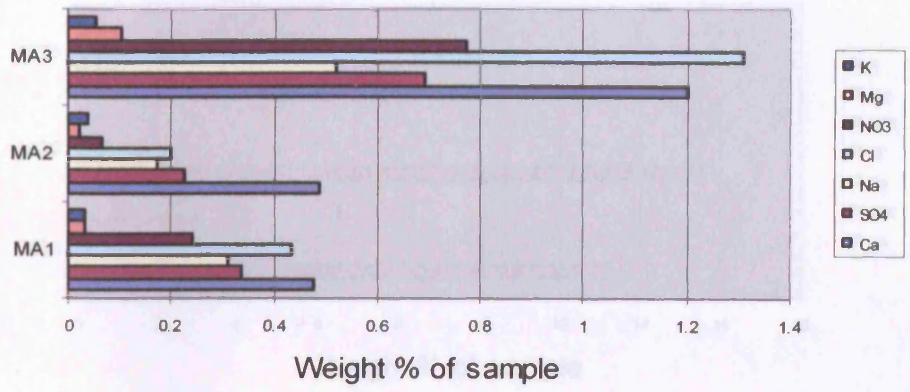

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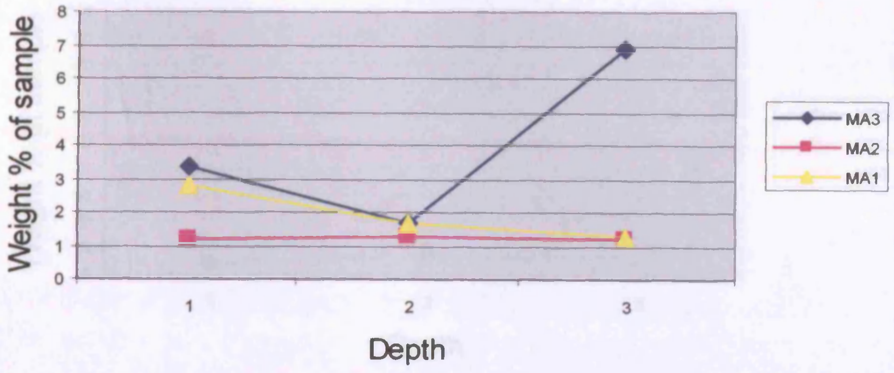


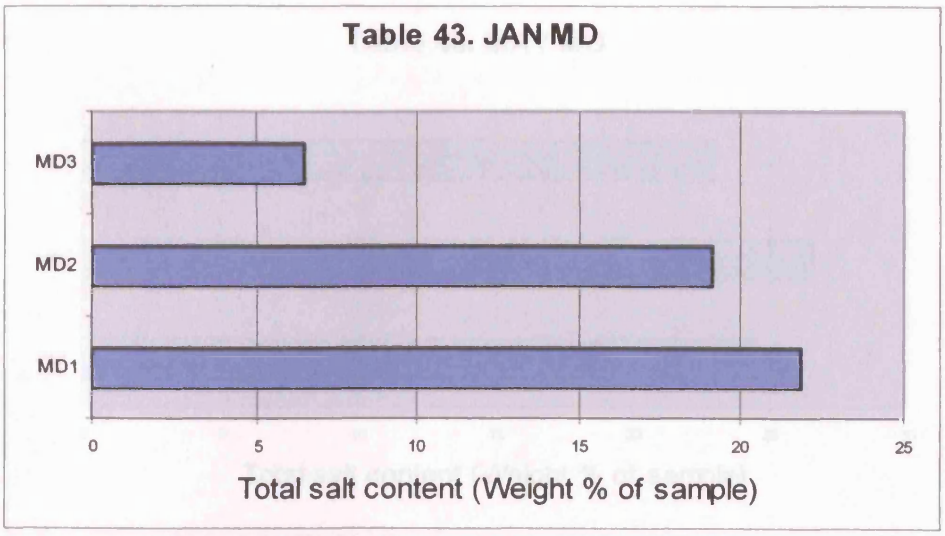


Table 43. JAN MD

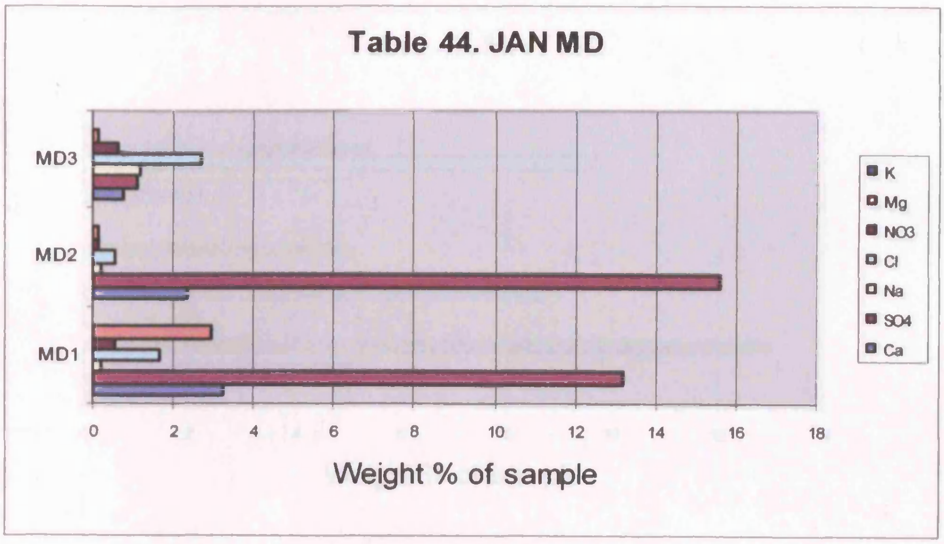


Table 44. JAN MD

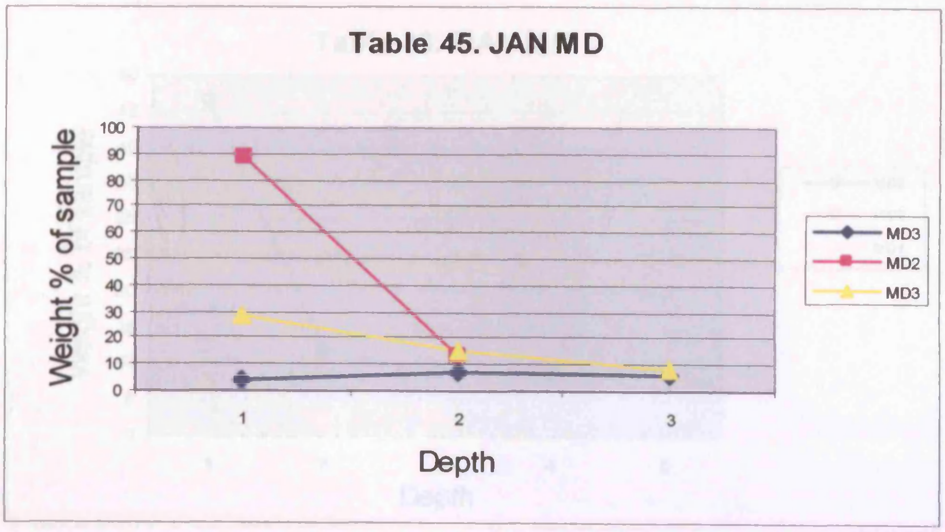


Table 45. JAN MD

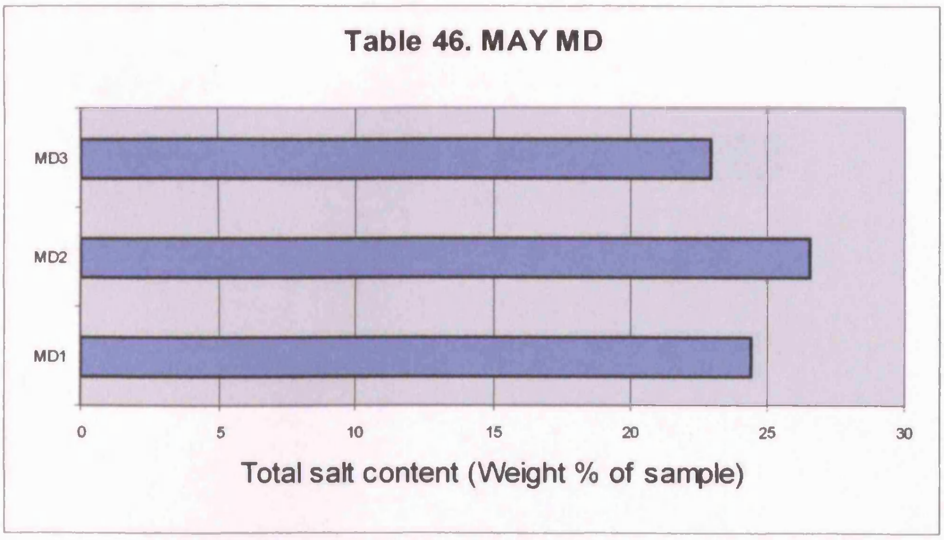
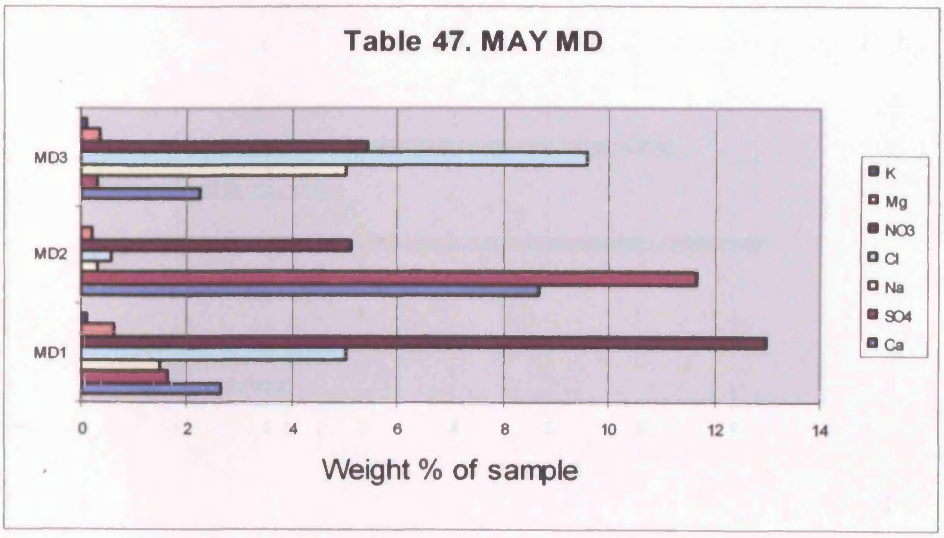


Table 46. MAY MD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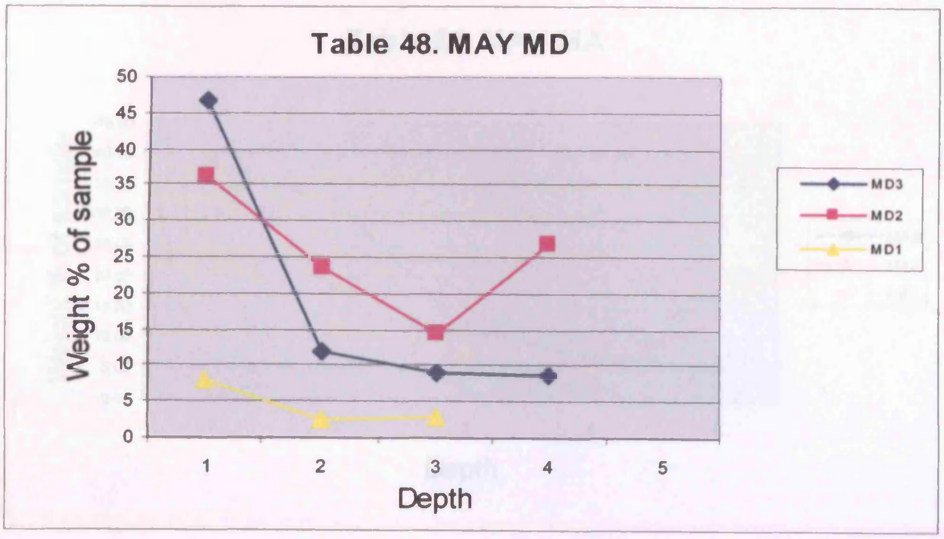


Table 48. MAY MD

Table 49. MAY MA

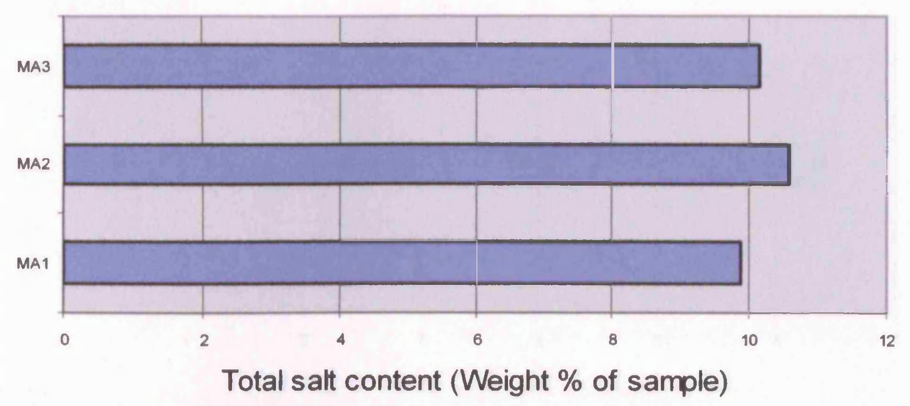
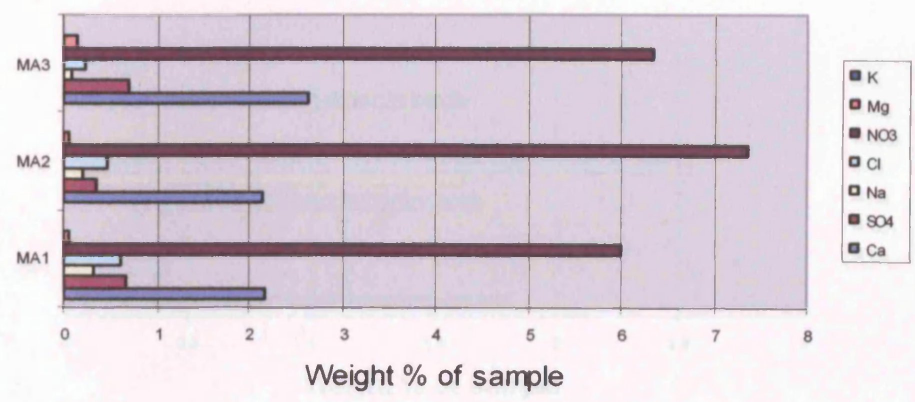


Table 50. MAY MA



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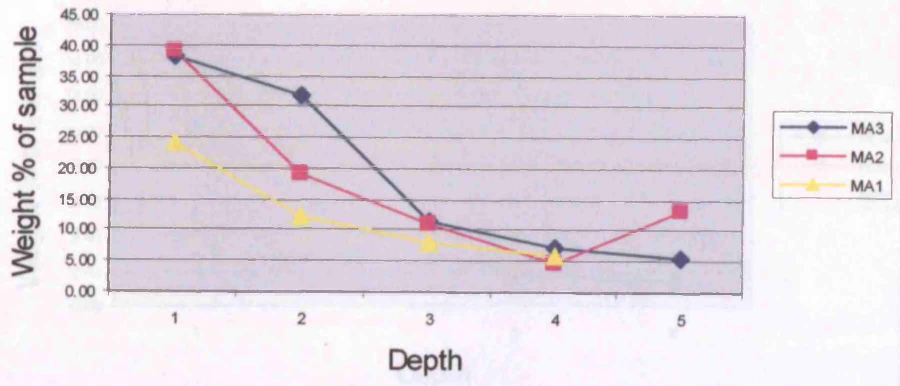
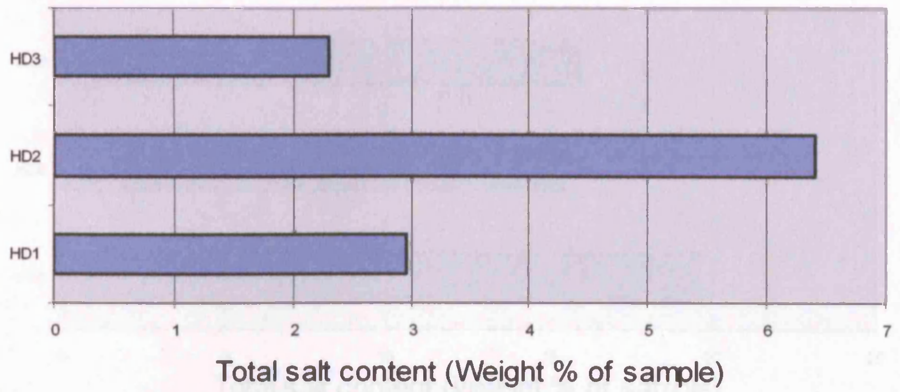


Table 52. MAY HD



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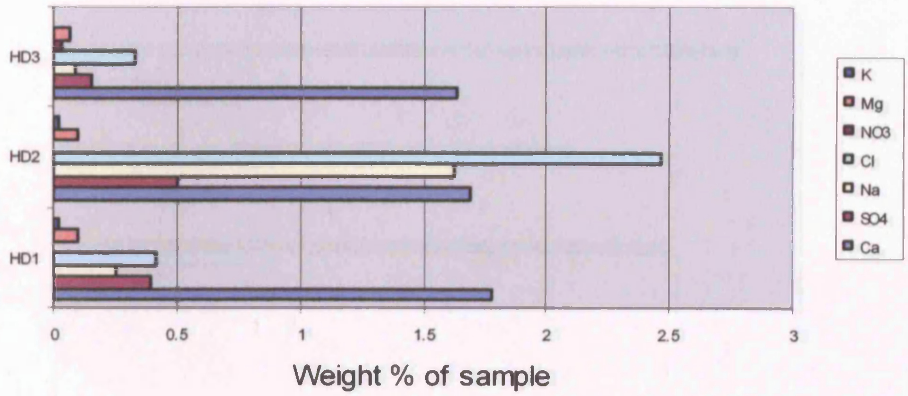
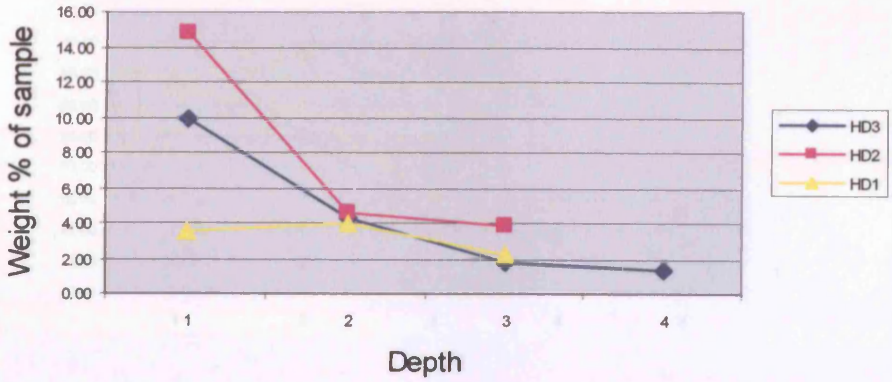


Table 54. MAY HD



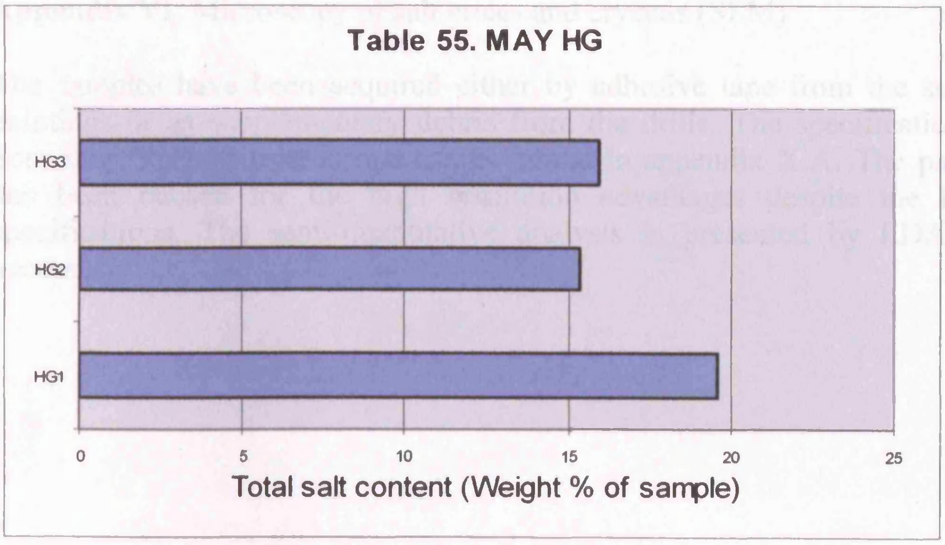


Table 55. MAY HG

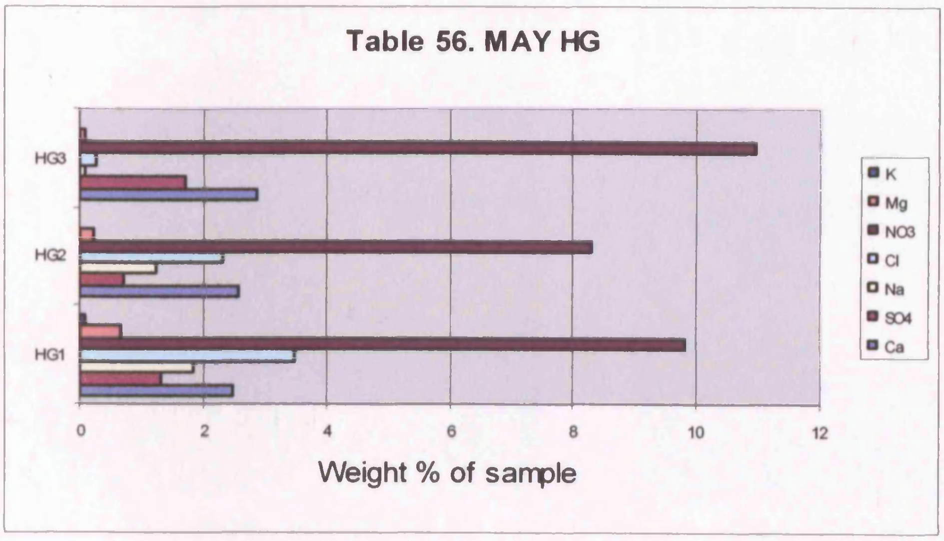


Table 56. MAY HG

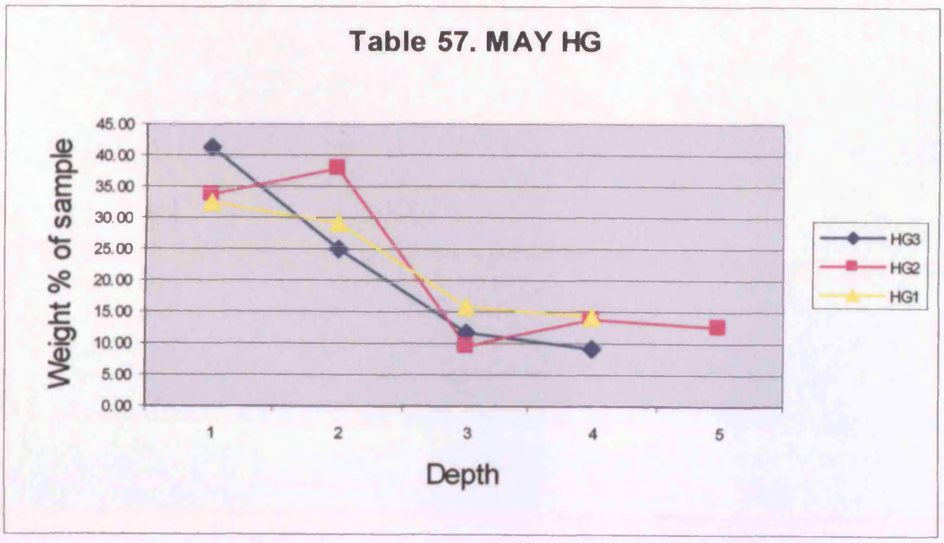


Table 57. MAY HG

Appendix VI: Microscopy of salt crusts and crystals (SEM)

The samples have been acquired either by adhesive tape from the surface of the wall paintings or as supplementary debris from the drills. The specifications of the Hitachi Scanning Electron microscope can be found in appendix X.A. The particular apparatus has been chosen for the high resolution advantages despite the limited analytical specifications. The semi-quantitative analysis is presented by EDAX spectra where necessary.

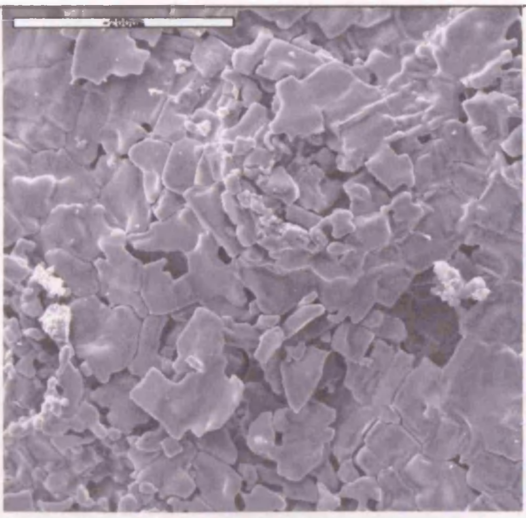


Fig. 1 Halite white crust MD2

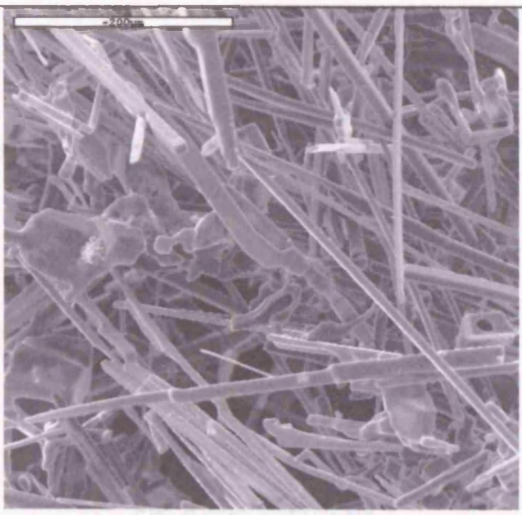


Fig. 2 Halite whiskers MD3

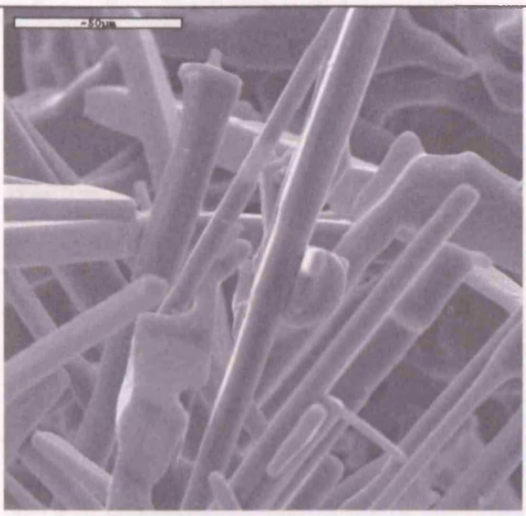


Fig. 3 Halite whiskers MD3

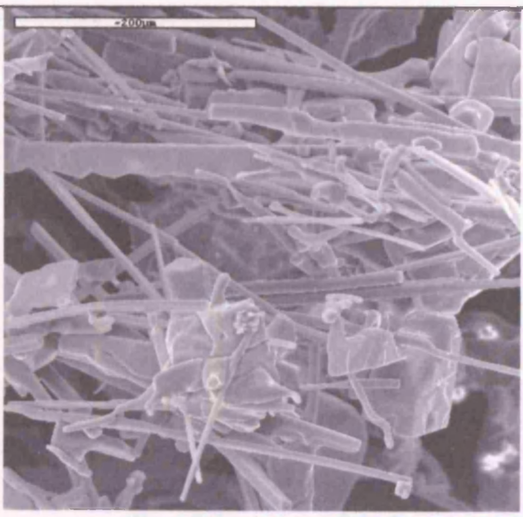


Fig. 4 Halite whiskers MD3

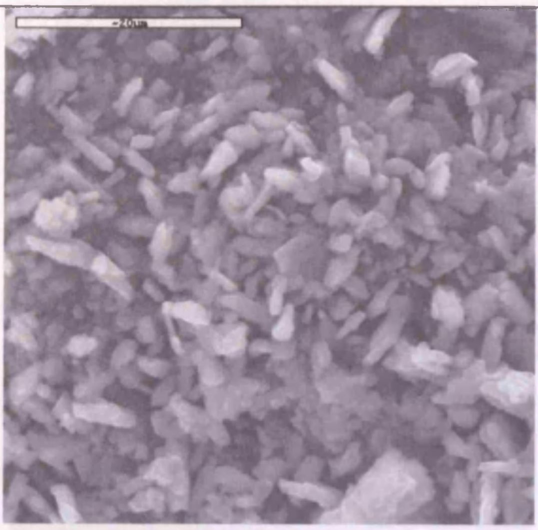


Fig. 5 Mixed crust MD2

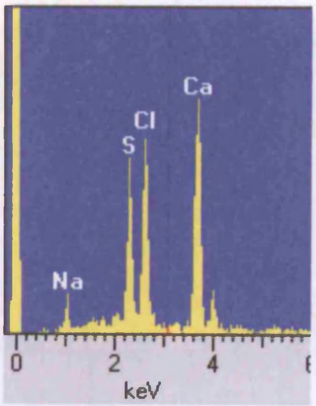


Fig. 6 Spectrum of fig.5

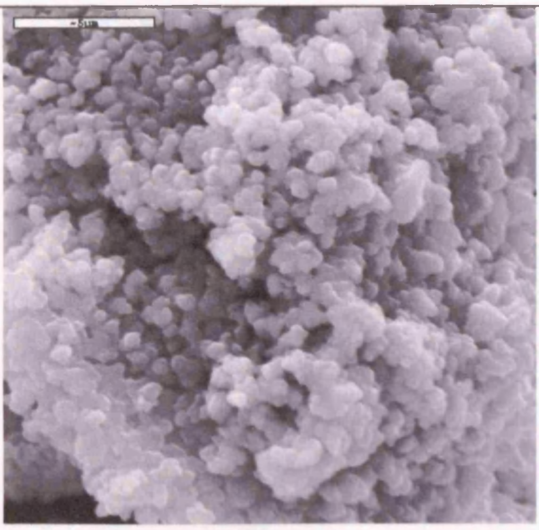


Fig. 7 Mg-K-Cl crystals on gypsum crust MD2

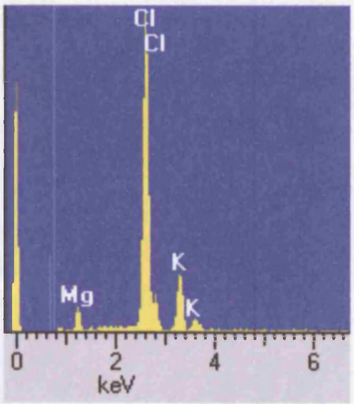


Fig. 8 Spectrum of fig.7

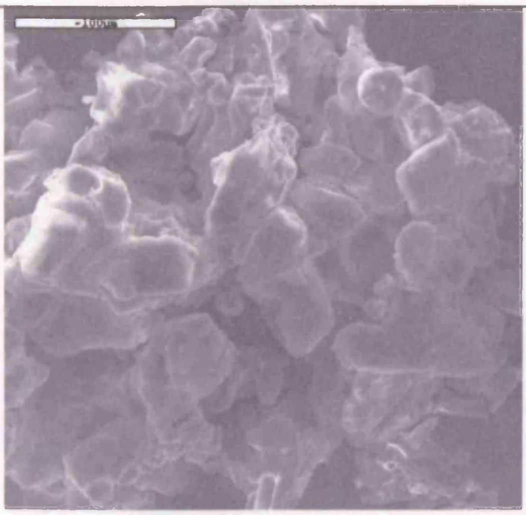


Fig. 9 Powdery white efflorescence MD1

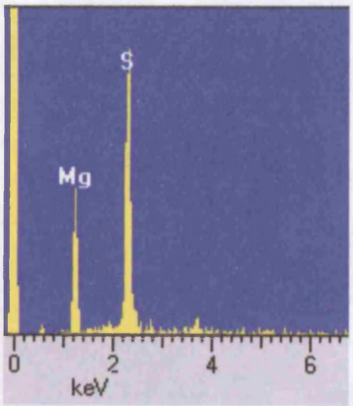


Fig. 10 Spectrum of fig.9

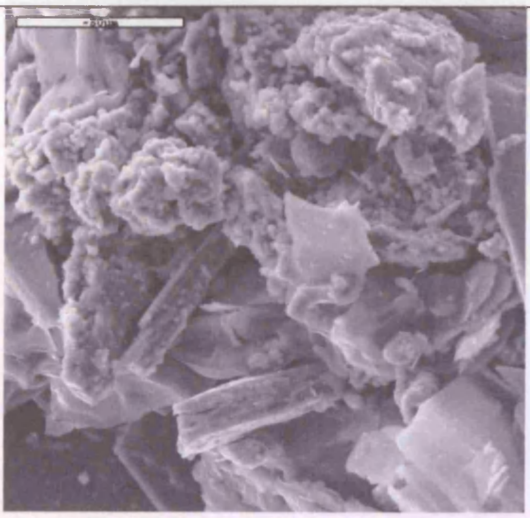


Fig. 11 Mixed Ca-Mg-S species MD1

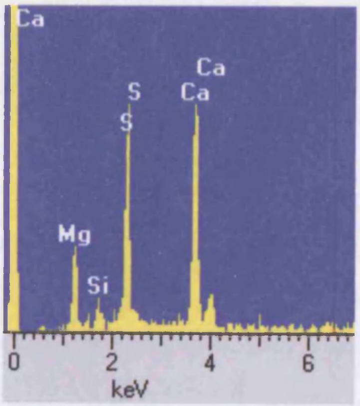


Fig. 12 Spectrum of fig.11

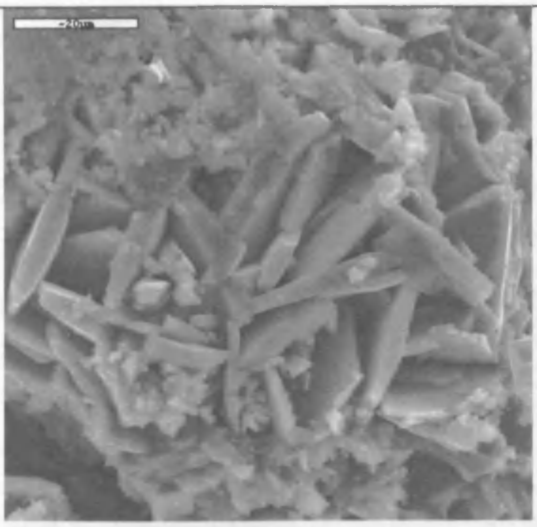


Fig. 13 Sea salt particles on yellow gypsum crust

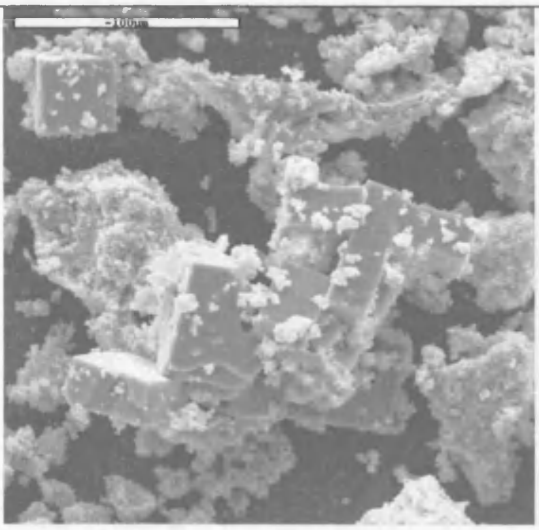


Fig. 14 Halite crystals in pulverized mortar MD3

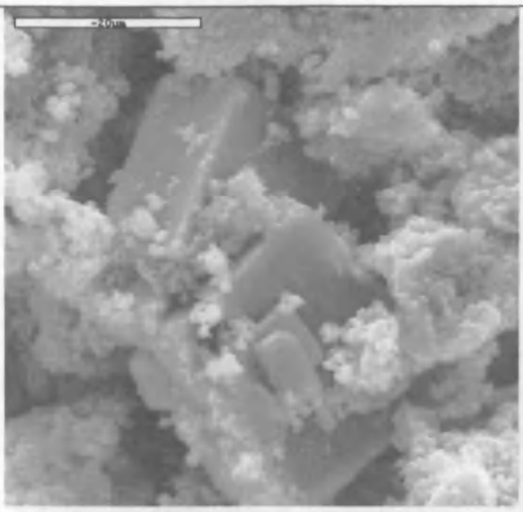


Fig. 15 As in fig.14

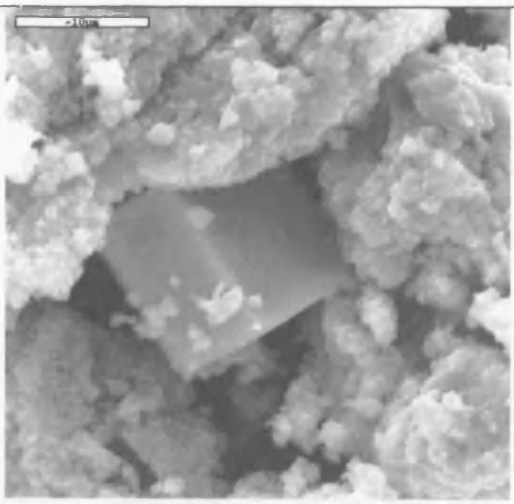


Fig. 16 As in fig.14

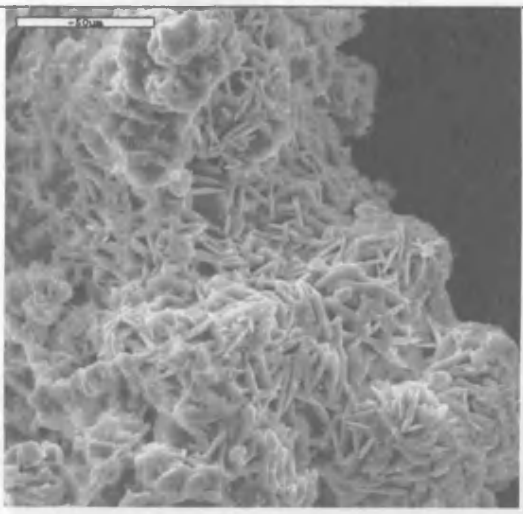


Fig. 17 Gypsum thick crust HG3

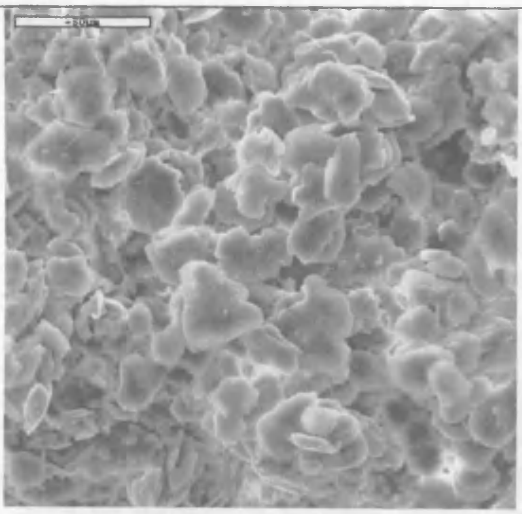


Fig. 18 Gypsum powdery efflorescence HG3

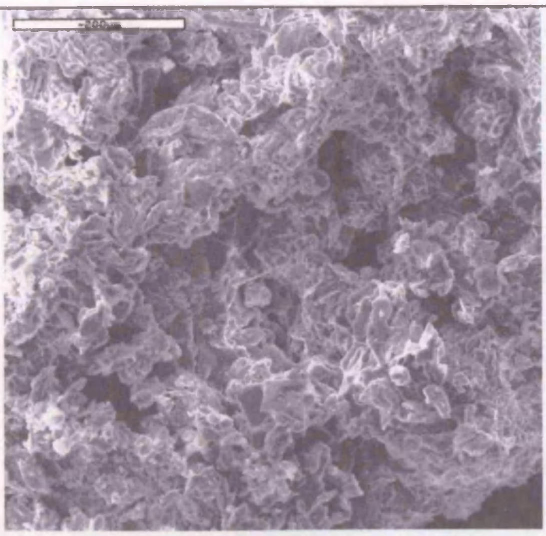


Fig. 19 Compound, hard gypsum grey crust HG1

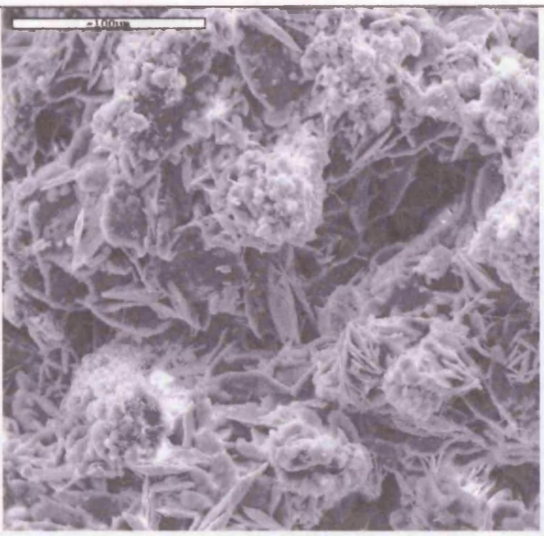


Fig. 20 White gypsum crust with sea salt deposits

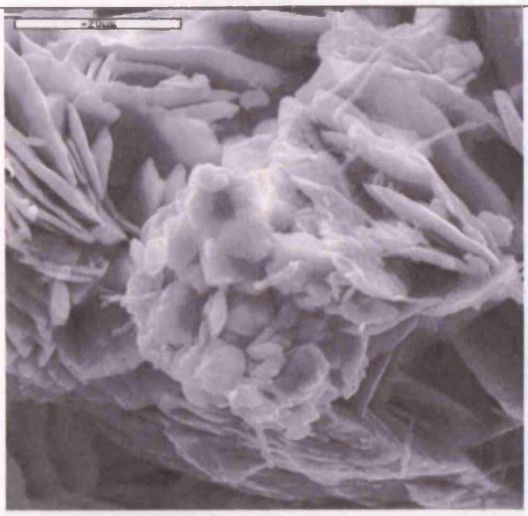


Fig. 21 (det.20) Sea salt particle on gypsum HG2

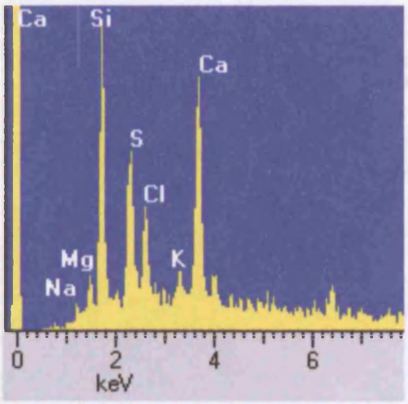


Fig. 22 Spectrum of fig.21

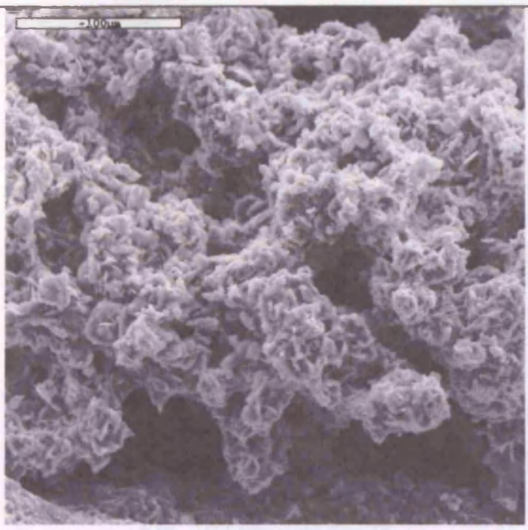


Fig. 23 Porous gypsum crust HG3

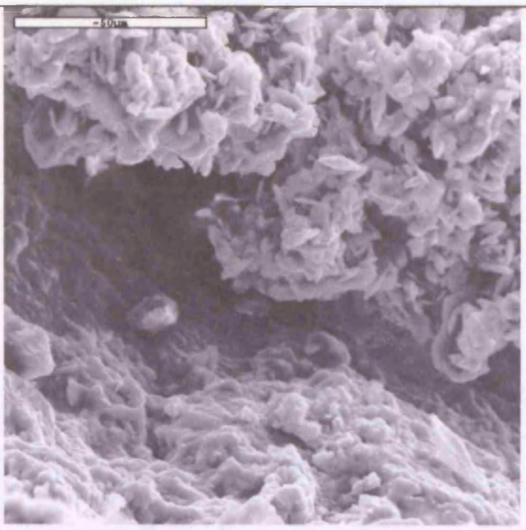


Fig. 24 Gypsum crust detached from the mortar

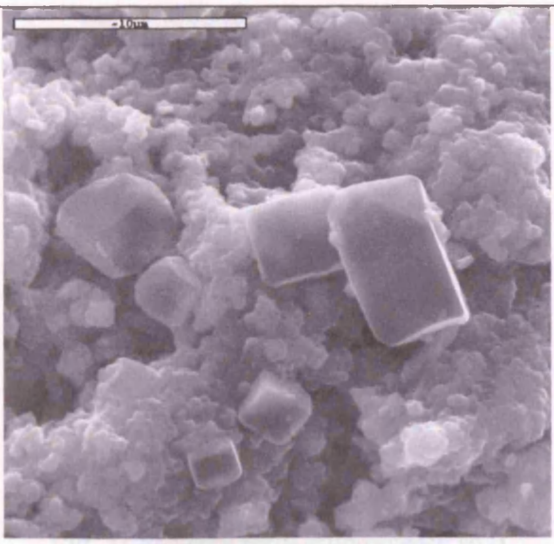


Fig. 25 Halite deposits MA

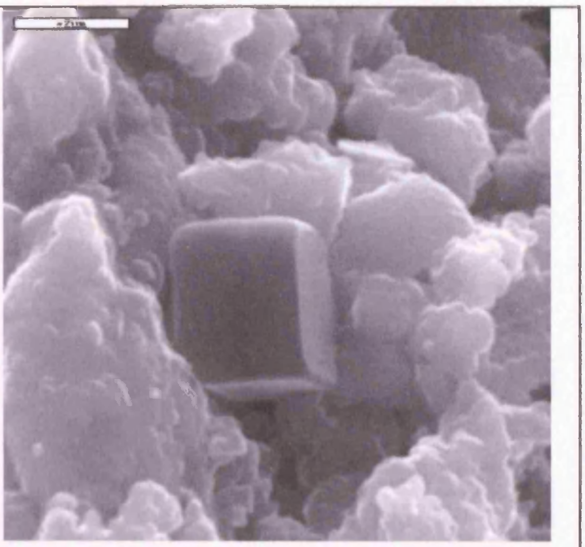


Fig. 26 Small halite crystal MA

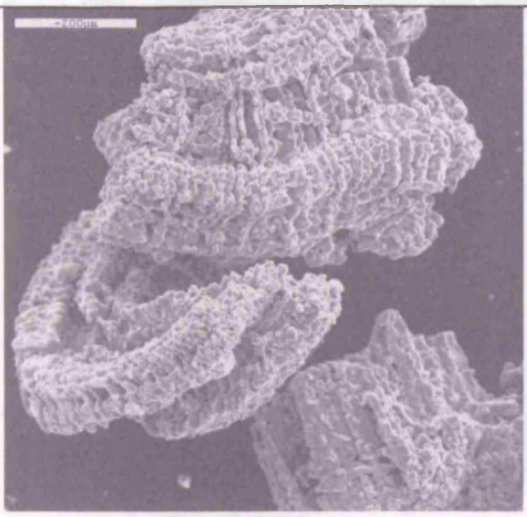


Fig. 27 Columnar Na-Cl crystals HG2

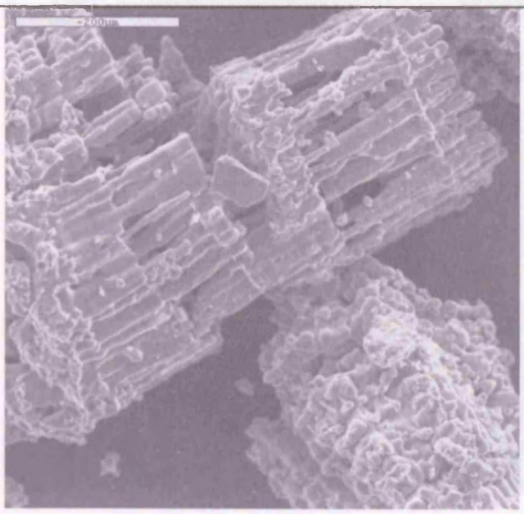


Fig. 28 (As in fig.27)

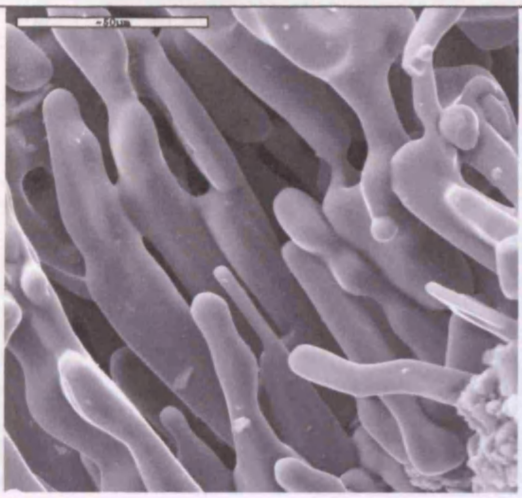


Fig. 29 Detail of fig.28

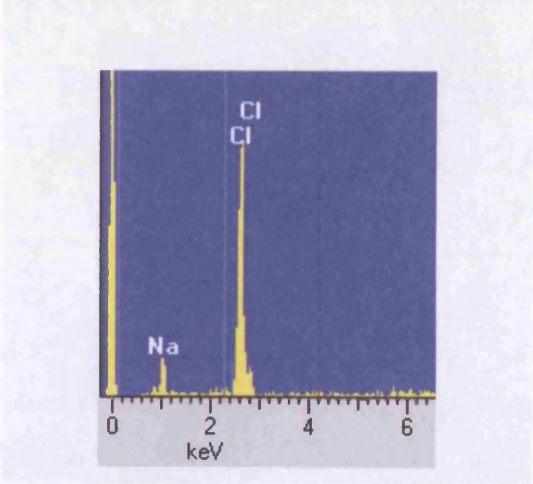


Fig. 30 Spectrum of fig.29

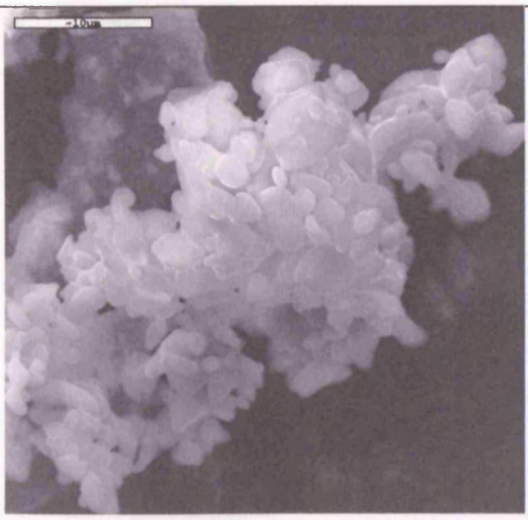


Fig. 31 Powdery Na-S efflorescence HG1

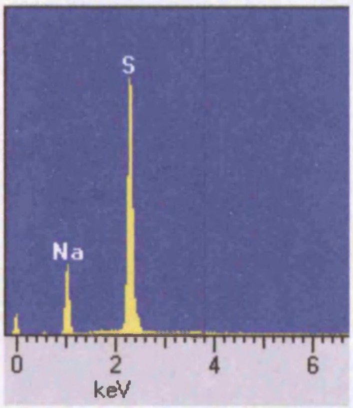


Fig. 32 Spectrum of fig.31

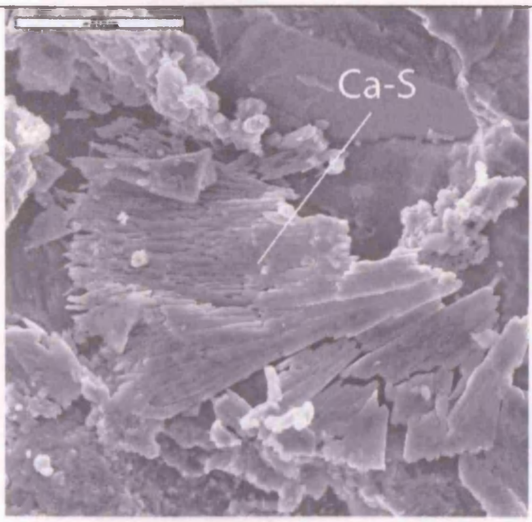


Fig. 33 Sulphation

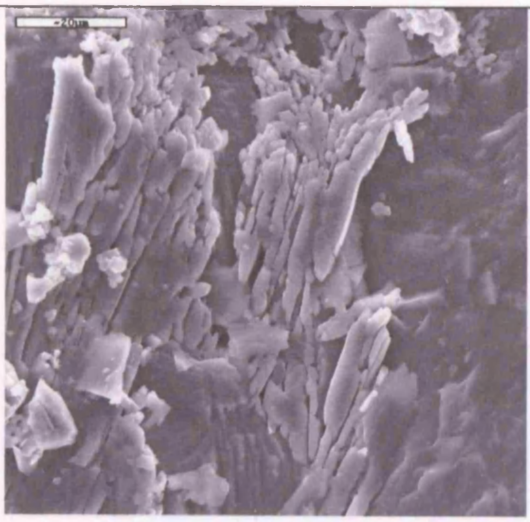


Fig. 34 Sulphation

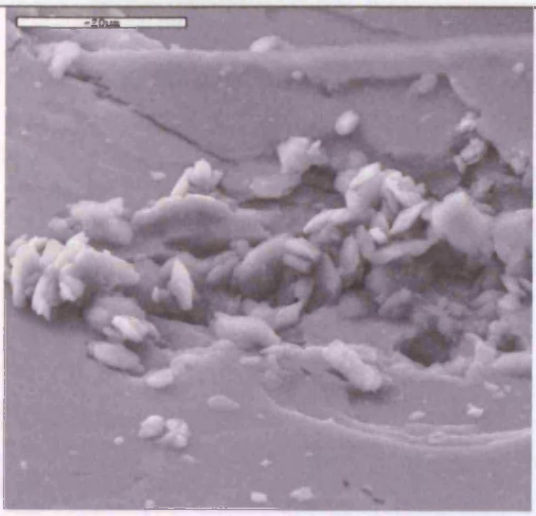


Fig. 35 Sulphation

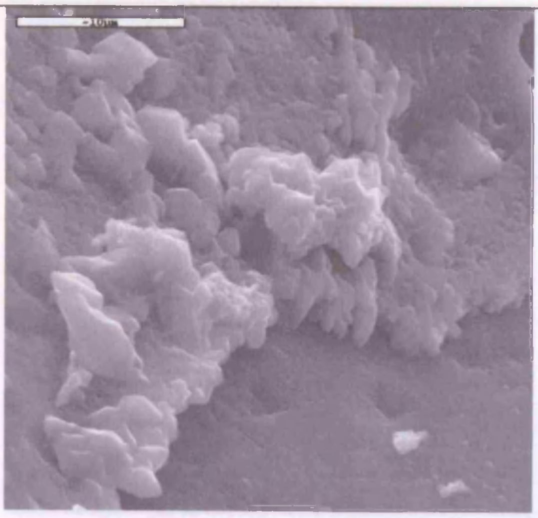


Fig. 36 Advancing gypsum crust

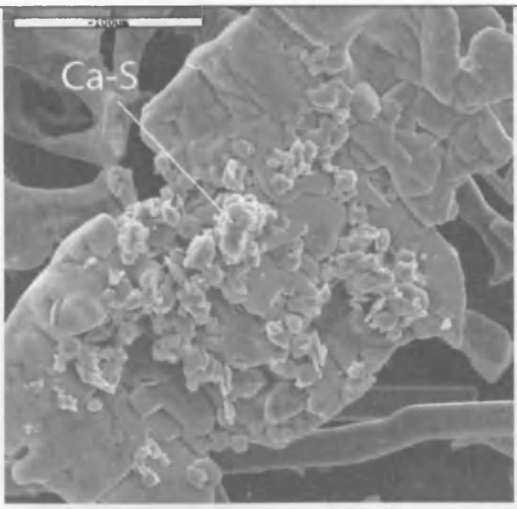


Fig. 37 Gypsum efflorescence on halite crust

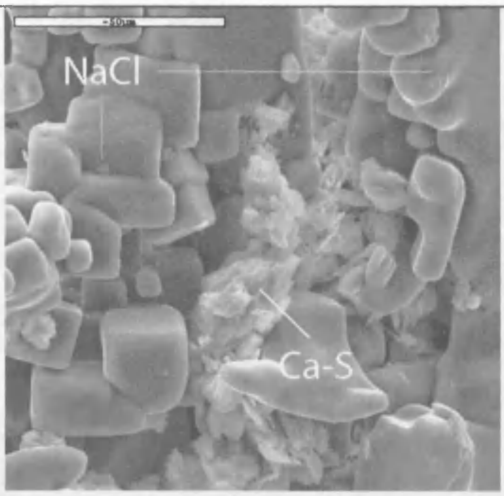


Fig. 38 Gypsum growing through a crack of the halite crust

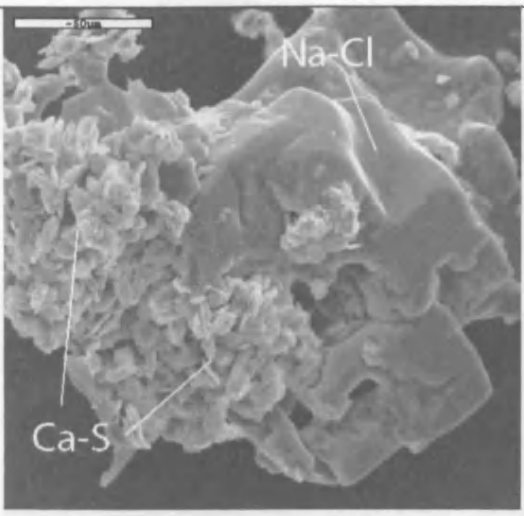


Fig. 39 Mixed species

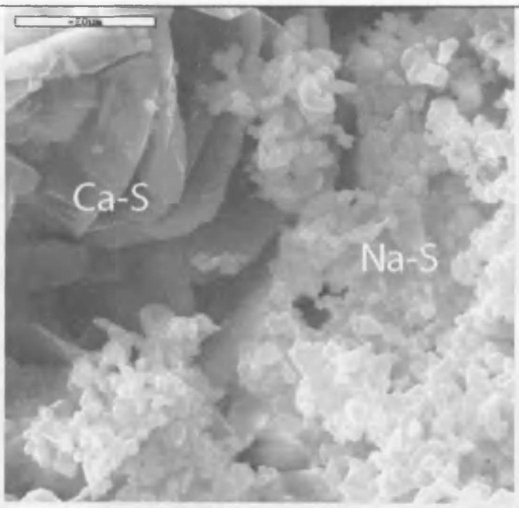


Fig. 40 Mixed efflorescence

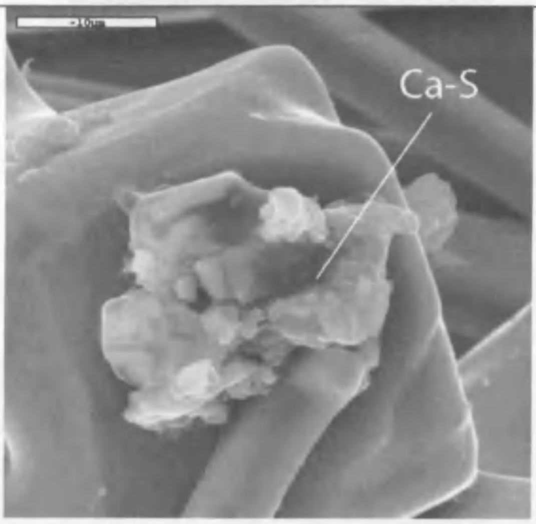


Fig. 41 Gypsum on halite crystal

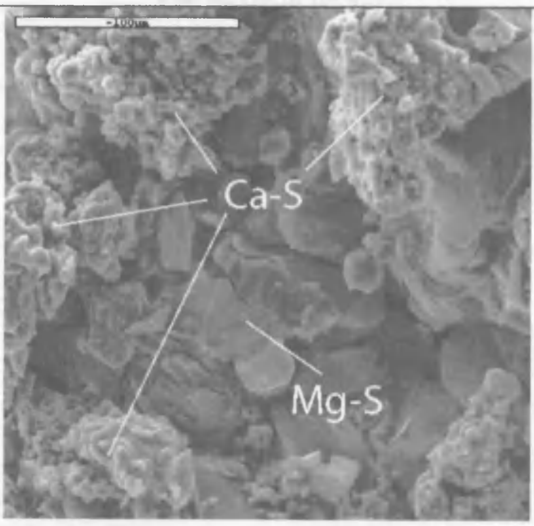


Fig. 42 Mixed efflorescence

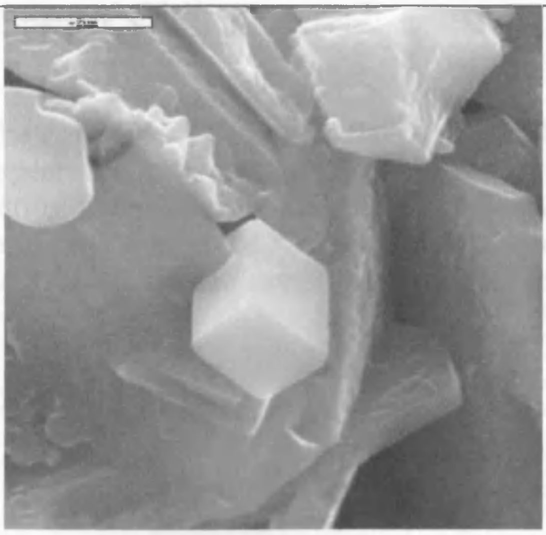


Fig. 43 Halite and gypsum crystals complex

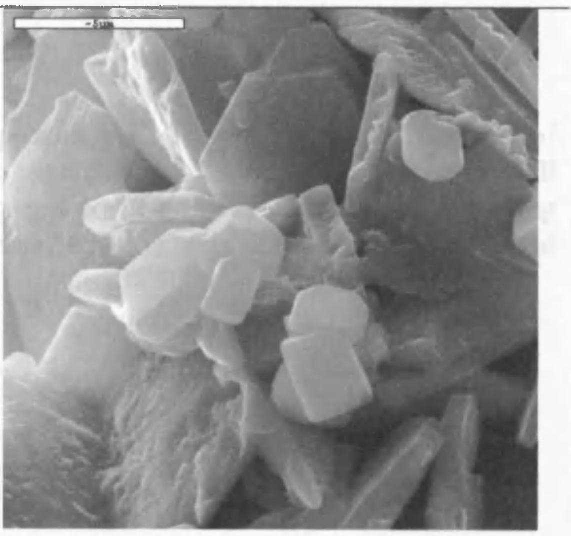


Fig. 44 (as in fig.43)

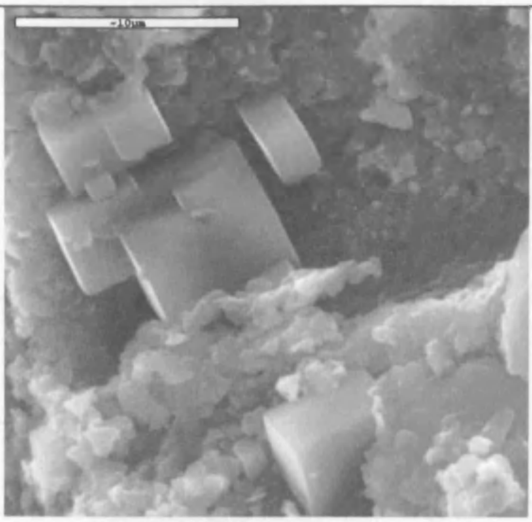


Fig. 45 Halite crystals growing in a pore

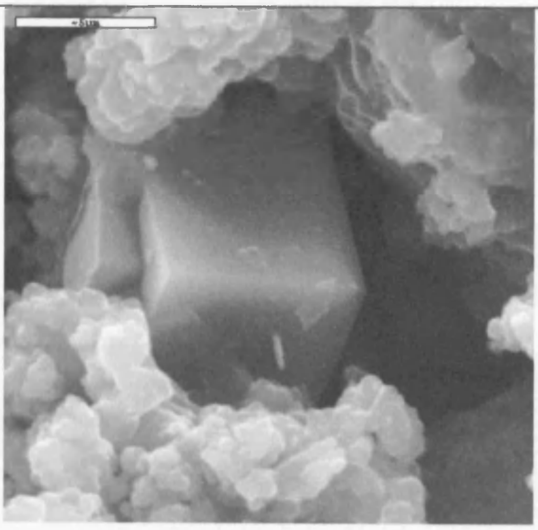
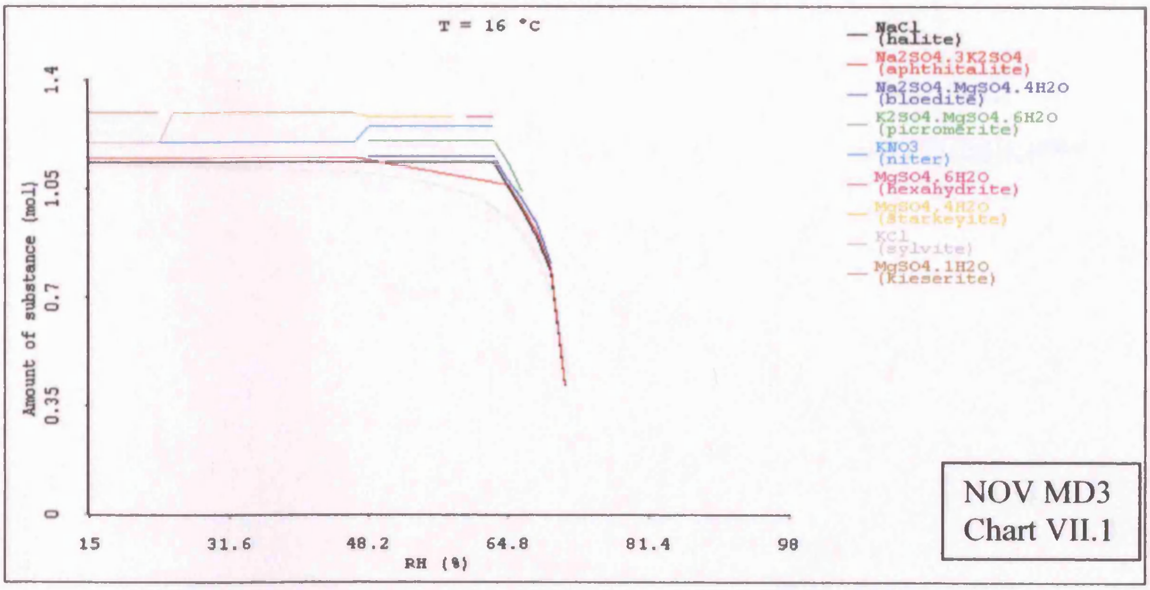


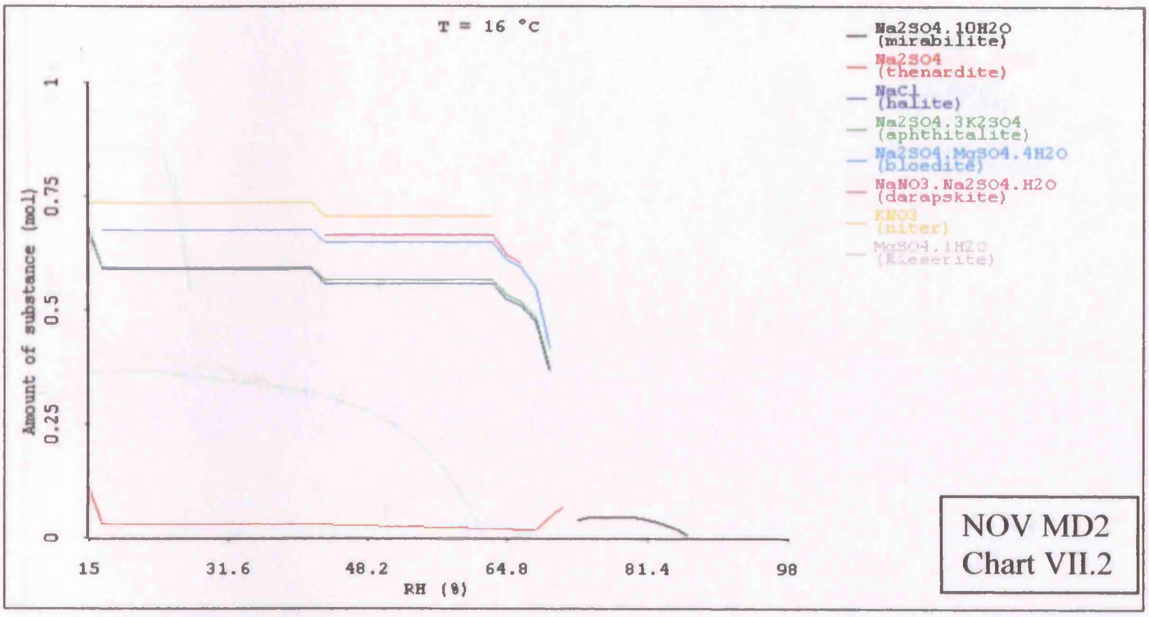
Fig. 46 (as in fig.45)

Appendix VII: ECOS graphs

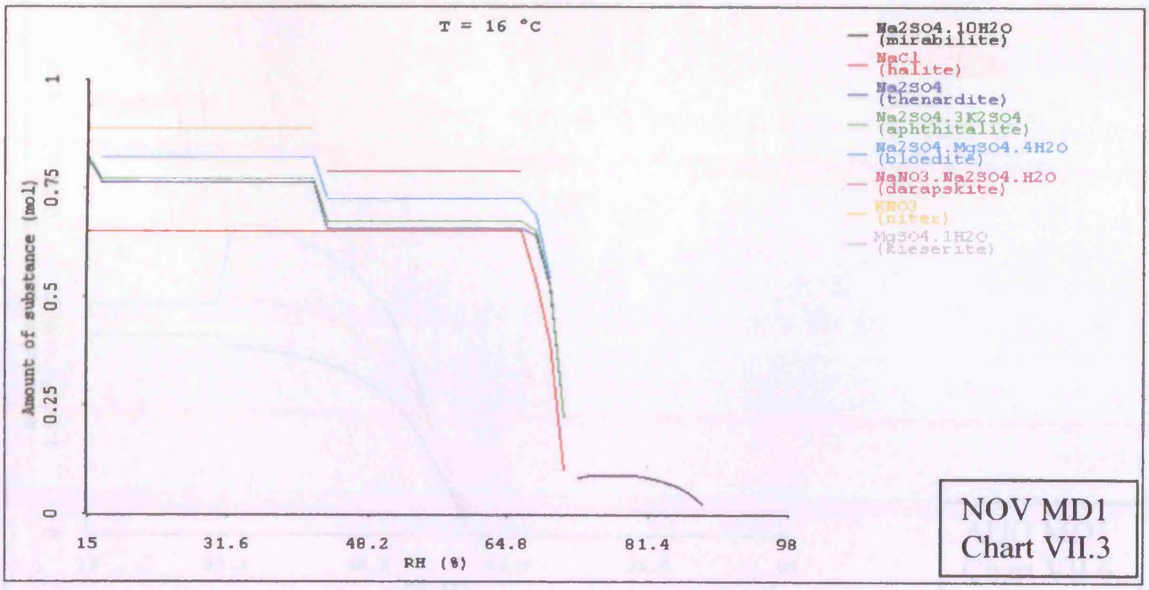
The graphs derive from the data on tables in appendix V.C. They are arranged in order of appearance in the text of chapter 9 so that each page contains graphs from the same wall during the same sampling period (the lowest graph corresponds to the lowest sampling location). The value "Amount of substance (mol)" on axis Y is cumulative. The legend refers to the time of sampling and the location.



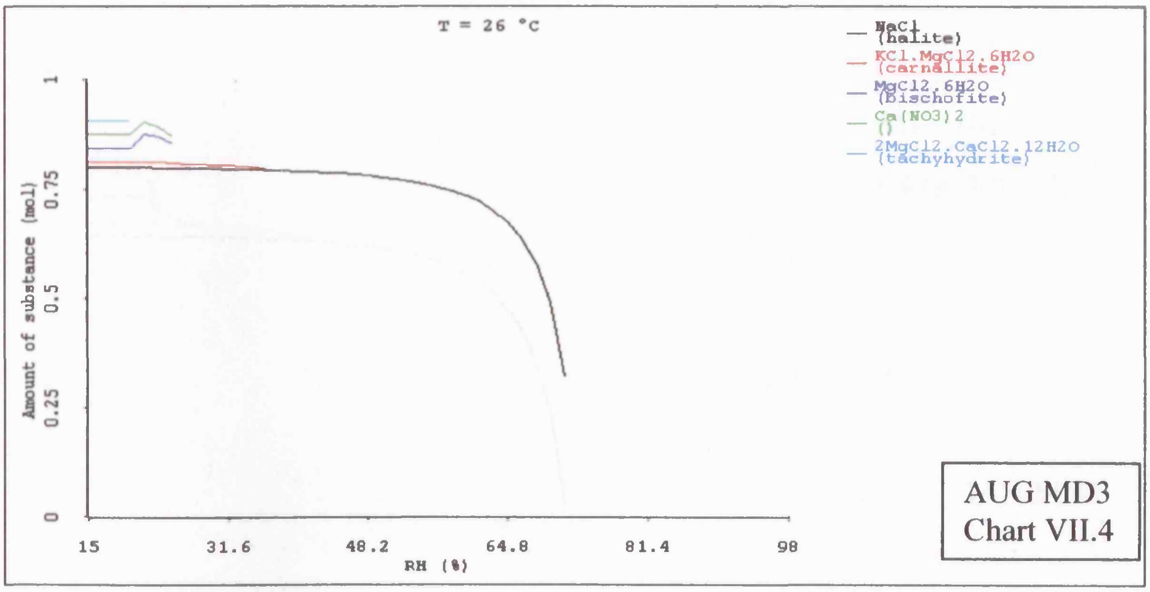
NOV MD3
Chart VII.1



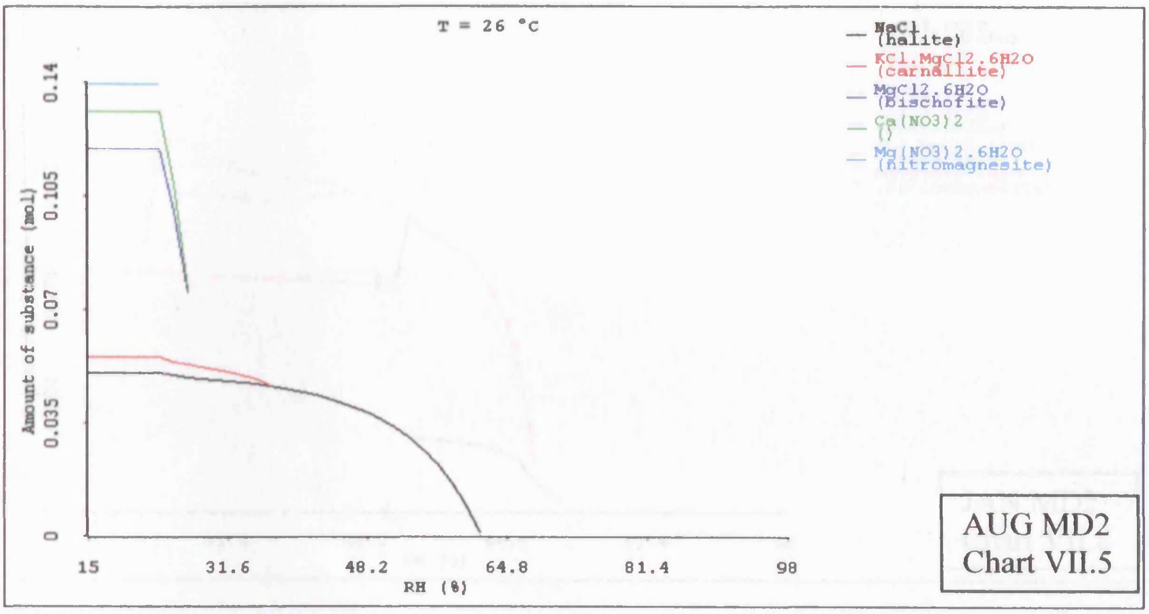
NOV MD2
Chart VII.2



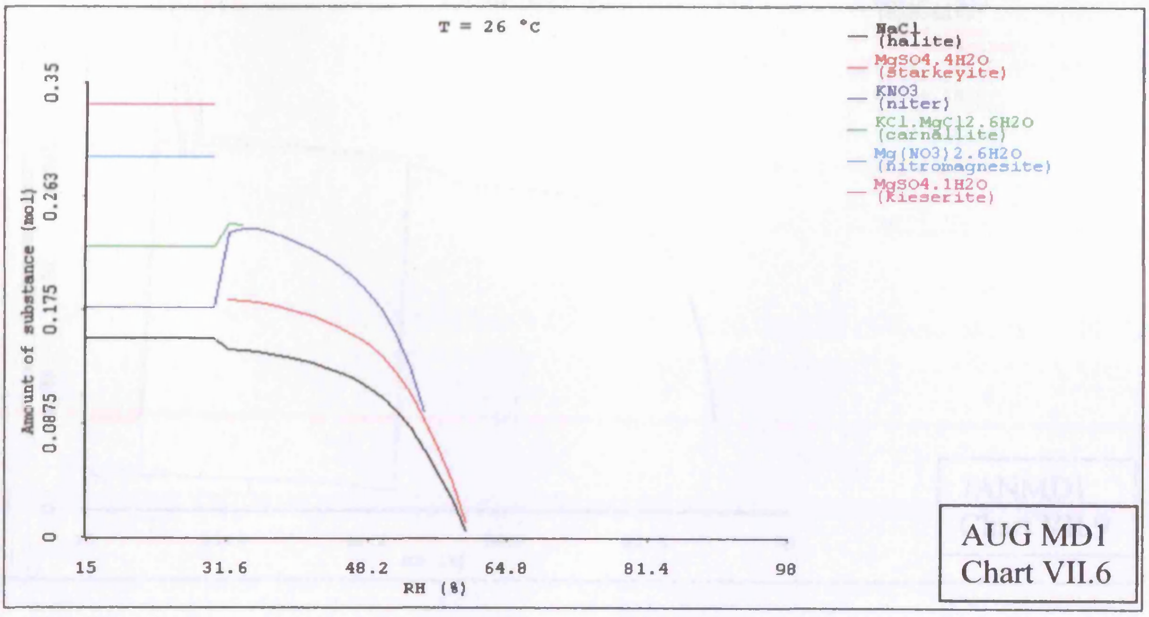
NOV MD1
Chart VII.3



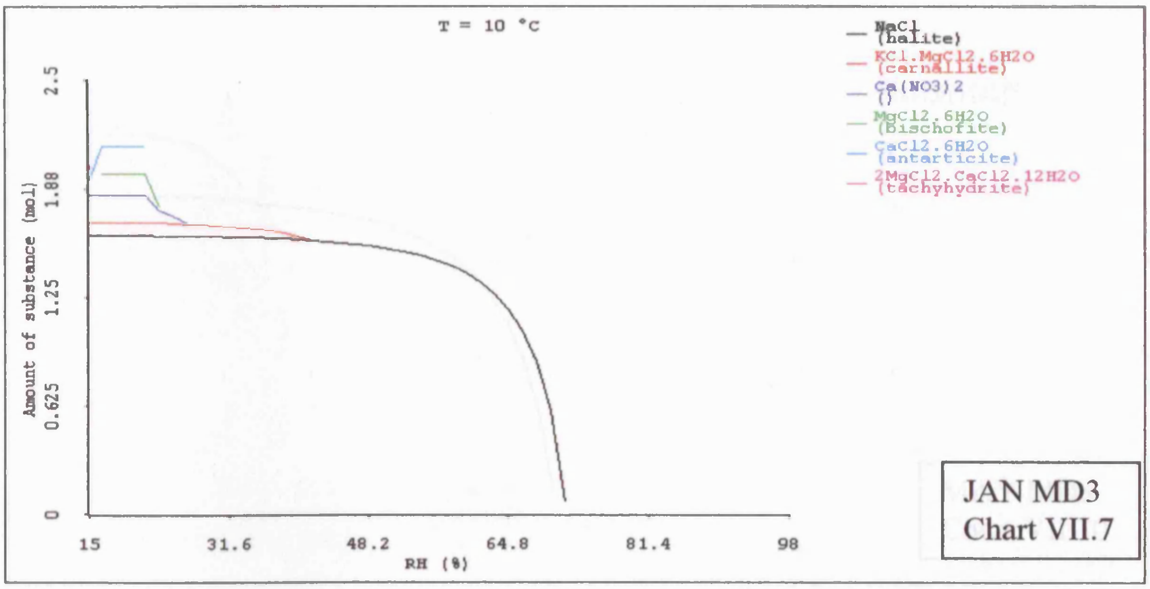
AUG MD3
Chart VII.4



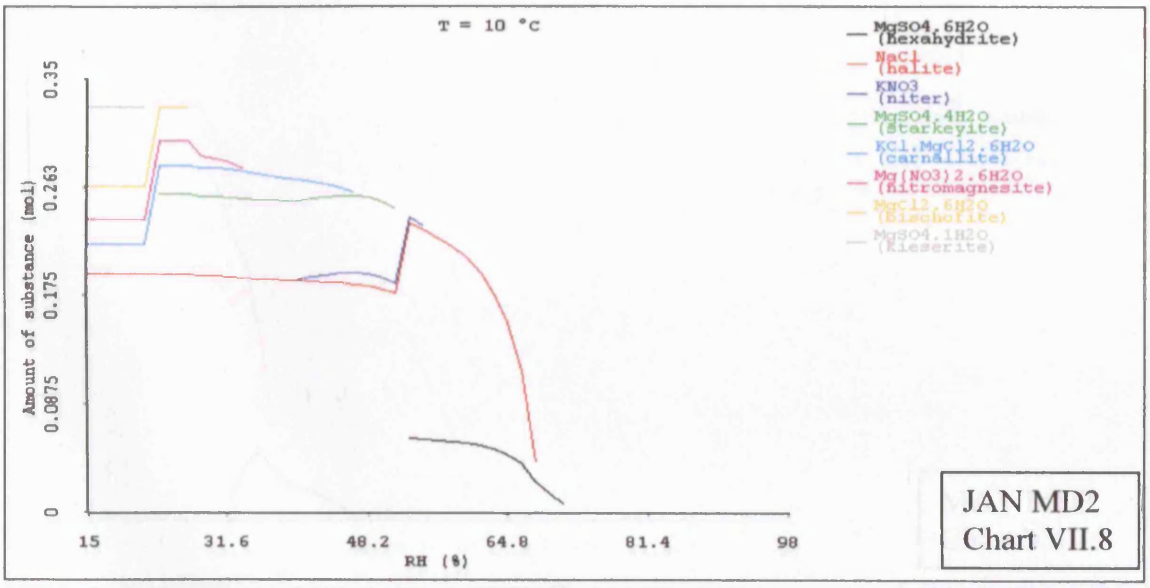
AUG MD2
Chart VII.5



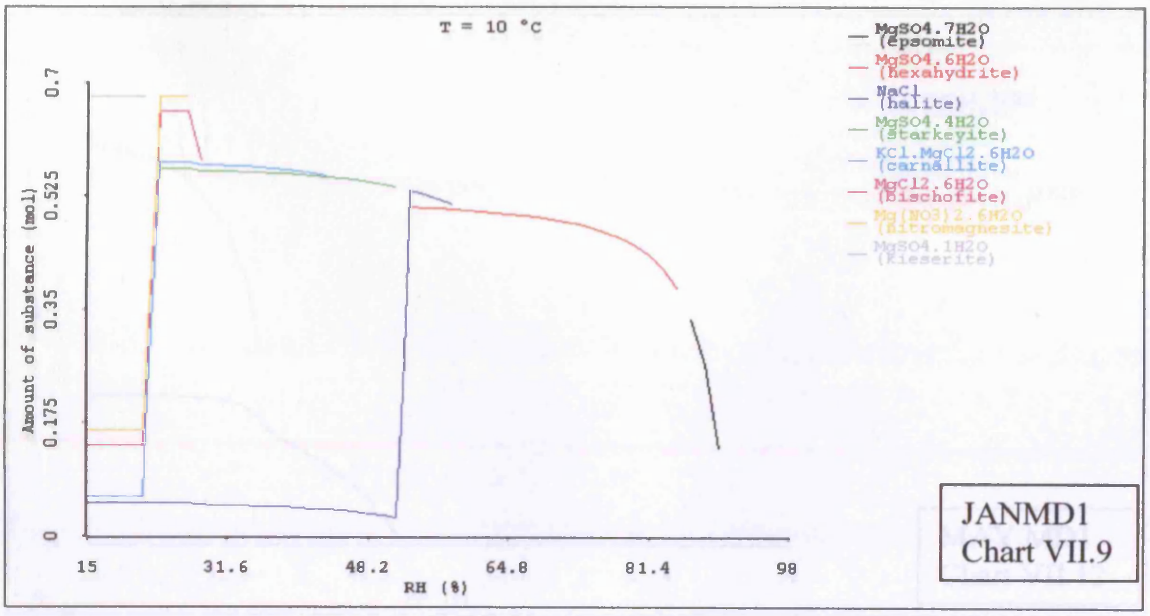
AUG MD1
Chart VII.6



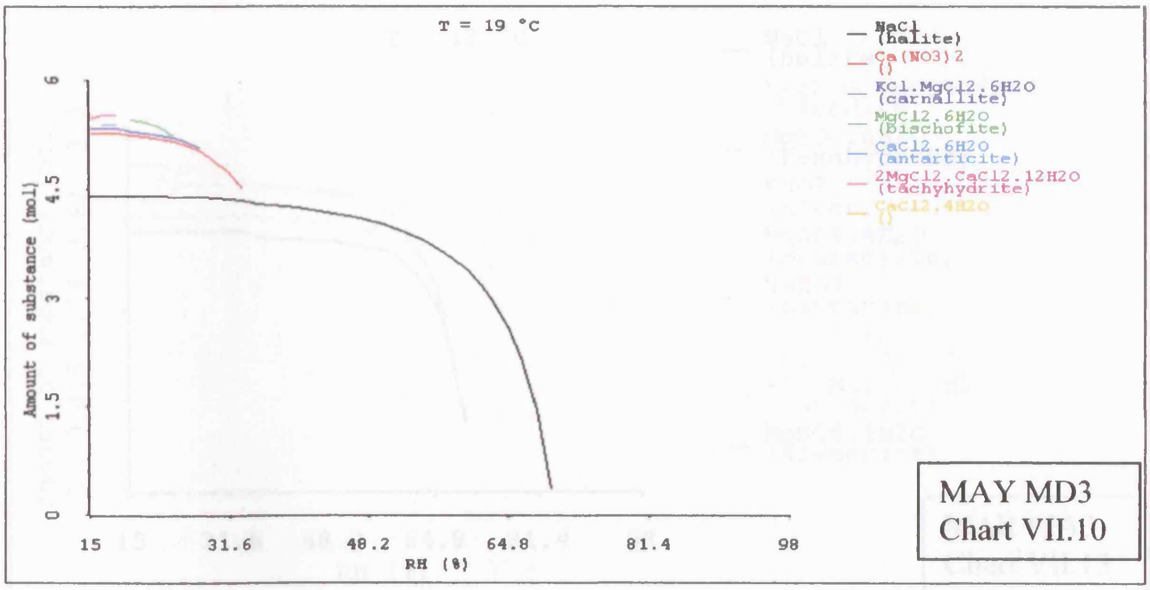
JAN MD3
Chart VII.7



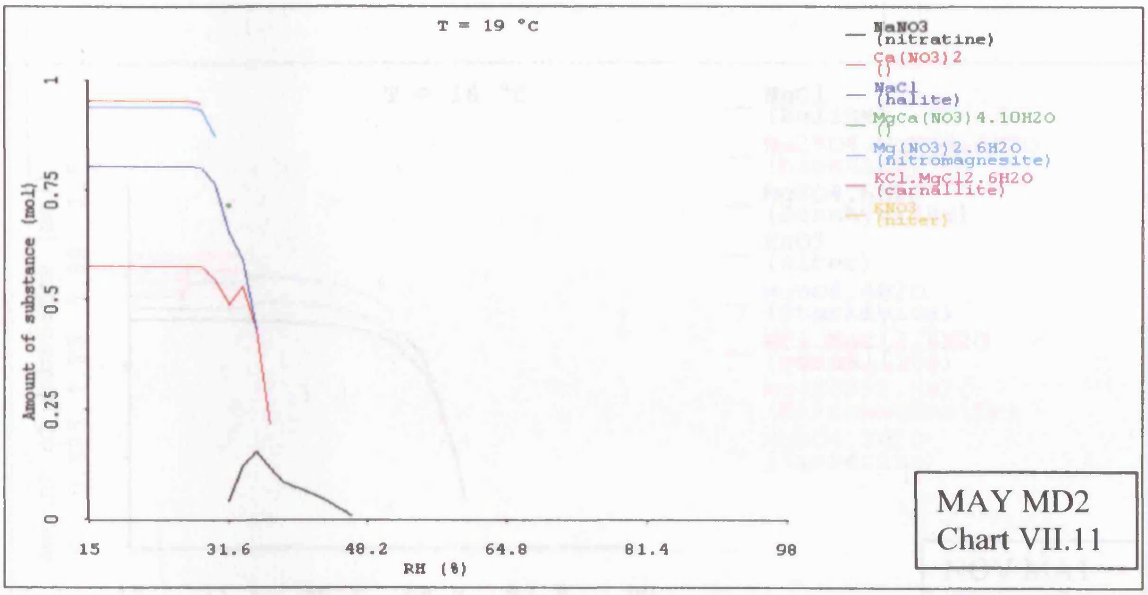
JAN MD2
Chart VII.8



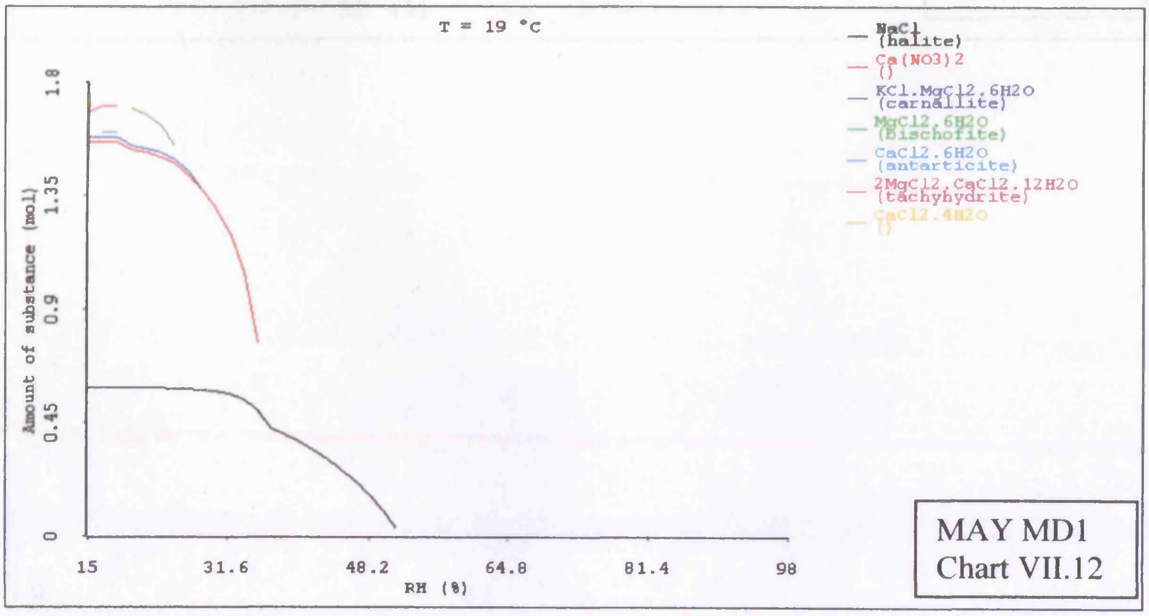
JANMD1
Chart VII.9



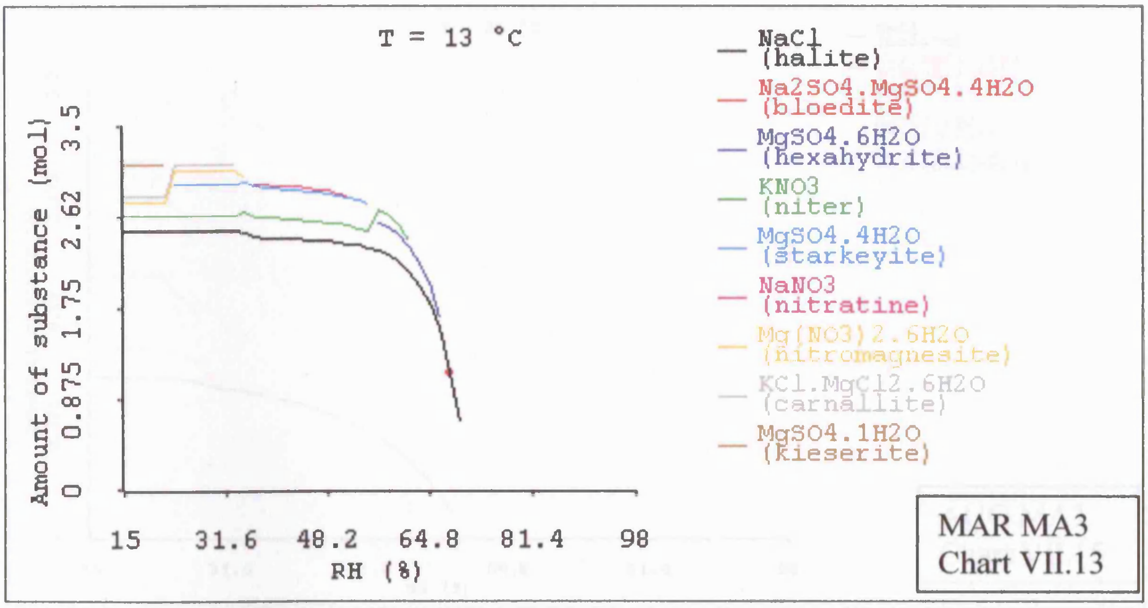
MAY MD3
Chart VII.10



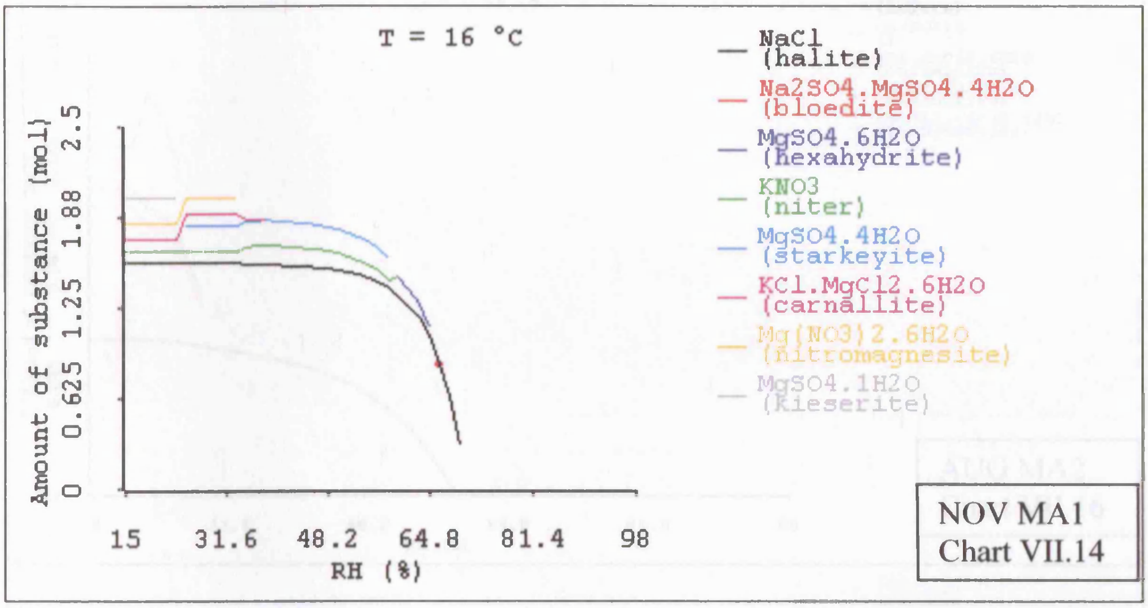
MAY MD2
Chart VII.11



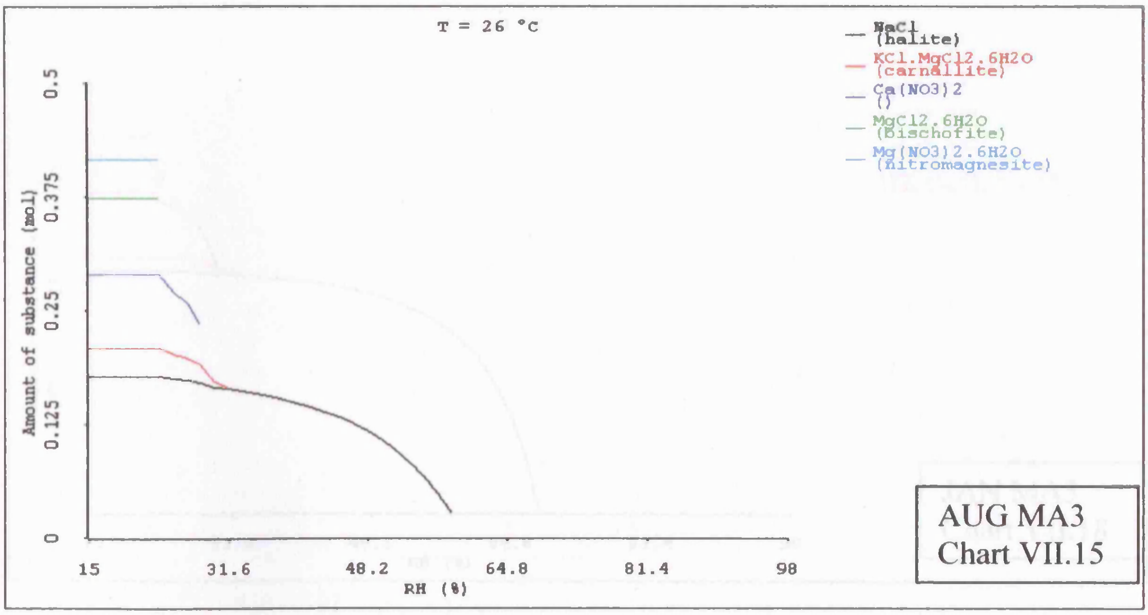
MAY MD1
Chart VII.12



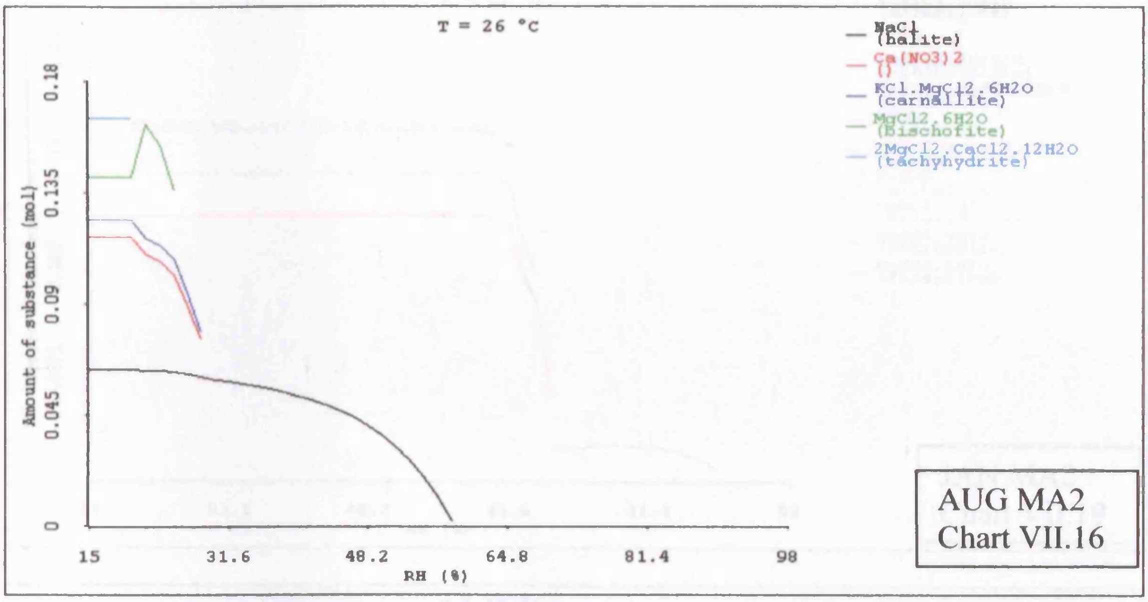
MAR MA3
Chart VII.13



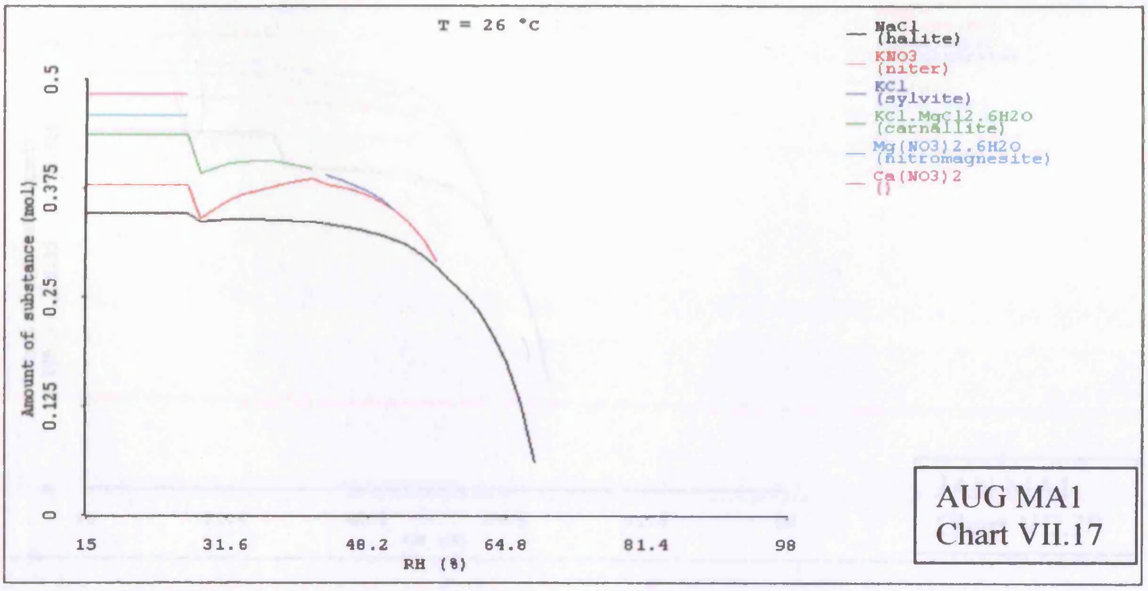
NOV MA1
Chart VII.14



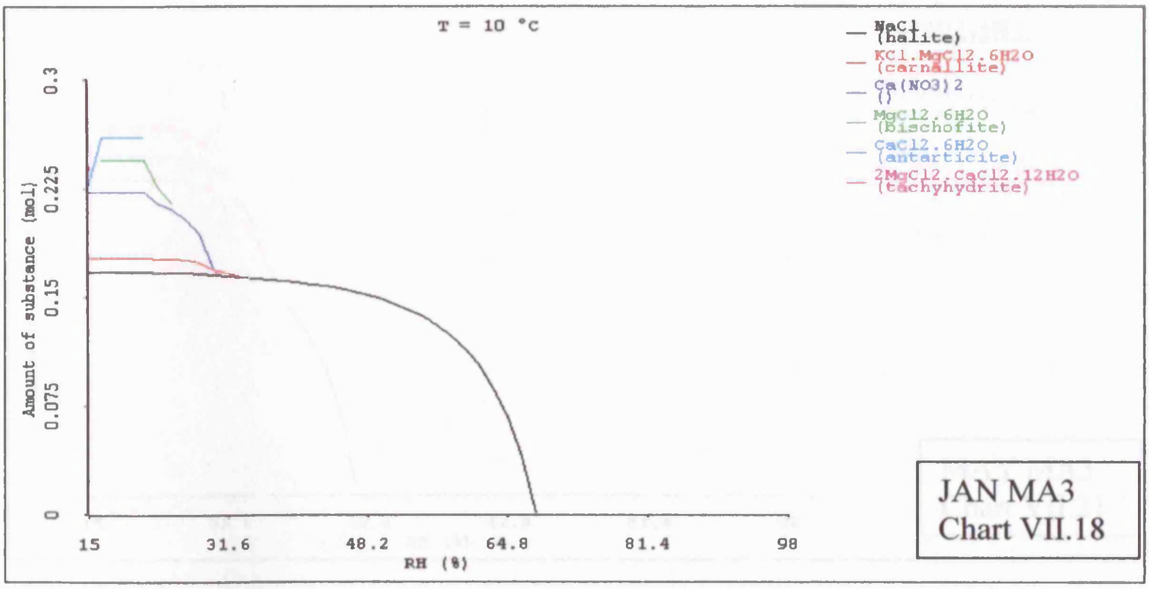
AUG MA3
Chart VII.15



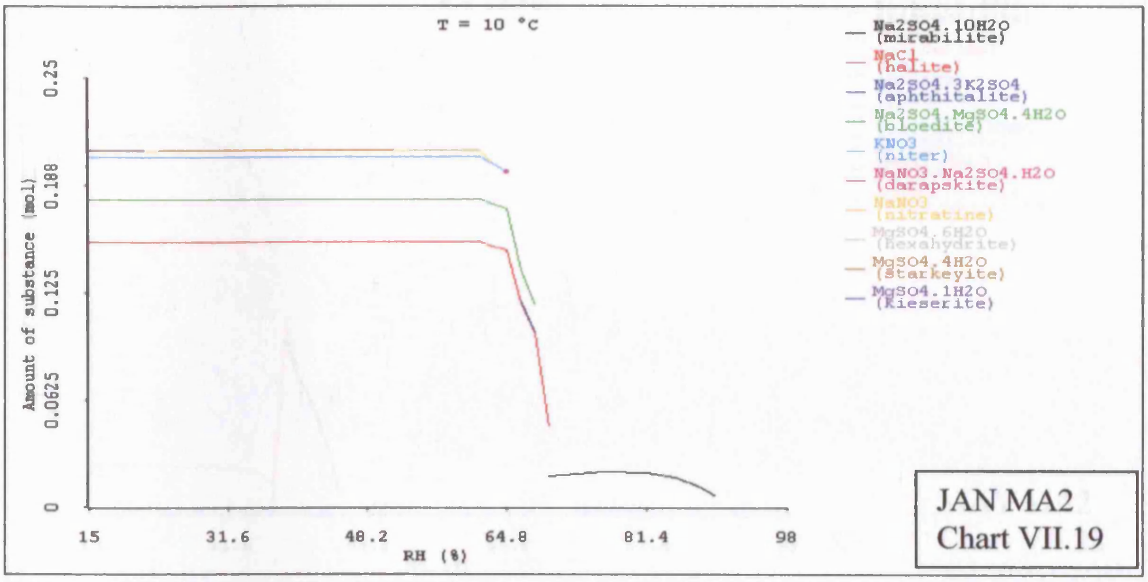
AUG MA2
Chart VII.16



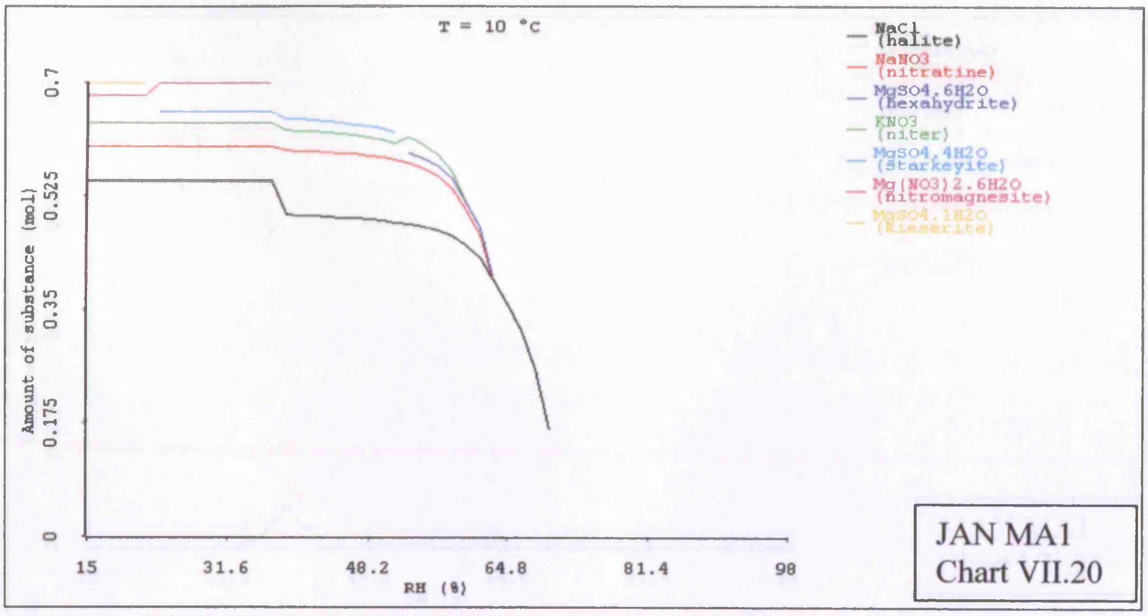
AUG MA1
Chart VII.17



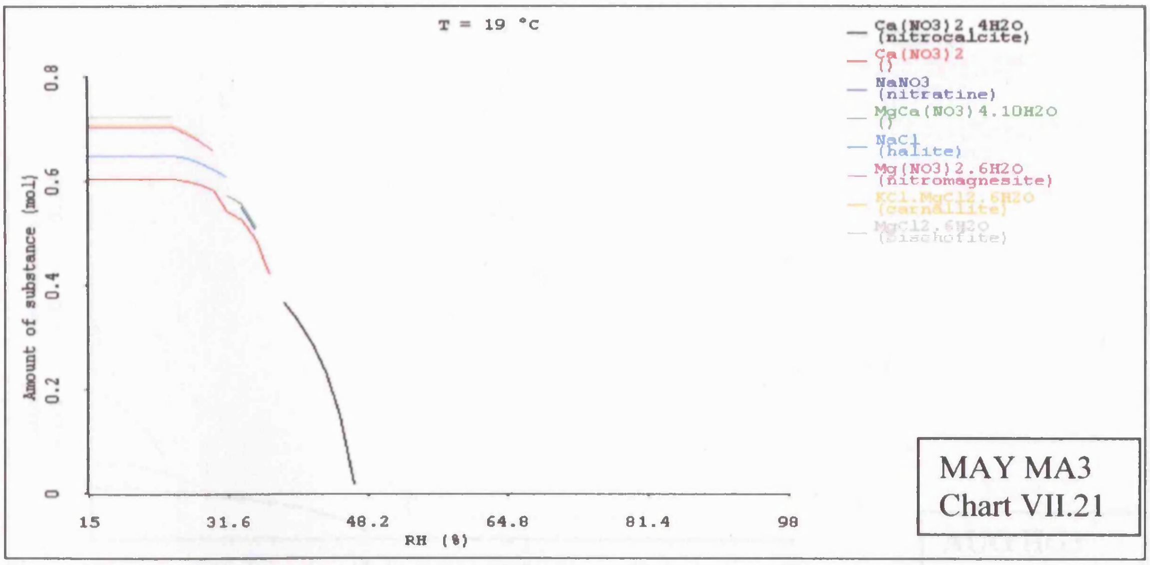
JAN MA3
Chart VII.18



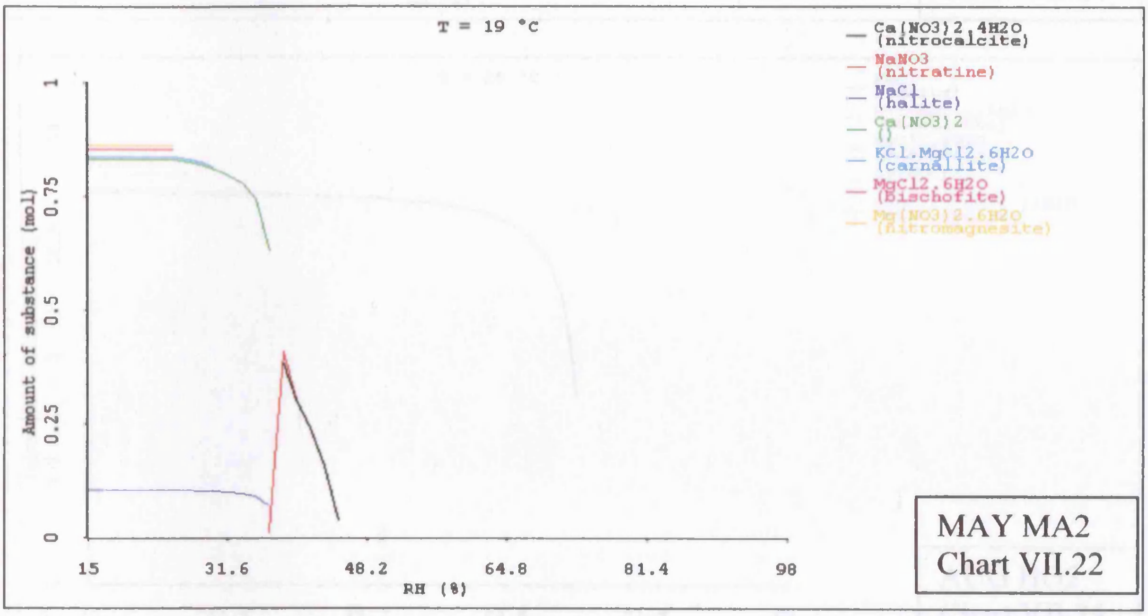
JAN MA2
Chart VII.19



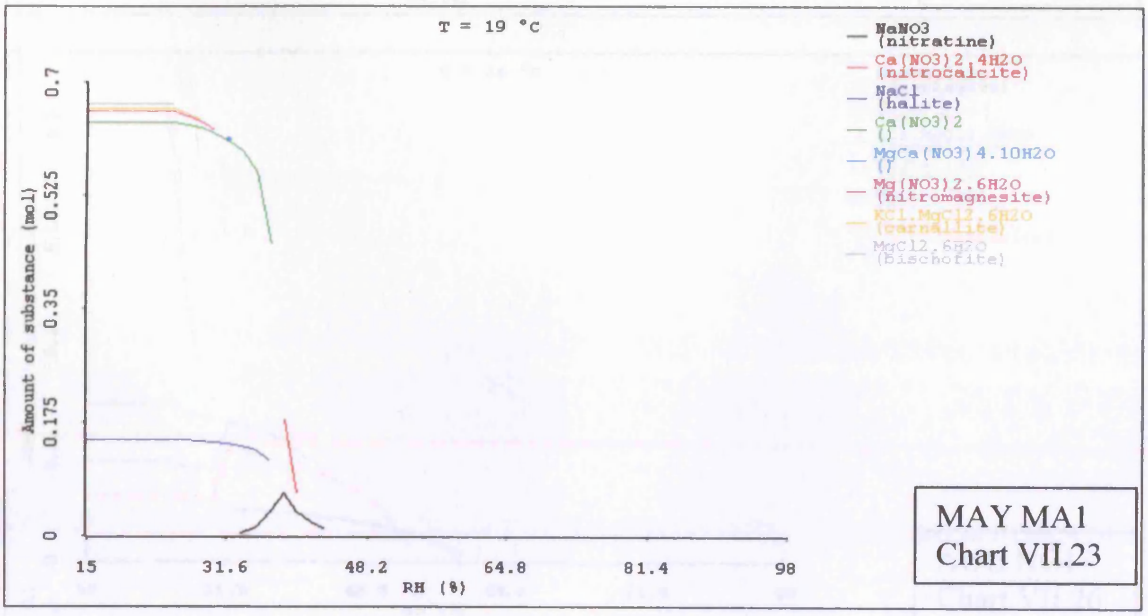
JAN MA1
Chart VII.20



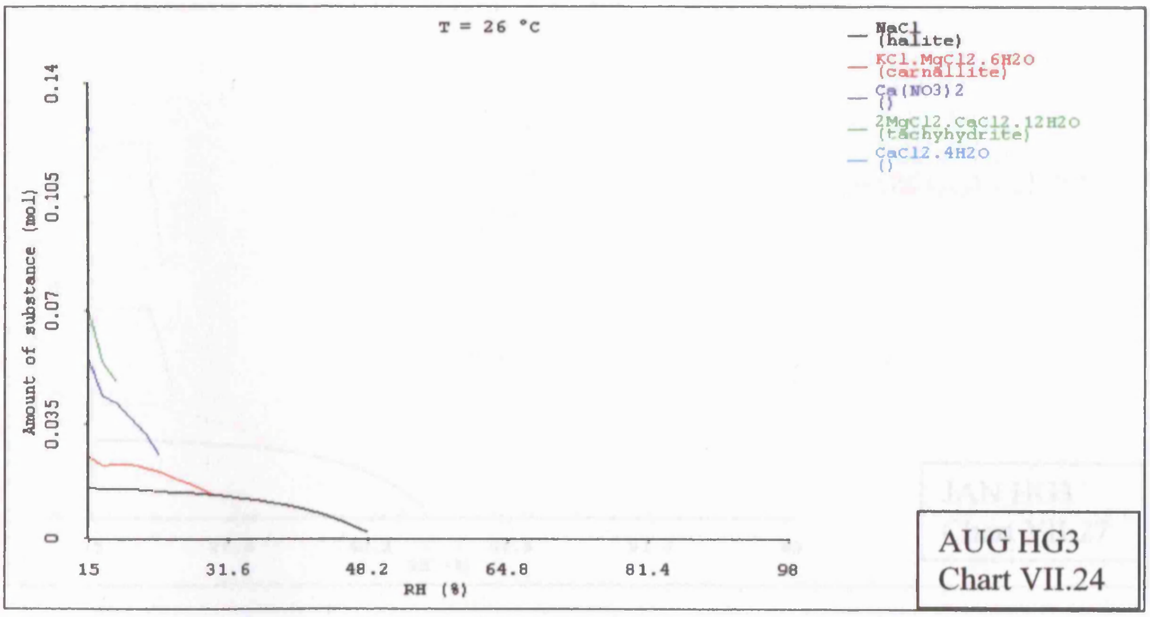
MAY MA3
Chart VII.21



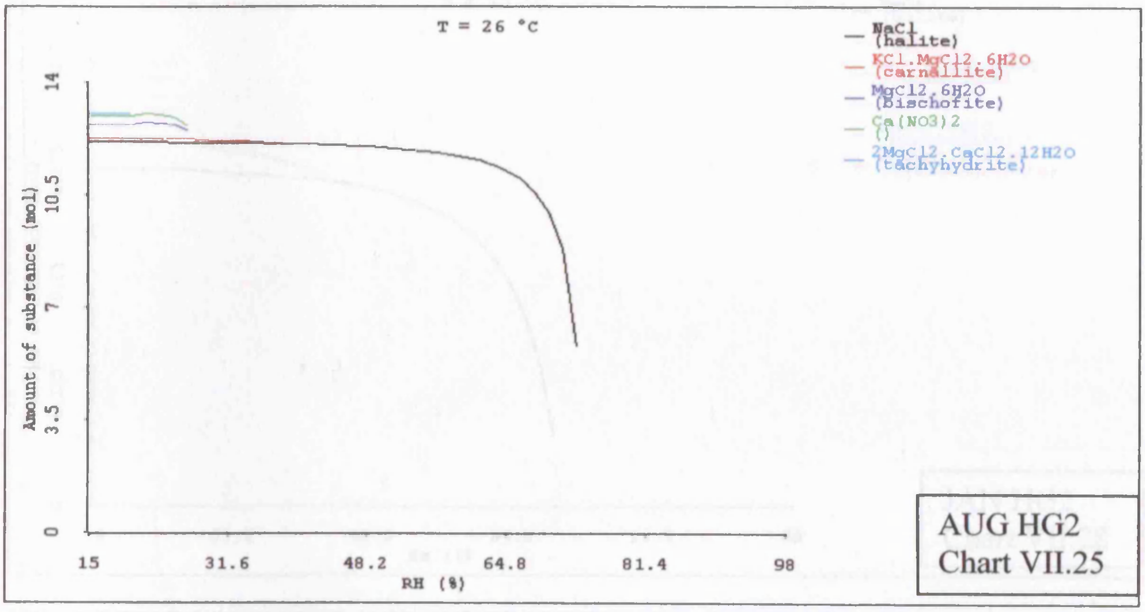
MAY MA2
Chart VII.22



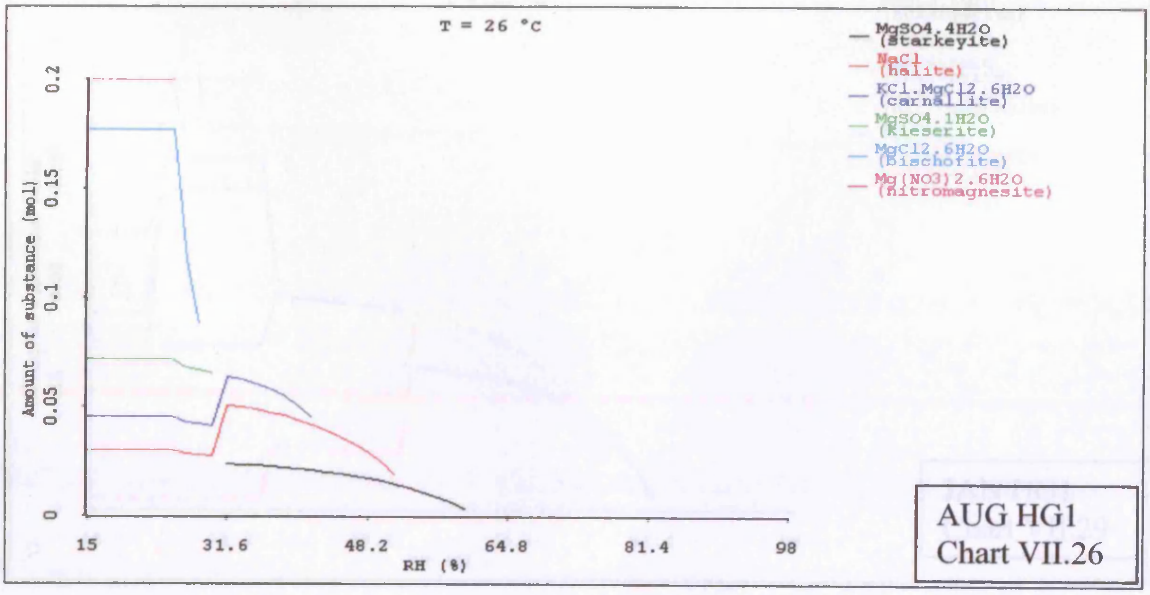
MAY MA1
Chart VII.23



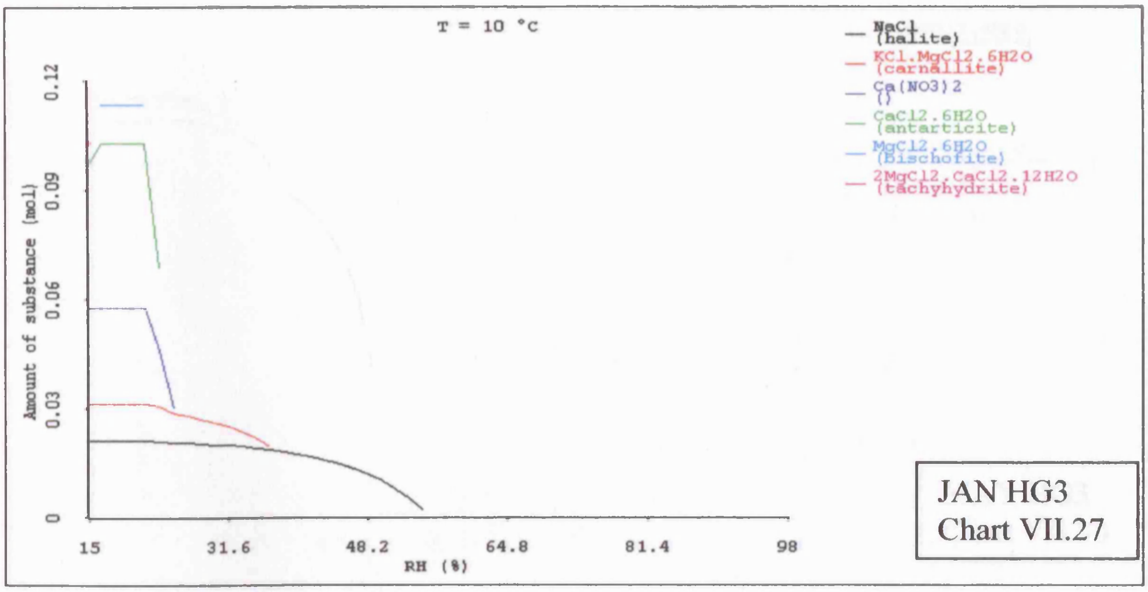
AUG HG3
Chart VII.24



AUG HG2
Chart VII.25



AUG HG1
Chart VII.26



JAN HG3
Chart VII.27

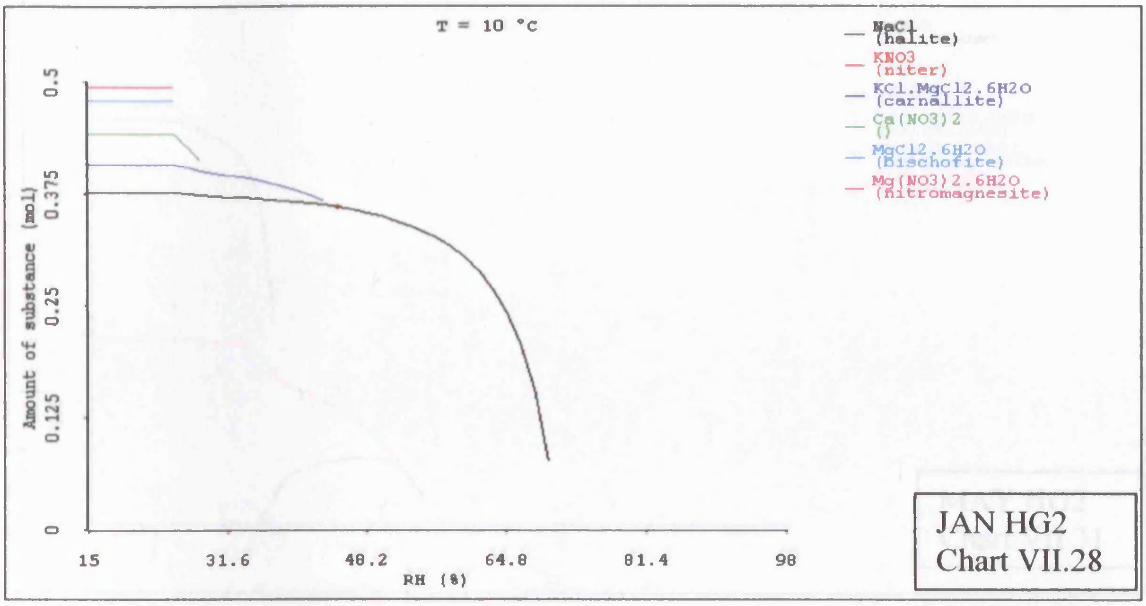


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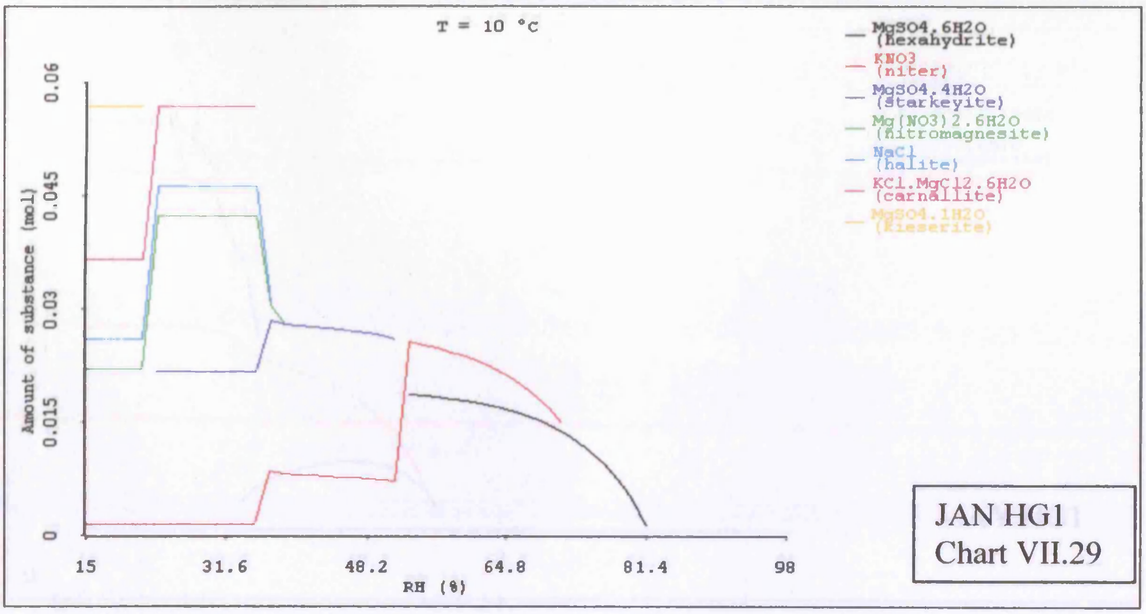
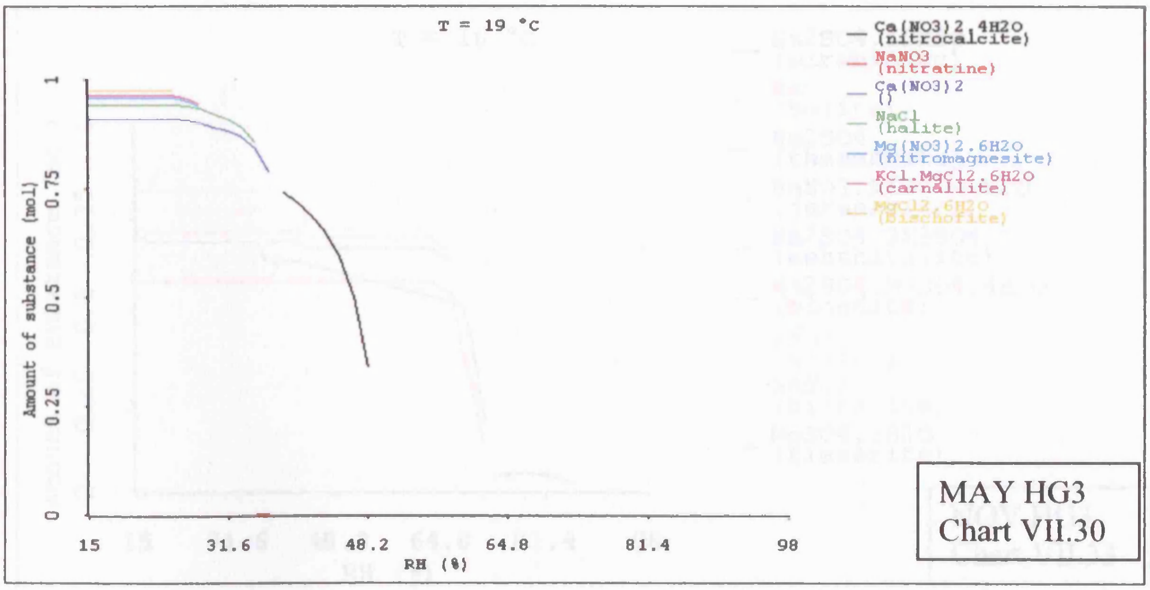
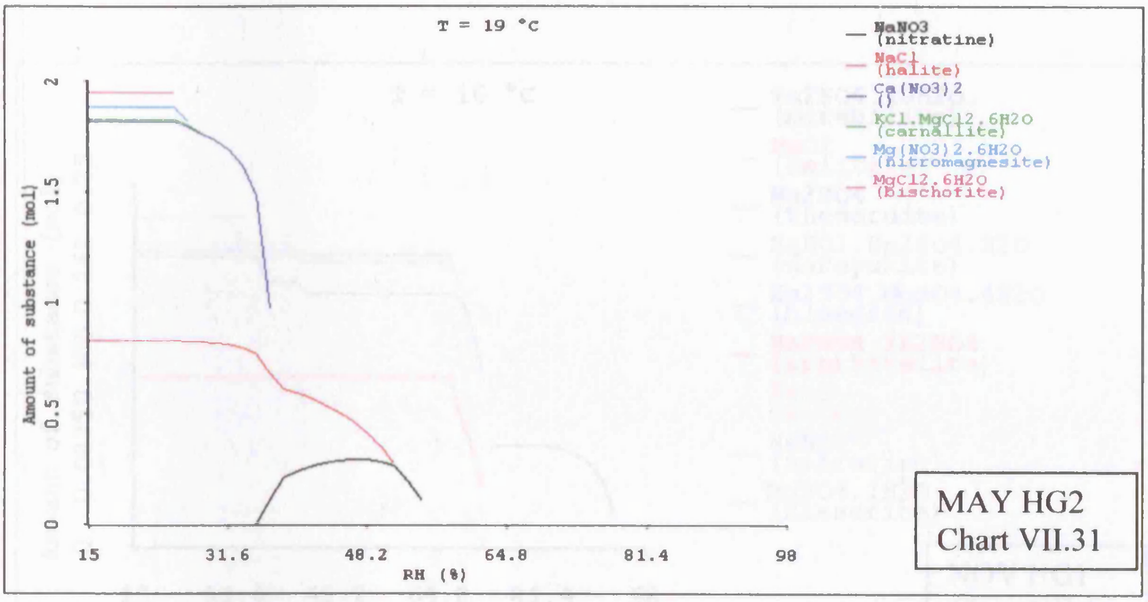
Chart VII.28



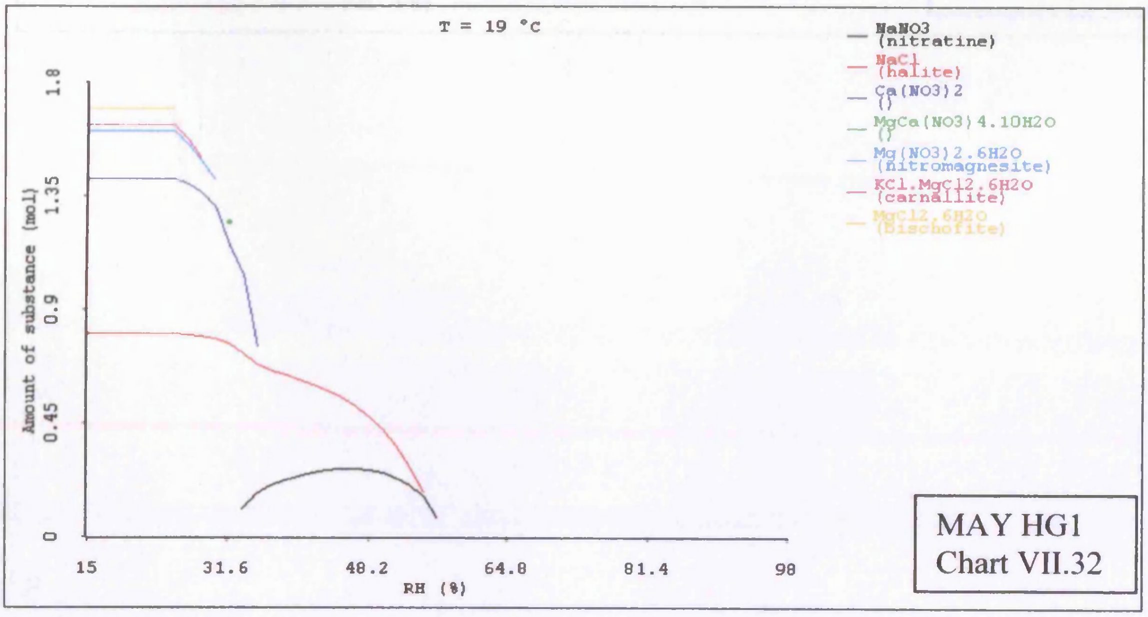
JAN HG1
Chart VII.29



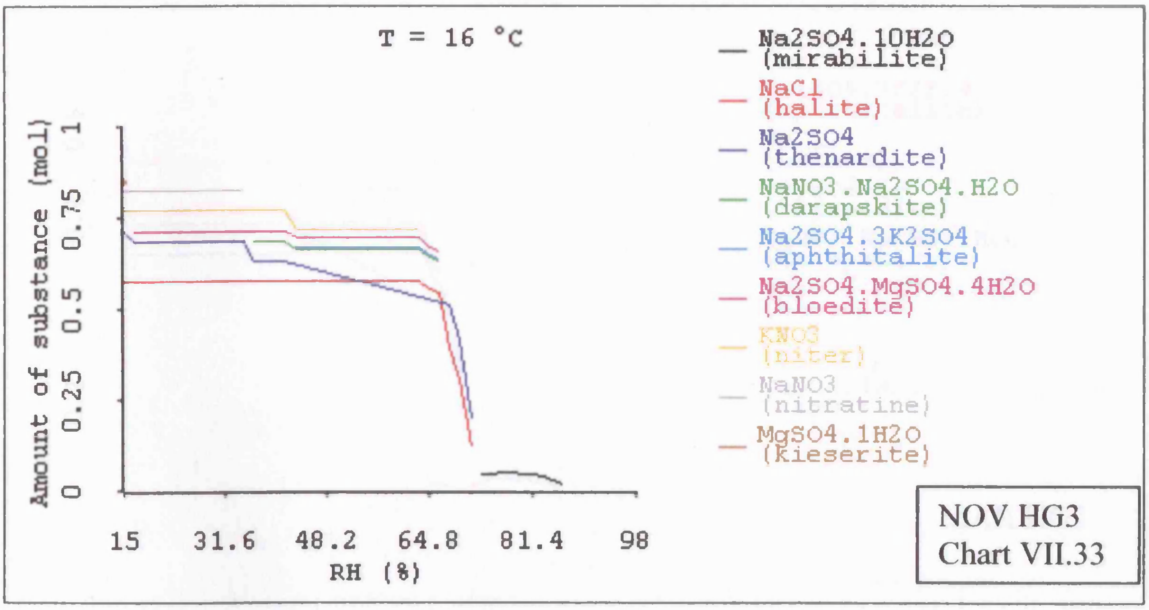
MAY HG3
Chart VII.30



MAY HG2
Chart VII.31



MAY HG1
Chart VII.32



NOV HG3
Chart VII.33

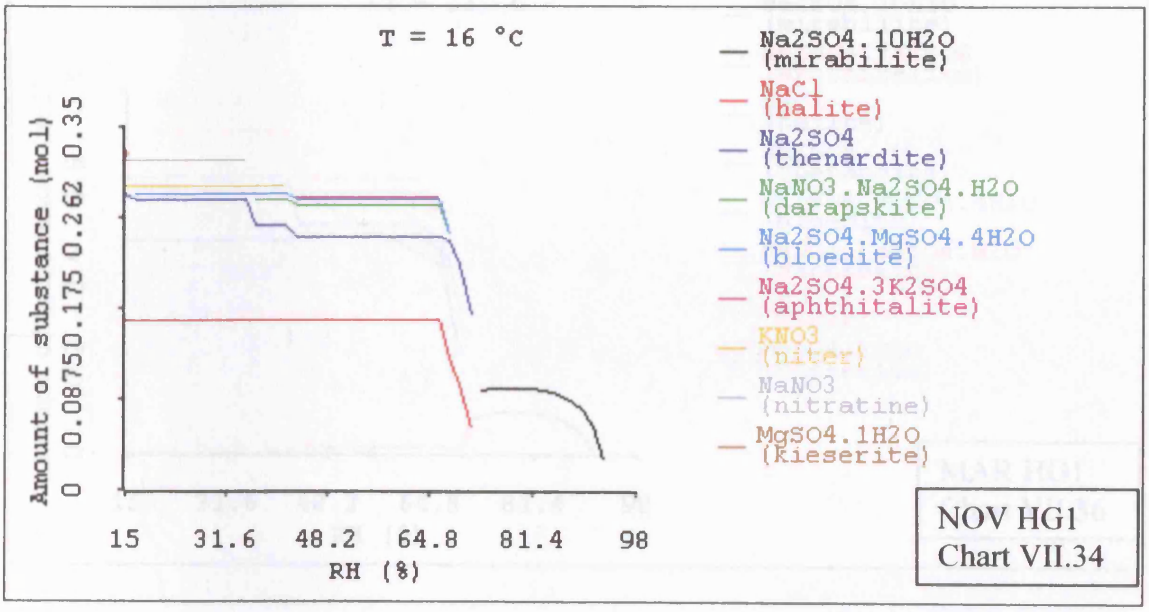


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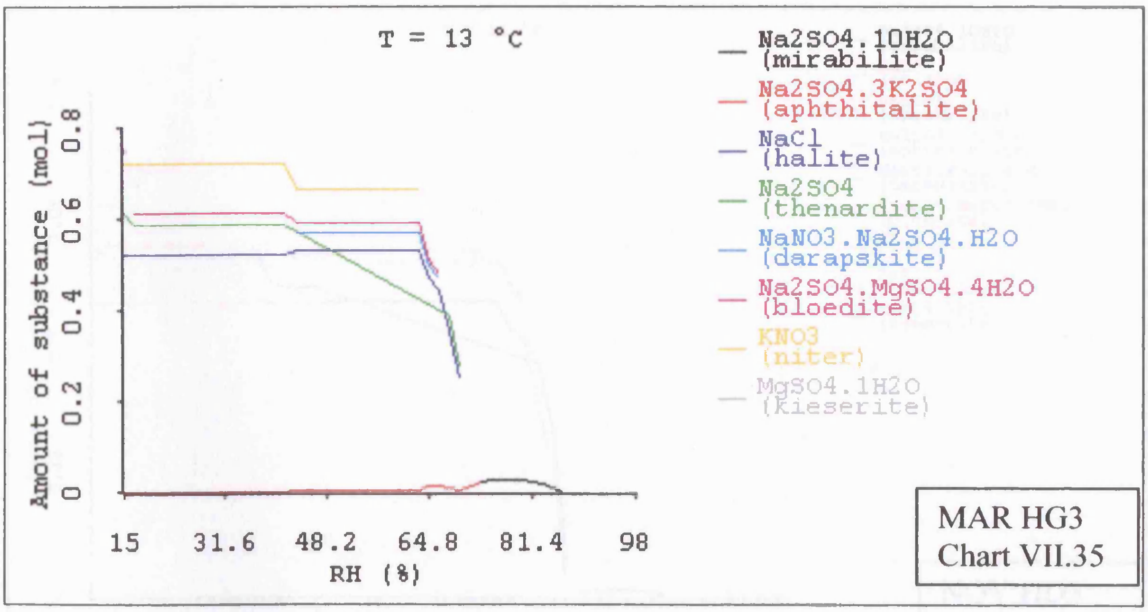
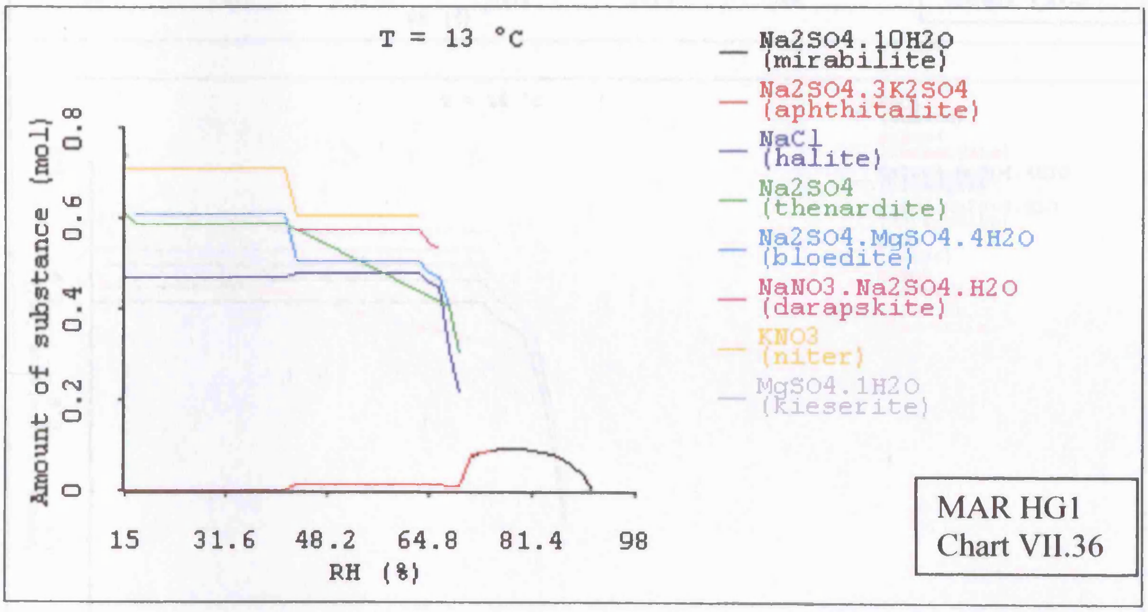
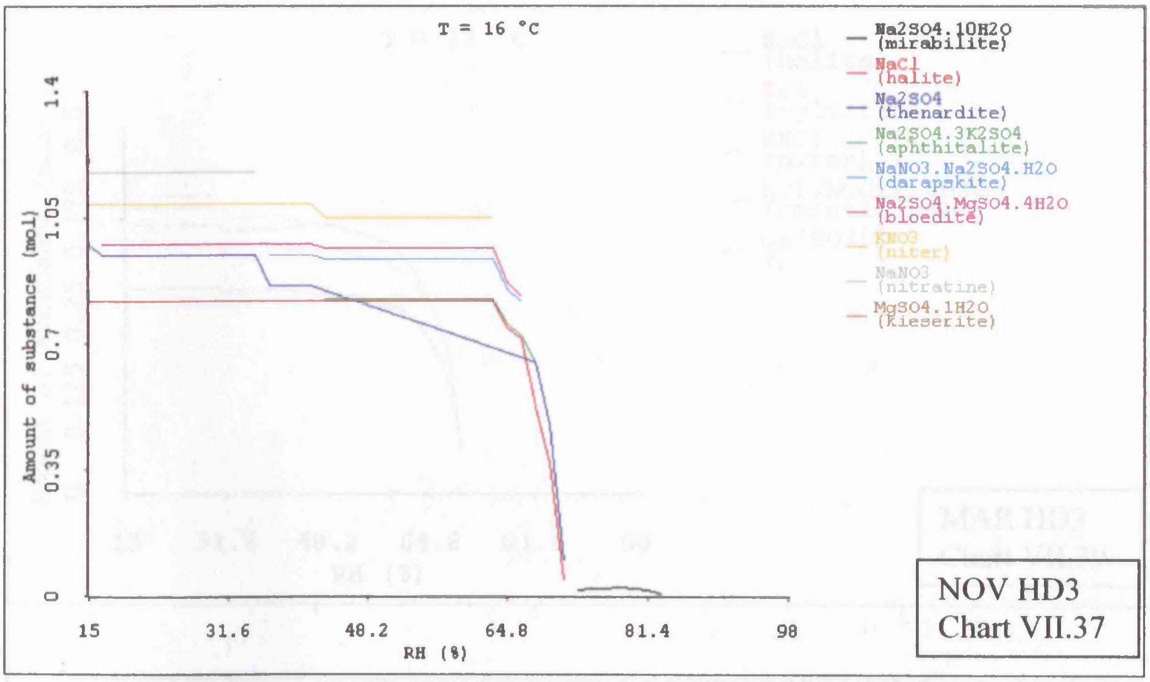
Chart VII.34



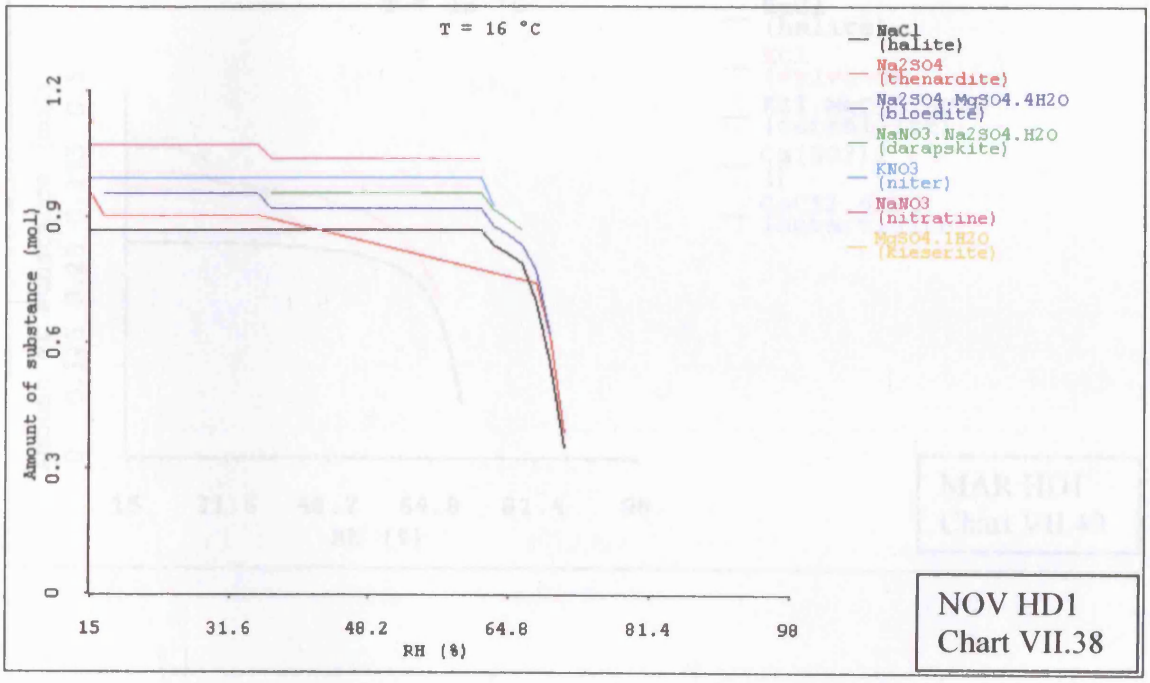
MAR HG3
Chart VII.35



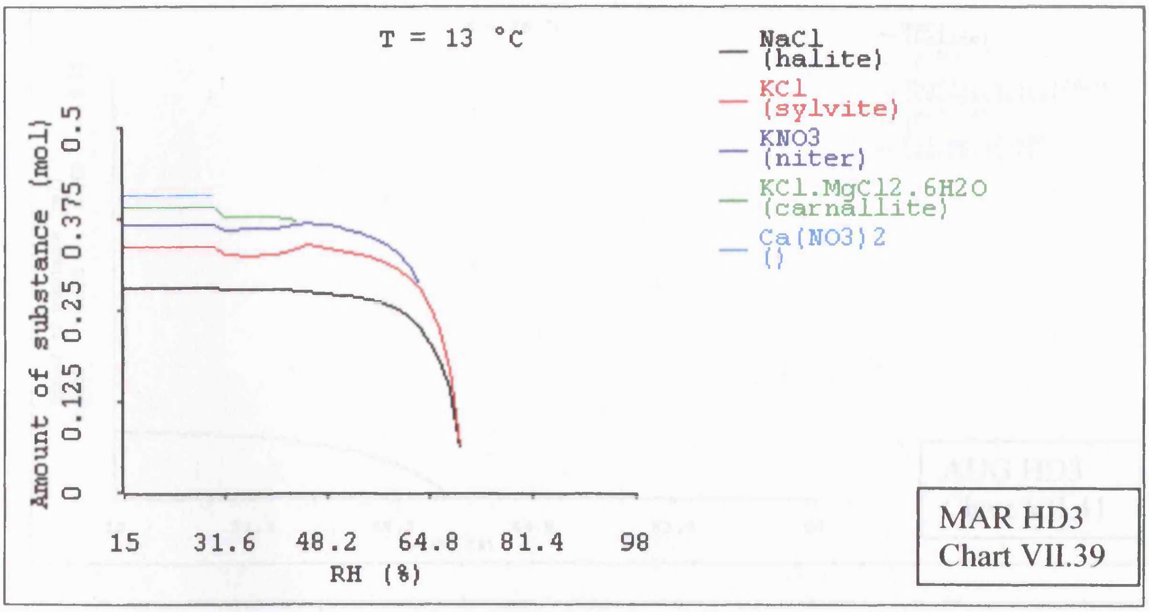
MAR HG1
Chart VII.36



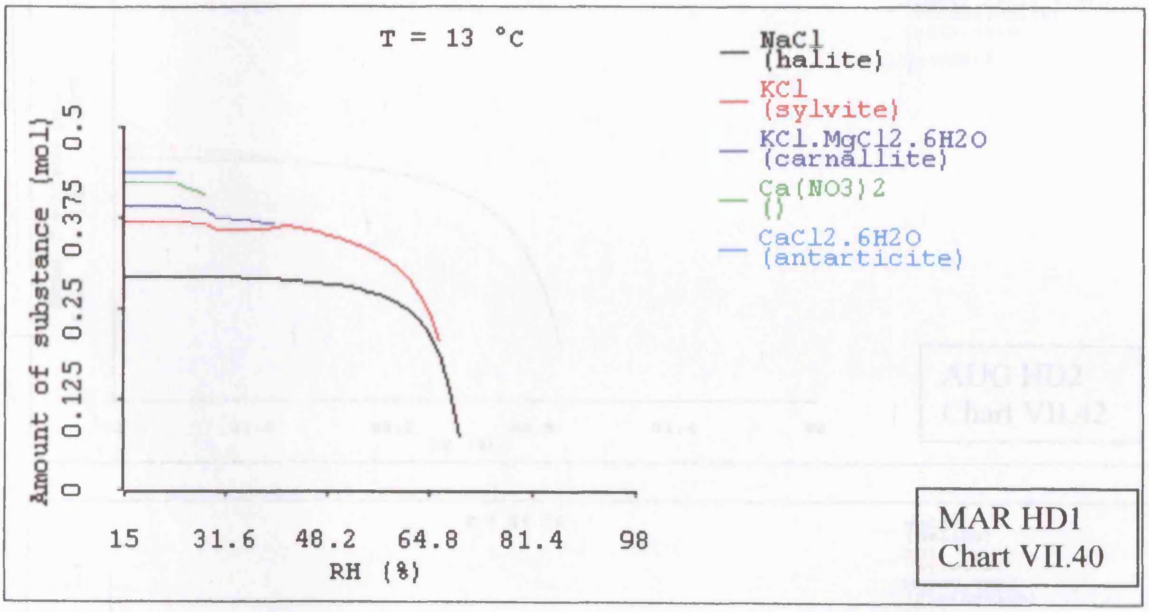
NOV HD3
Chart VII.37



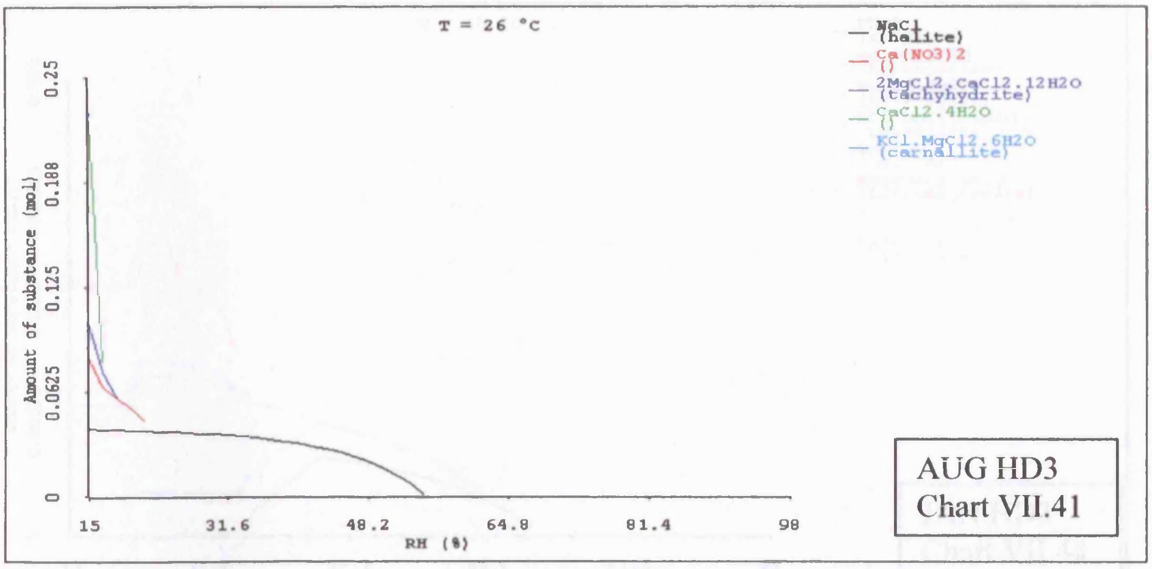
NOV HD1
Chart VII.38



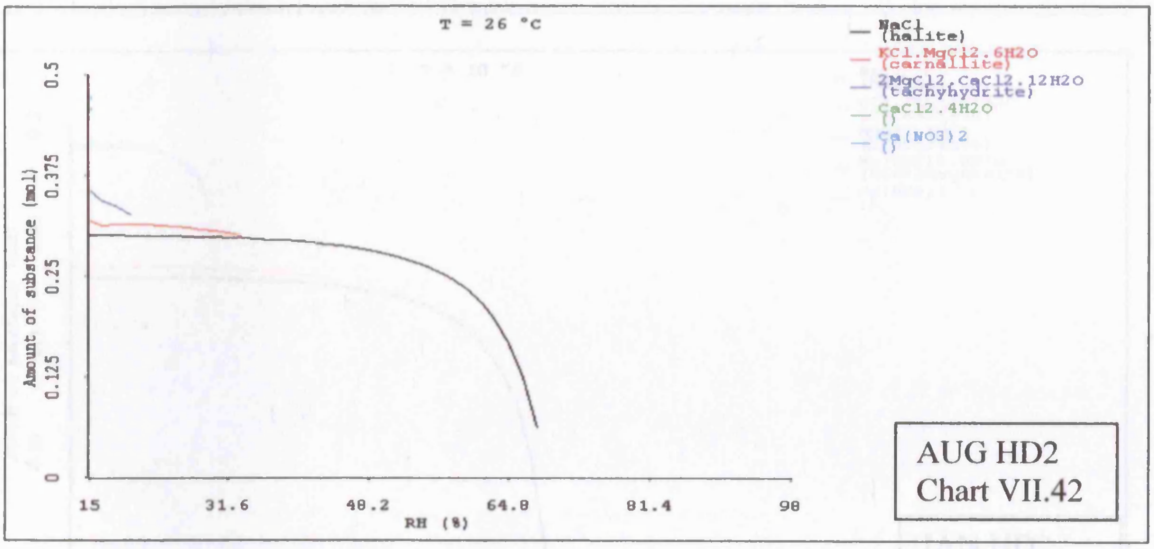
MAR HD3
Chart VII.39



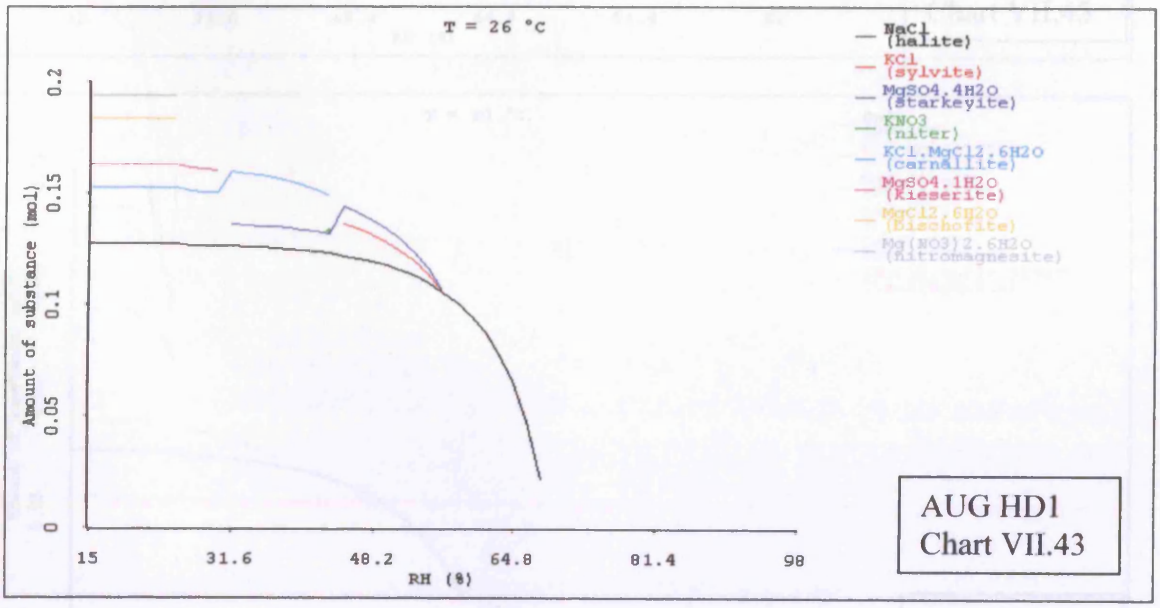
MAR HD1
Chart VII.40



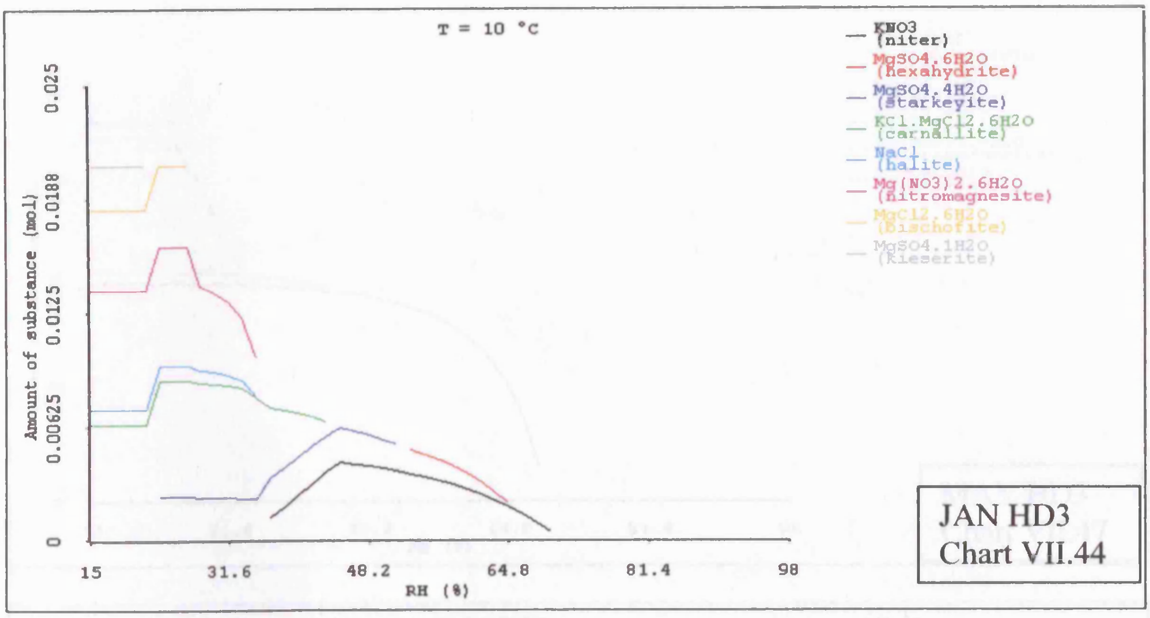
AUG HD3
Chart VII.41



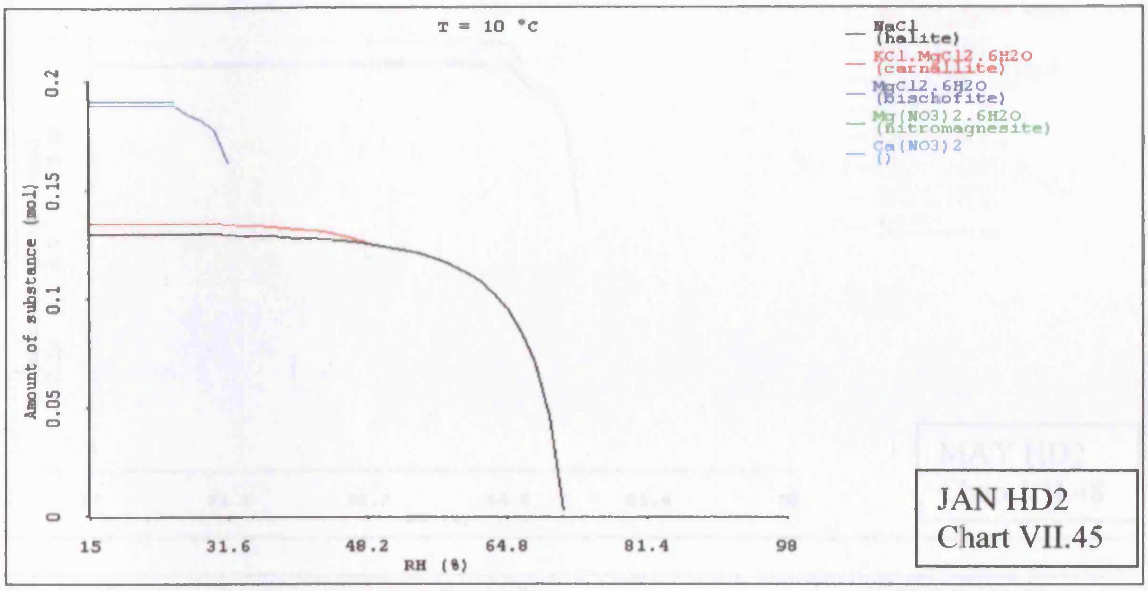
AUG HD2
Chart VII.42



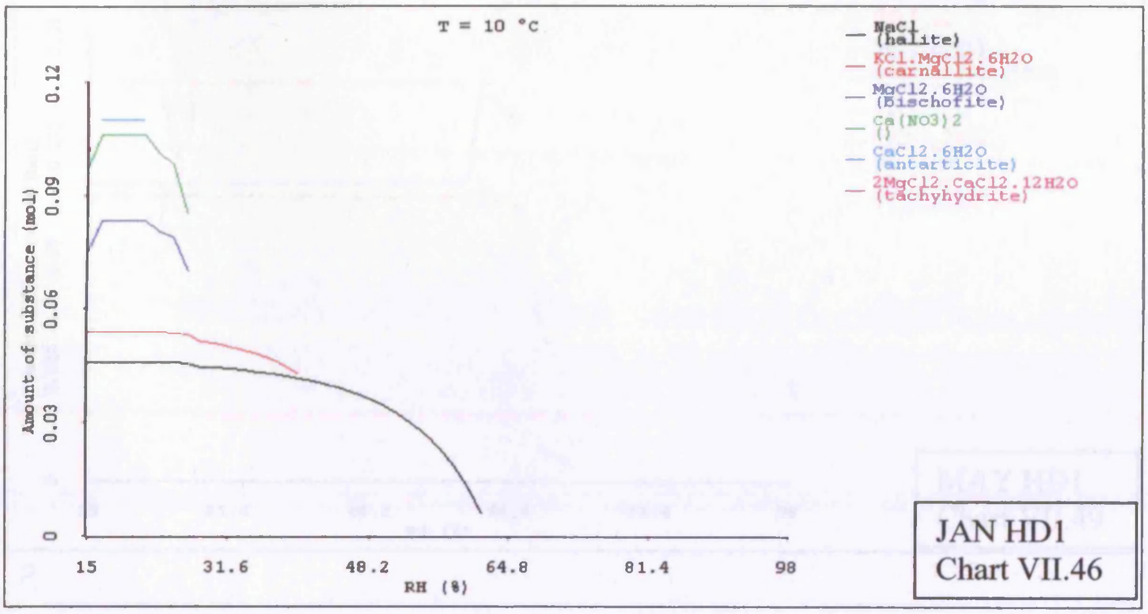
AUG HD1
Chart VII.43



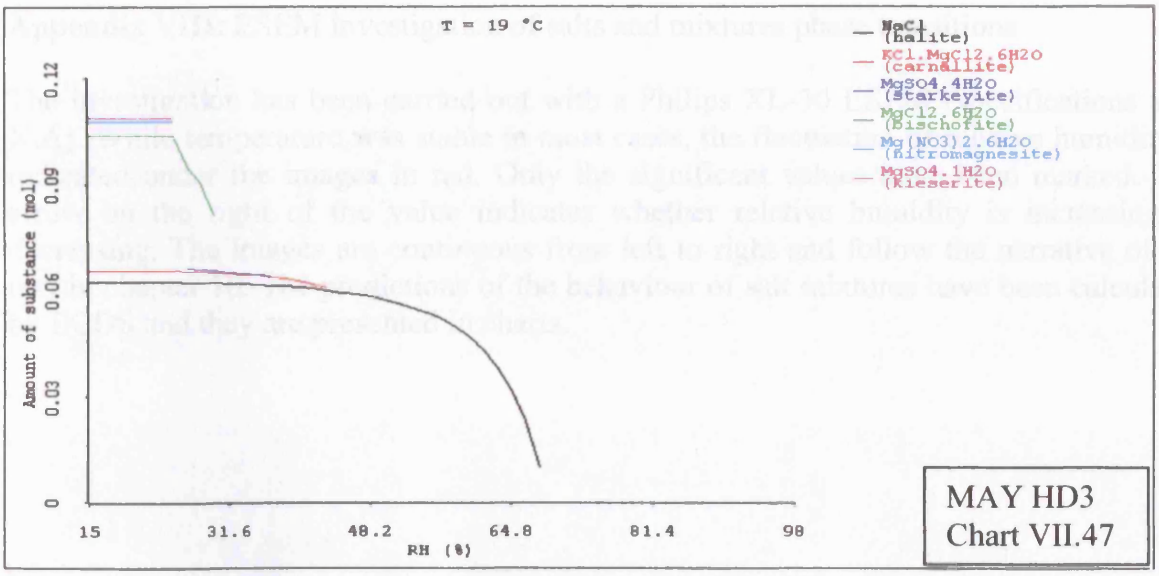
JAN HD3
Chart VII.44



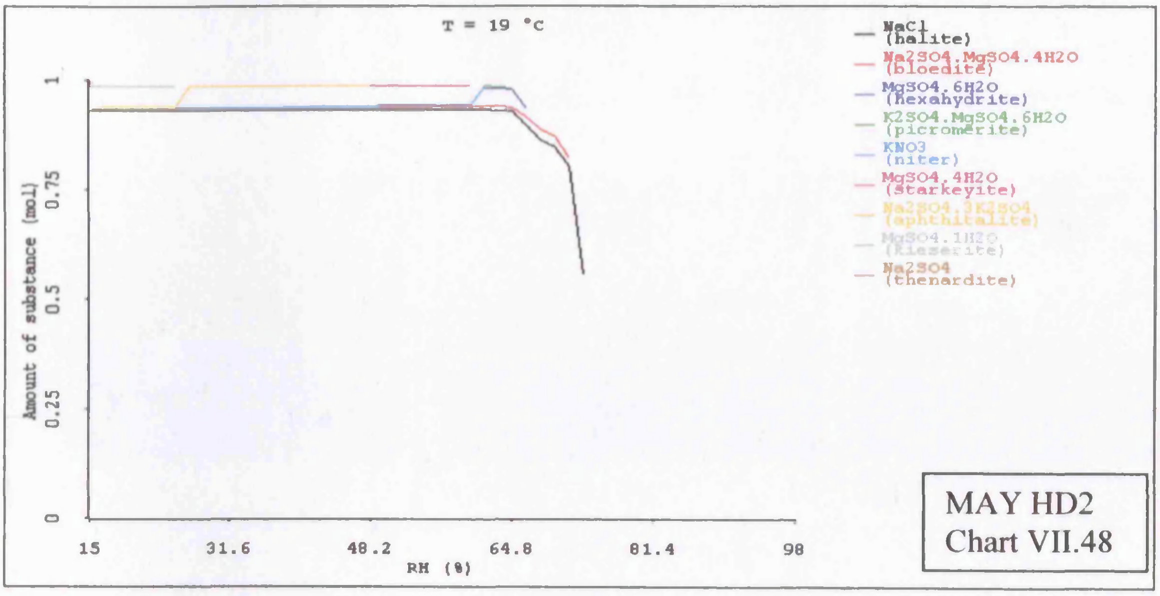
JAN HD2
Chart VII.45



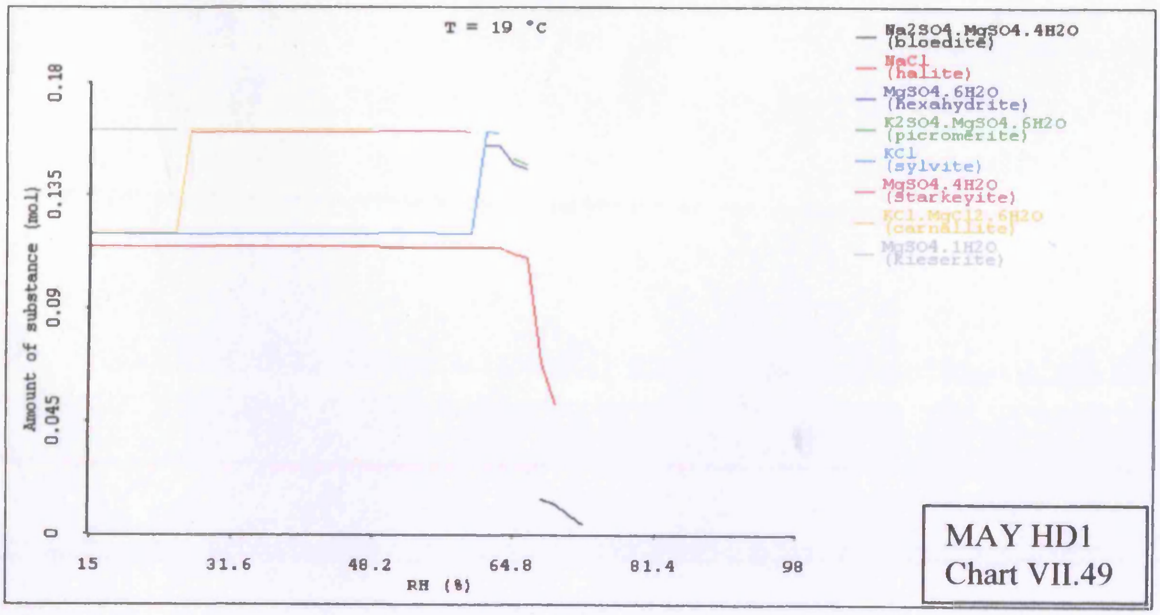
JAN HD1
Chart VII.46



MAY HD3
Chart VII.47



MAY HD2
Chart VII.48



MAY HD1
Chart VII.49

Appendix VIII: ESEM investigation of salts and mixtures phase transitions

The investigation has been carried out with a Philips XL-30 ESEM (specifications app. X.A). While temperature was stable in most cases, the fluctuation of relative humidity is indicated under the images in red. Only the significant values have been marked. The arrow on the right of the value indicates whether relative humidity is increasing or decreasing. The images are continuous from left to right and follow the narrative of the text in chapter 10. The predictions of the behaviour of salt mixtures have been calculated by ECOS and they are presented in charts.

Table 1. NaCl

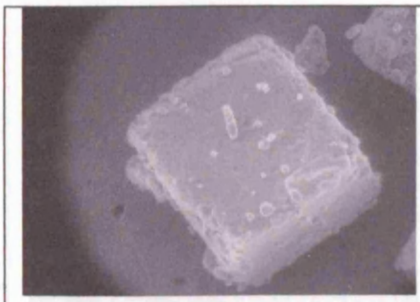
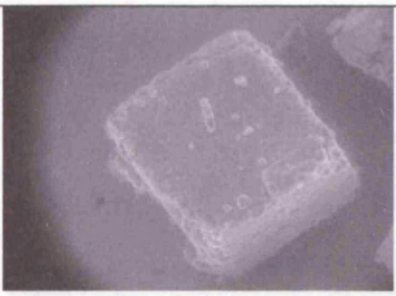
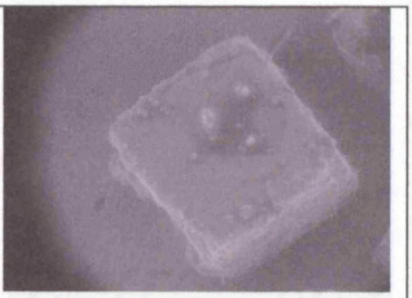
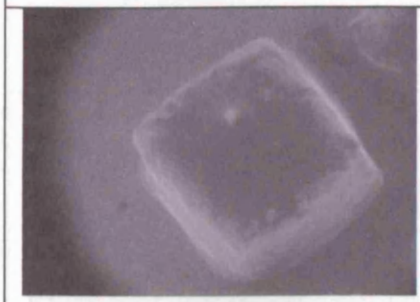
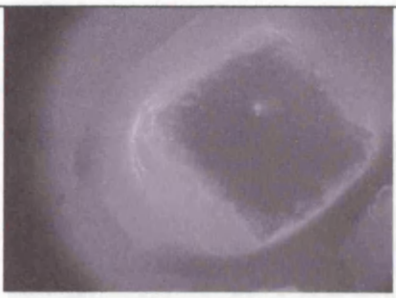
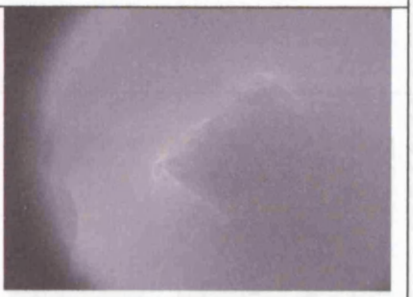
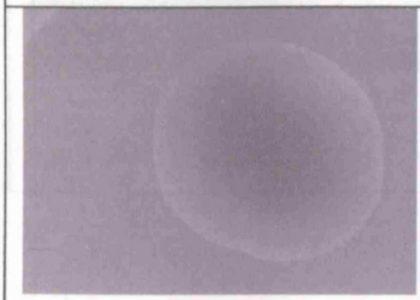
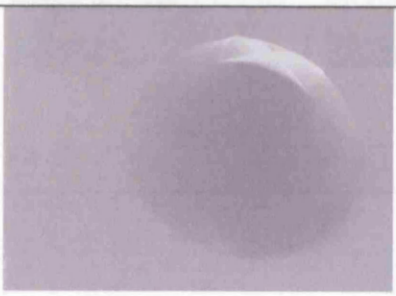
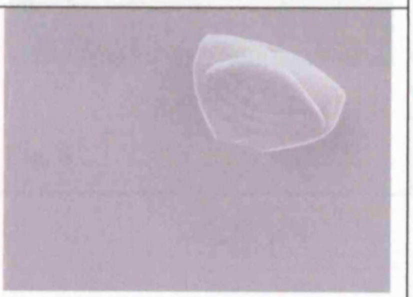
 **Fig. 1**	 **Fig. 2** 71.7%▲	 **Fig. 3**
 **Fig. 4**	 **Fig. 5**	 **Fig. 6**
 **Fig. 7** 73.4%▼	 **Fig. 8** 53.4%	 **Fig. 9**

Table 2. Mg_2SO_4

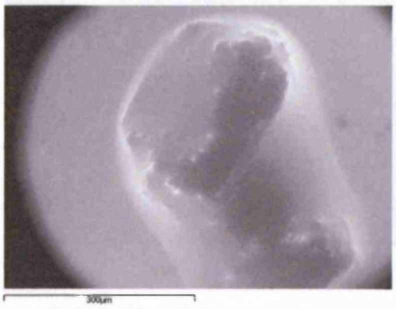
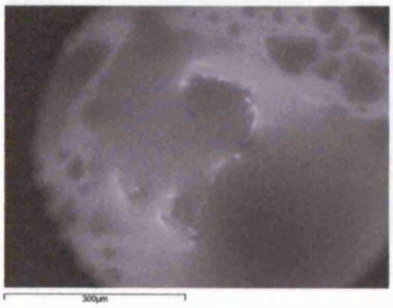
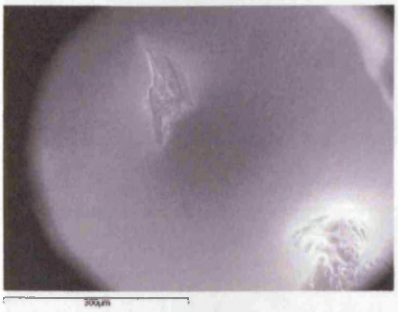
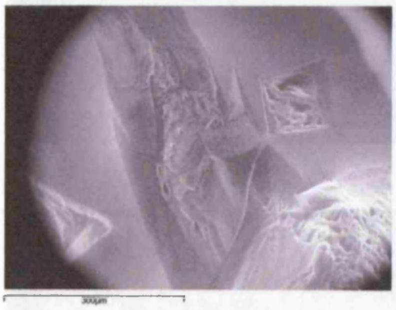
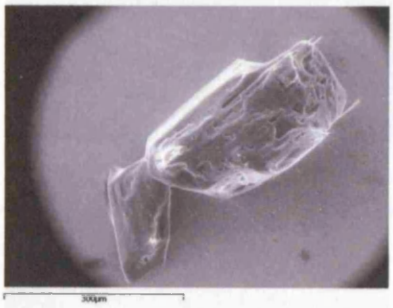
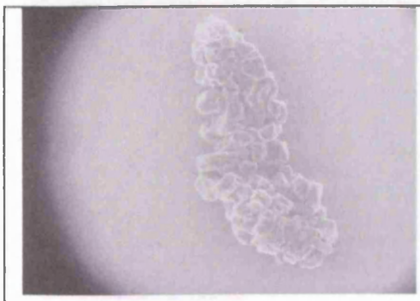
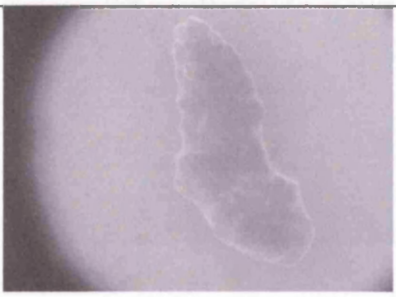
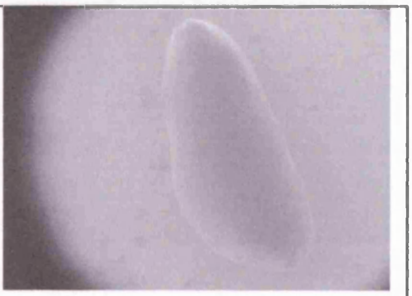
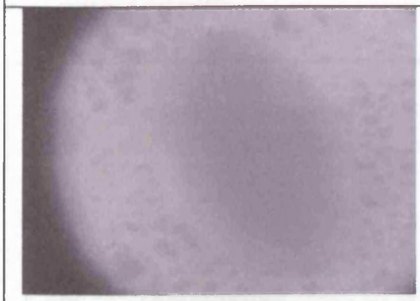
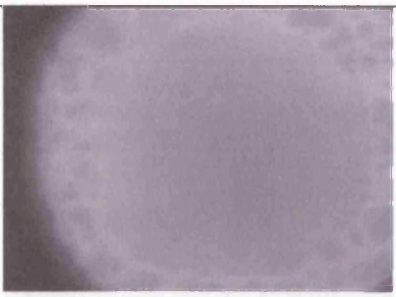
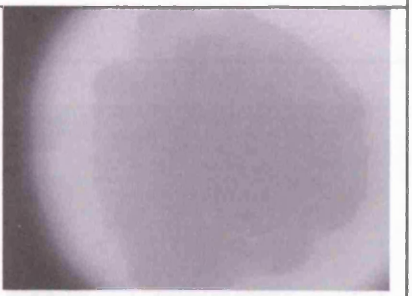
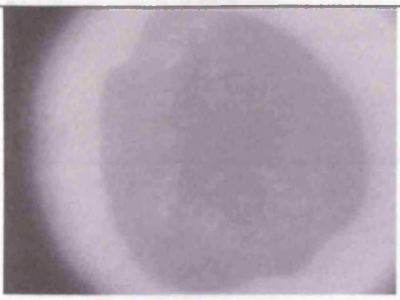
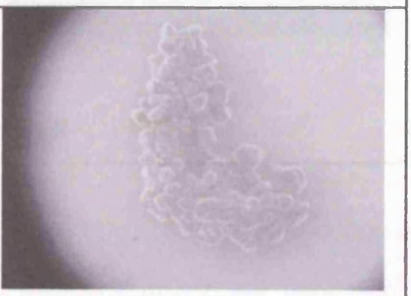
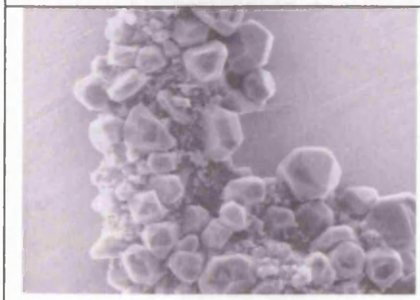
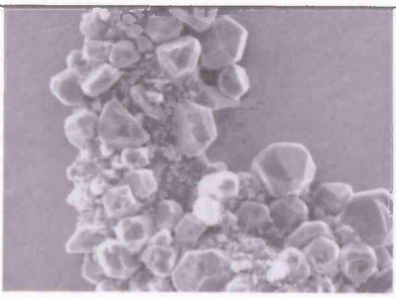
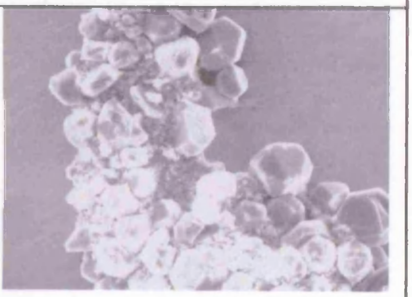
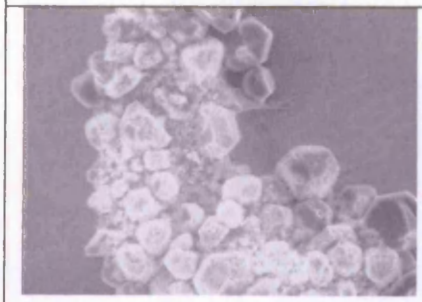
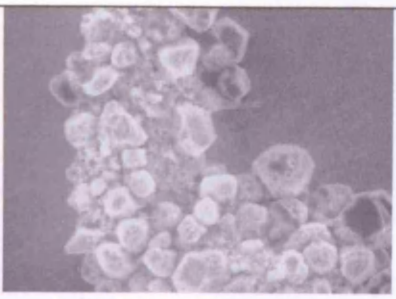
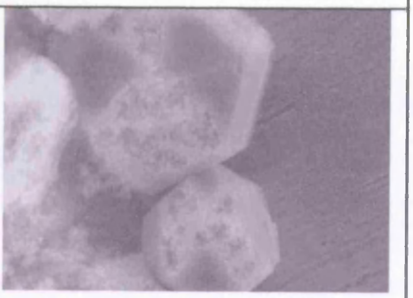
 **Fig. 1** 90% ▲	 **Fig. 2**	 **Fig. 3** 95%
 **Fig. 4** 75% ▼	 **Fig. 5**	 **Fig. 6** 63.4%

Table 3. Na_2SO_4

 **Fig. 1**	 **Fig. 2** 90% ▲	 **Fig. 3** 95%
 **Fig. 4**	 **Fig. 5** 96.7%	 **Fig. 6** 90% ▼
 **Fig. 7**	 **Fig. 8**	 **Fig. 9** 90%
 **Fig. 10**	 **Fig. 11** 43.4% ▼	 **Fig. 12**
 **Fig. 13**	 **Fig. 14**	 **Fig. 15**

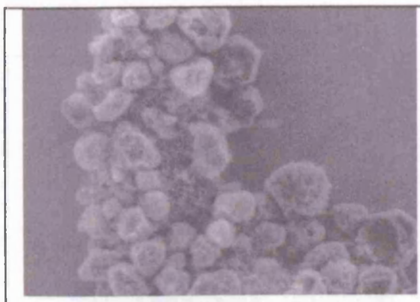
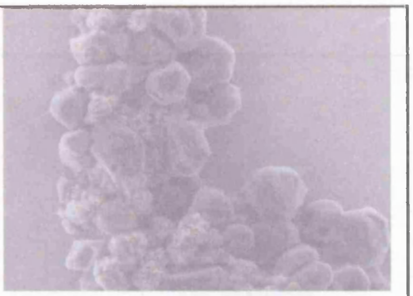
		

Fig. 16	**Fig. 17** 66.2% ▲	**Fig. 18** 68.7%

Table 4. **CaNO$_3$ - 20C^o**

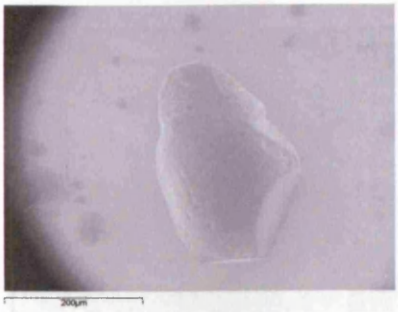
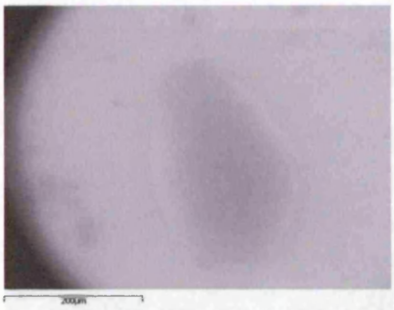
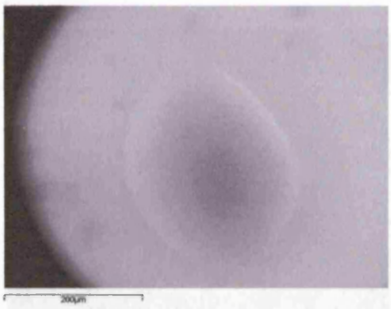
		

Fig. 1	**Fig. 2** 46.5%	**Fig. 9** 48.5%

Table 5. NaNO$_3$

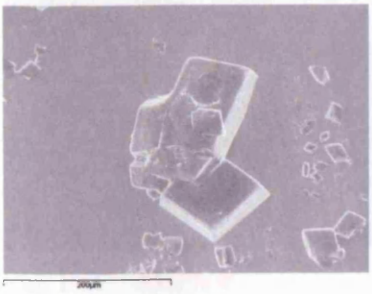
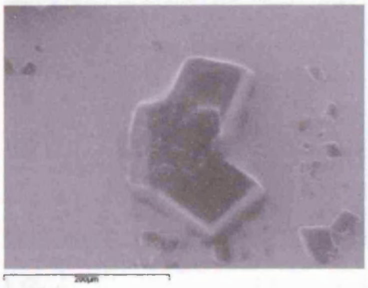
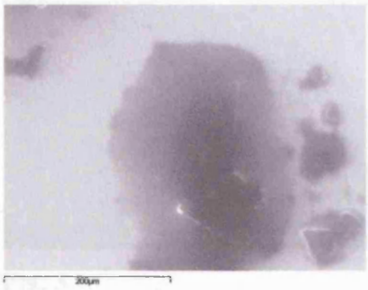
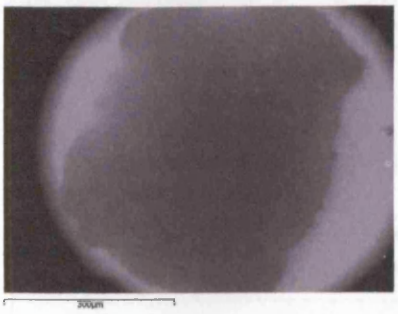
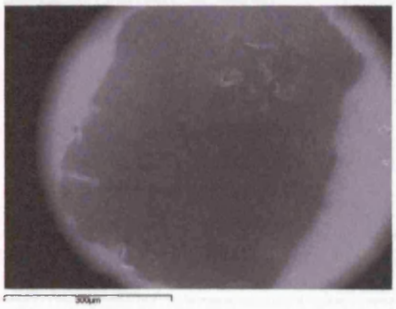
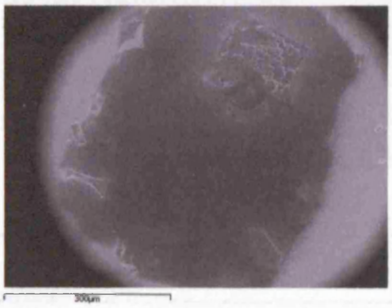
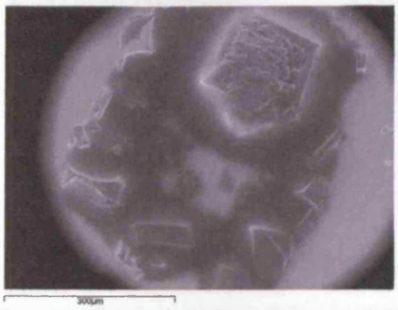
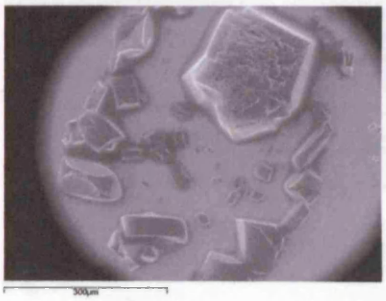
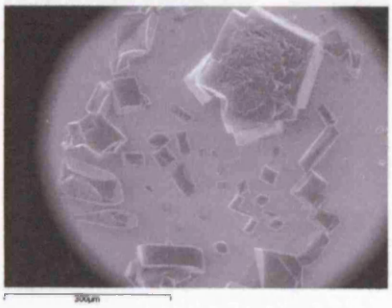
 **Fig. 1**	 **Fig. 2** 73.4%	 **Fig. 3** 76.7%
 **Fig. 4** 66.3% ▼	 **Fig. 5**	 **Fig. 6**
 **Fig. 7**	 **Fig. 8**	 **Fig. 9**

Table 6. NaCl – Na_2SO_4

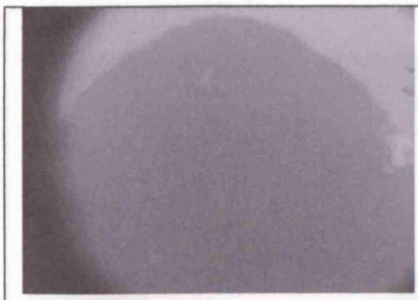


Fig. 1 58.4%▼

Fig. 2

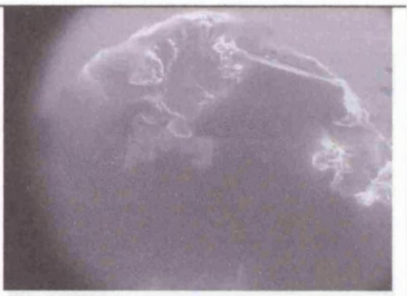
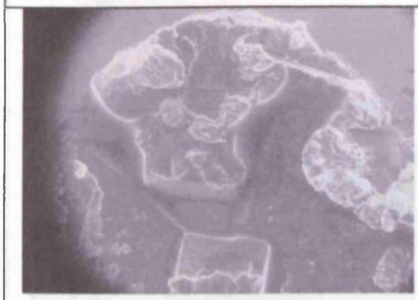


Fig. 3



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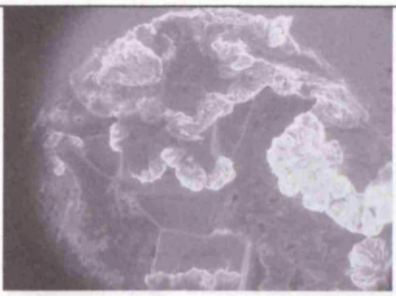


Fig. 5

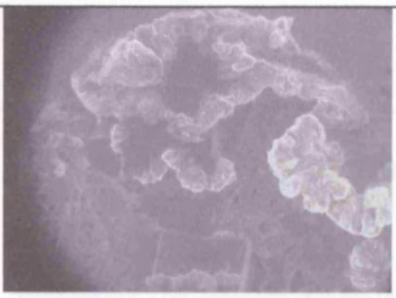


Fig. 6

Table 7. NaCl – $CaCl_2$

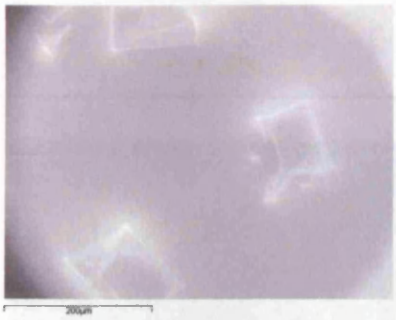


Fig. 1 47%

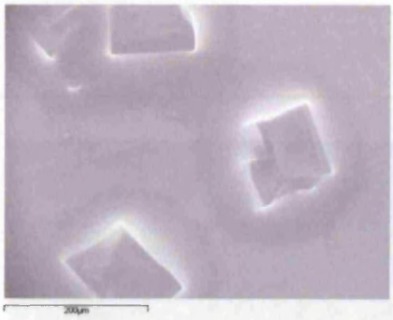


Fig. 2

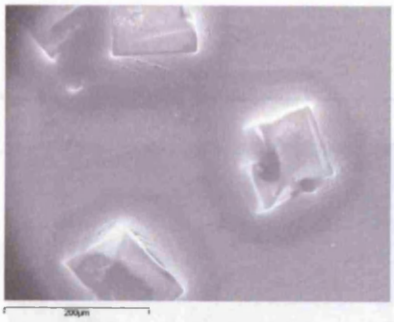


Fig. 3 25C^{O}

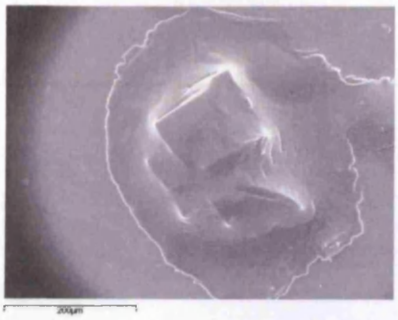


Fig. 4 60%▲

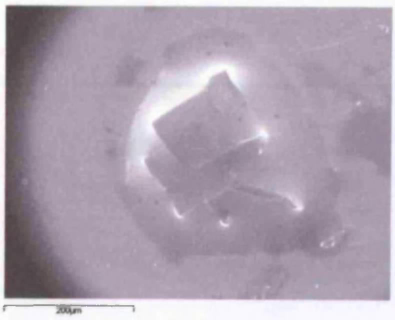


Fig. 5

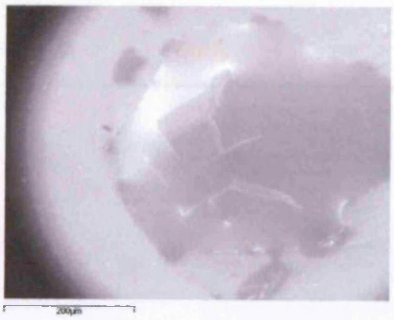


Fig. 6

Table 8. NaCl – $CaNO_3$

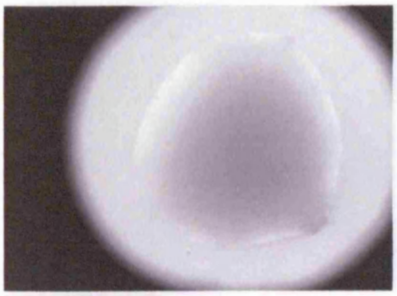


Fig. 1

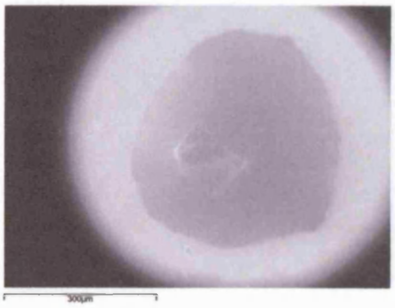


Fig. 2 55%▼

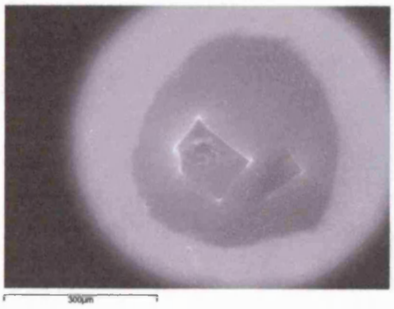


Fig. 3

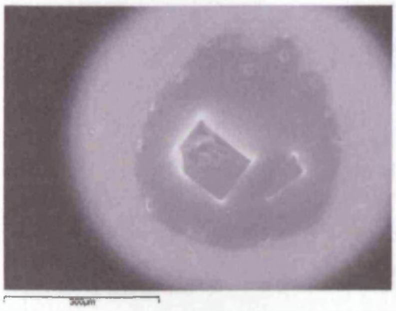


Fig. 4 47.5%

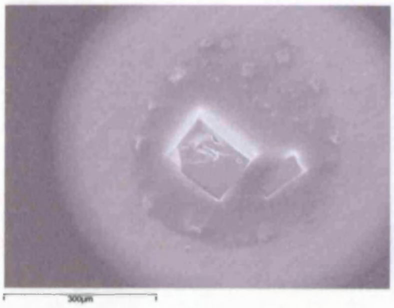


Fig. 5 15%

Fig. 6

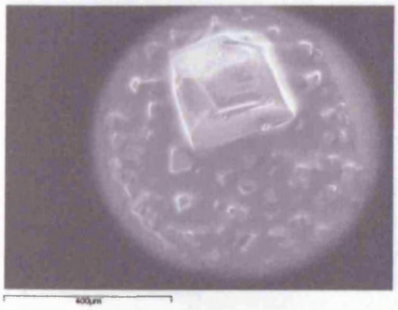


Fig. 7 45%▲

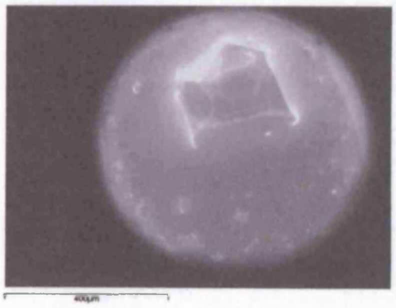


Fig. 8 55%

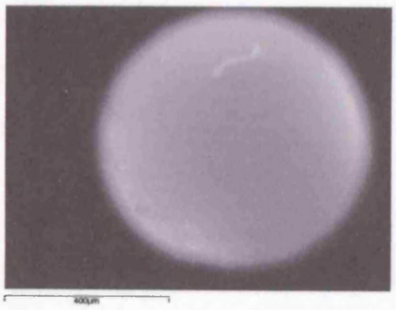


Fig. 9 60%

Table 9. NaCl – $MgSO_4$

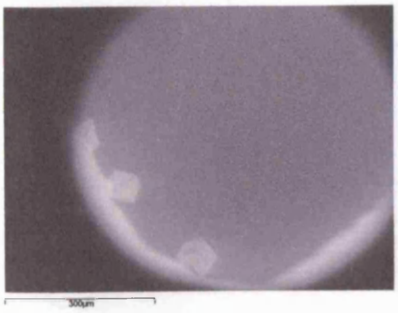
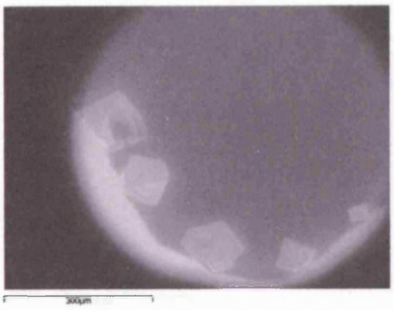
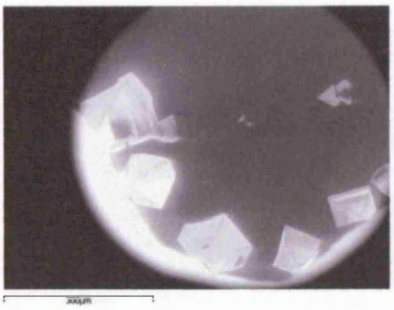
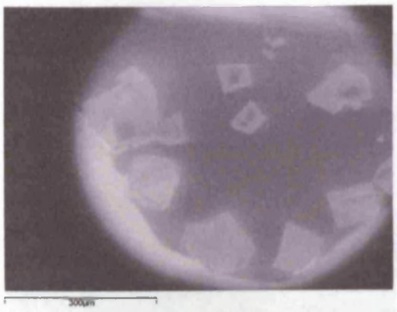
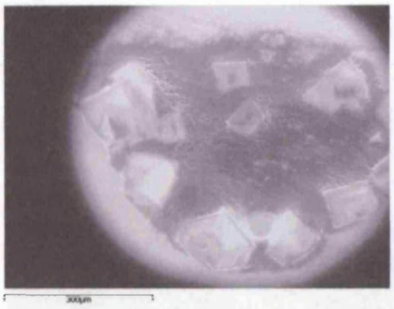
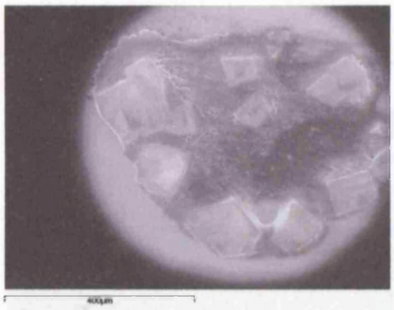
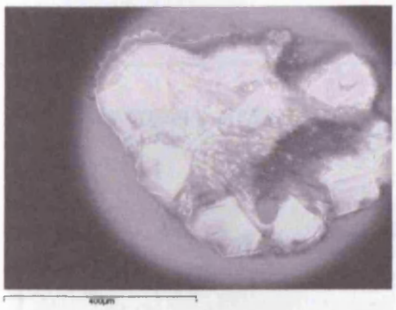
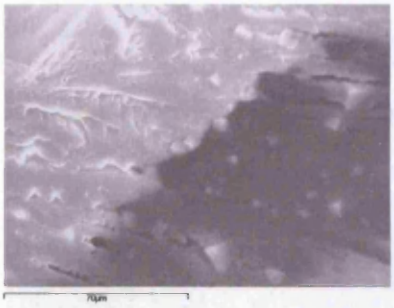
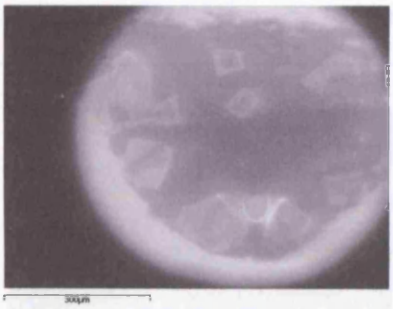
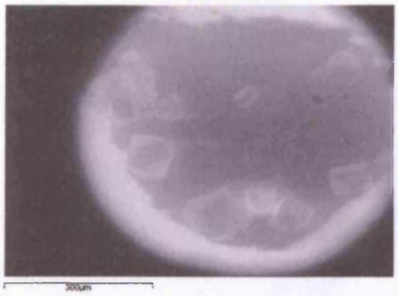
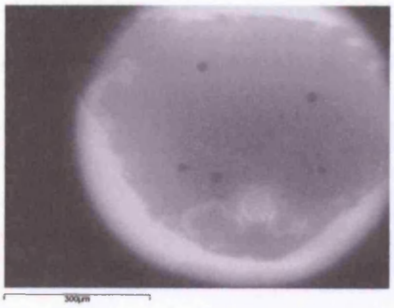
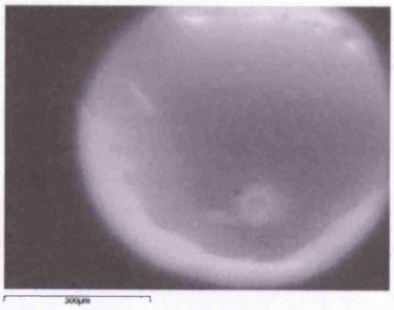
 **Fig. 1** 56.7% ▼	 **Fig. 2**	 **Fig. 3**
 **Fig. 4** 53.4%	 **Fig. 5** 45%	 **Fig. 6** 15%
 **Fig. 7**	 **Fig. 8**	 **Fig. 9** 66.2% ▲
 **Fig. 10**	 **Fig. 11**	 **Fig. 12** 80%

Table 10. NaCl – $CaSO_4$

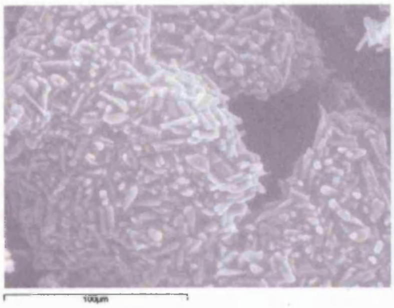
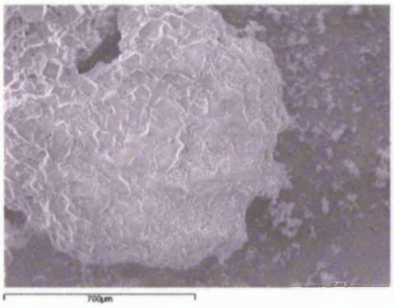
 **Fig. 1**	 **Fig. 2** 83.4%	 **Fig. 3** 55%

Table 11. NaCl – KCl – $MgCl_2$

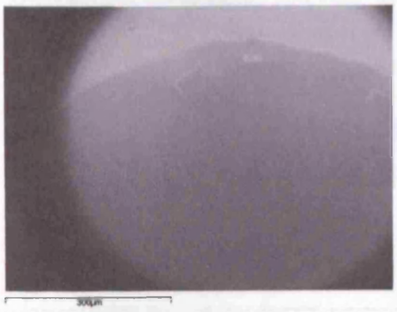
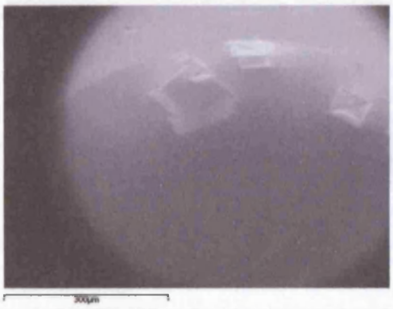
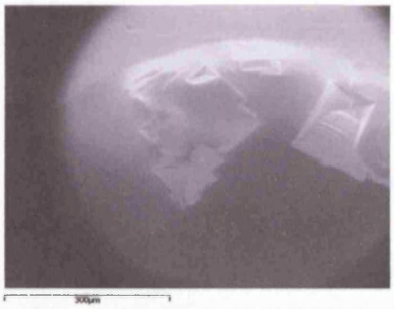
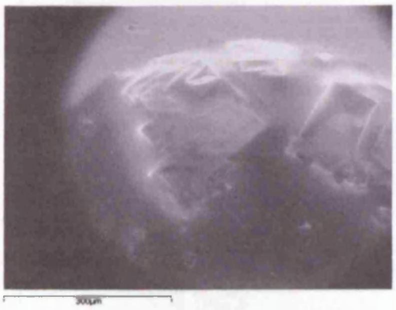
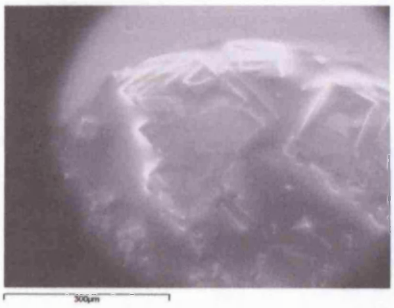
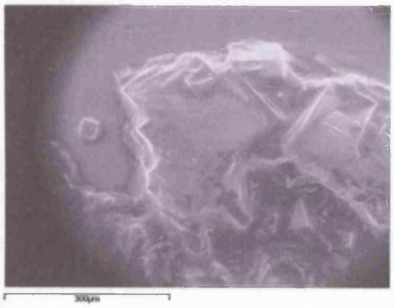
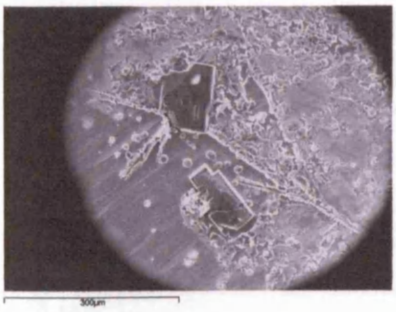
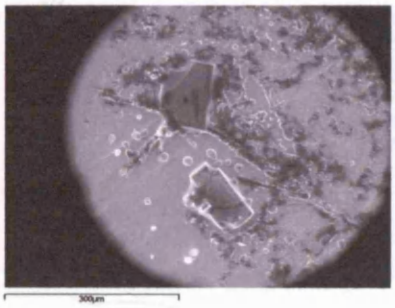
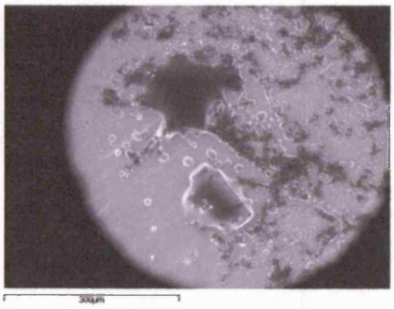
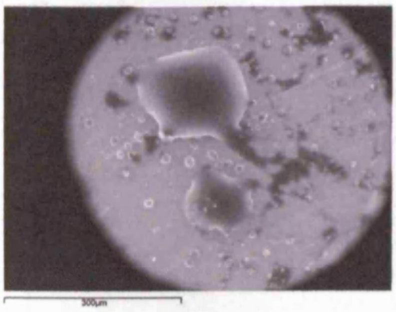
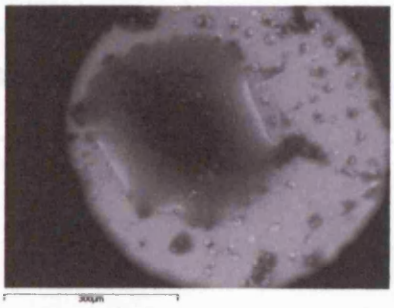
 **Fig. 1** 58.4% ▼	 **Fig. 2**	 **Fig. 3**
 **Fig. 4** 40%	 **Fig. 5**	 **Fig. 6** 25C°

Table 12. Sea water

 **Fig. 1**	 **Fig. 2** 50%▲	 **Fig. 3**
 **Fig. 4** 70%	 **Fig. 5** 90%	

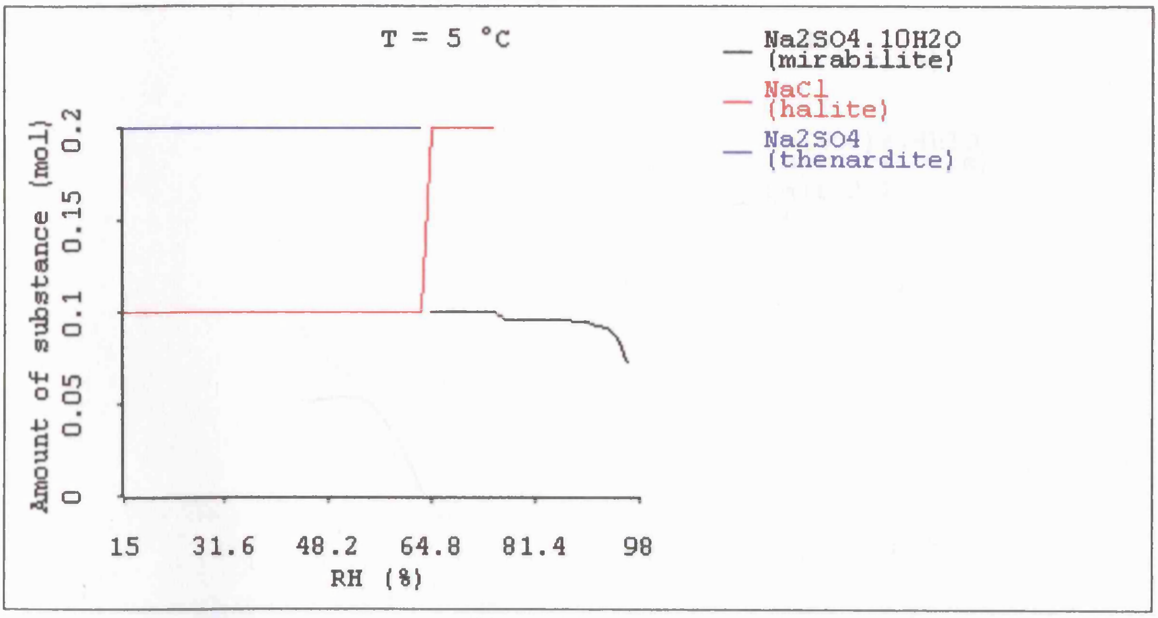


Chart 1 Na – Cl – SO_4

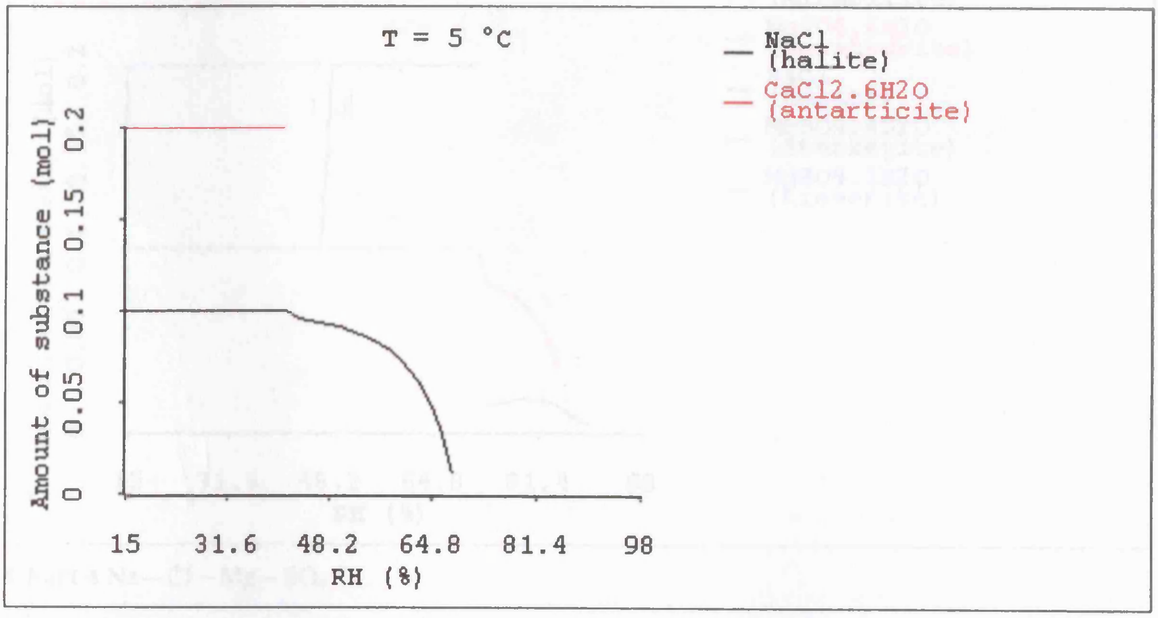


Chart 2 Na – Ca – Cl

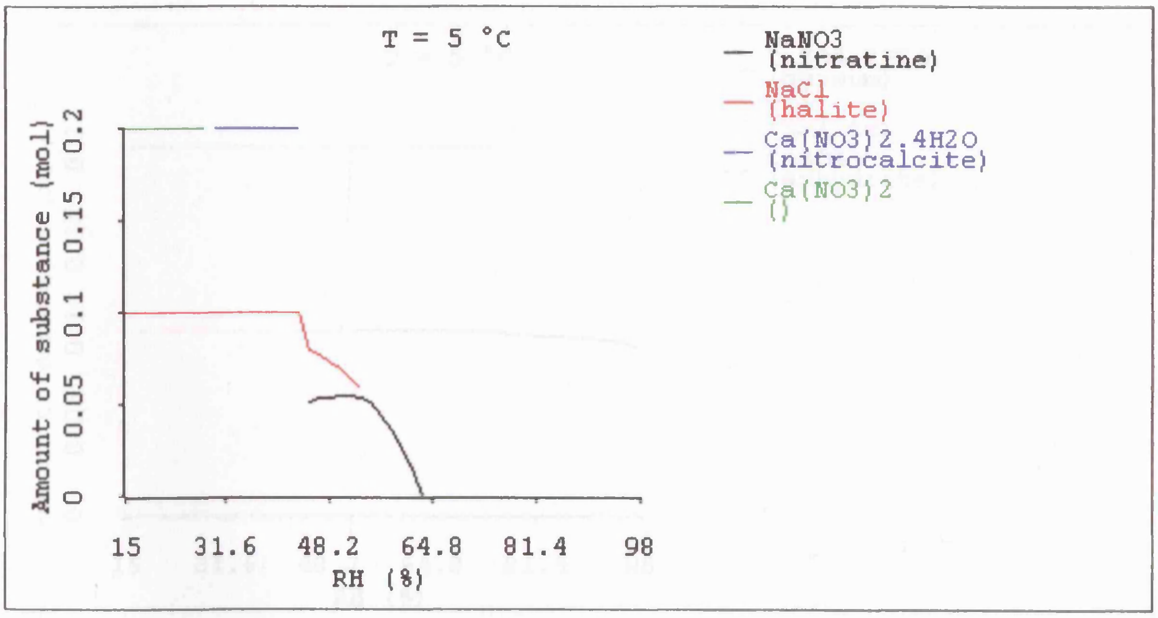


Chart 3 Na – Cl – Ca – NO_3

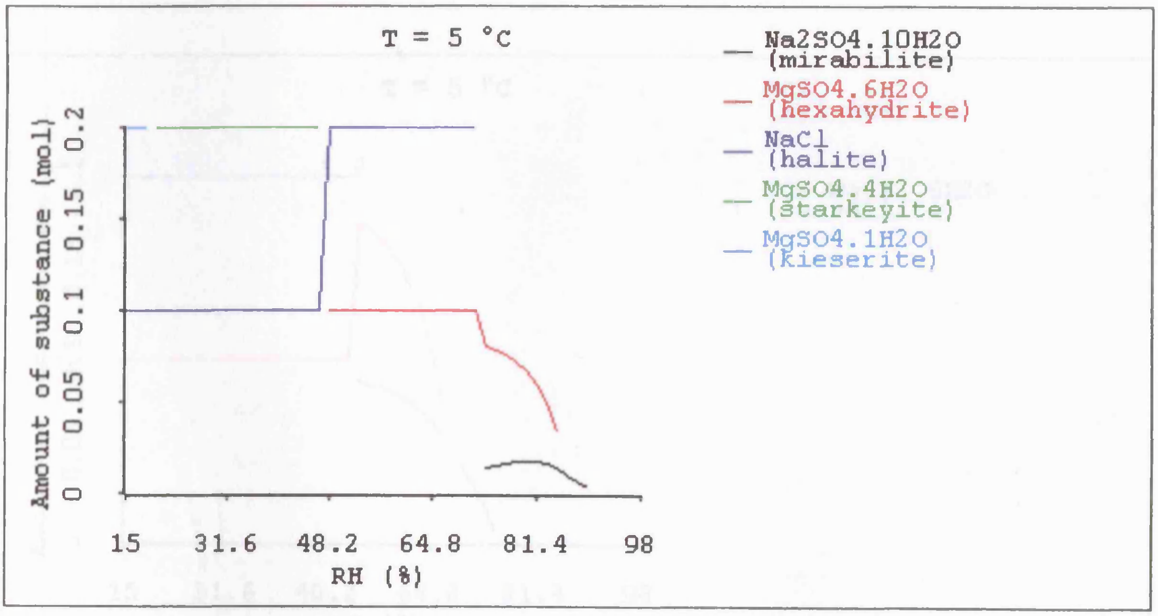


Chart 4 Na – Cl – Mg – SO_4

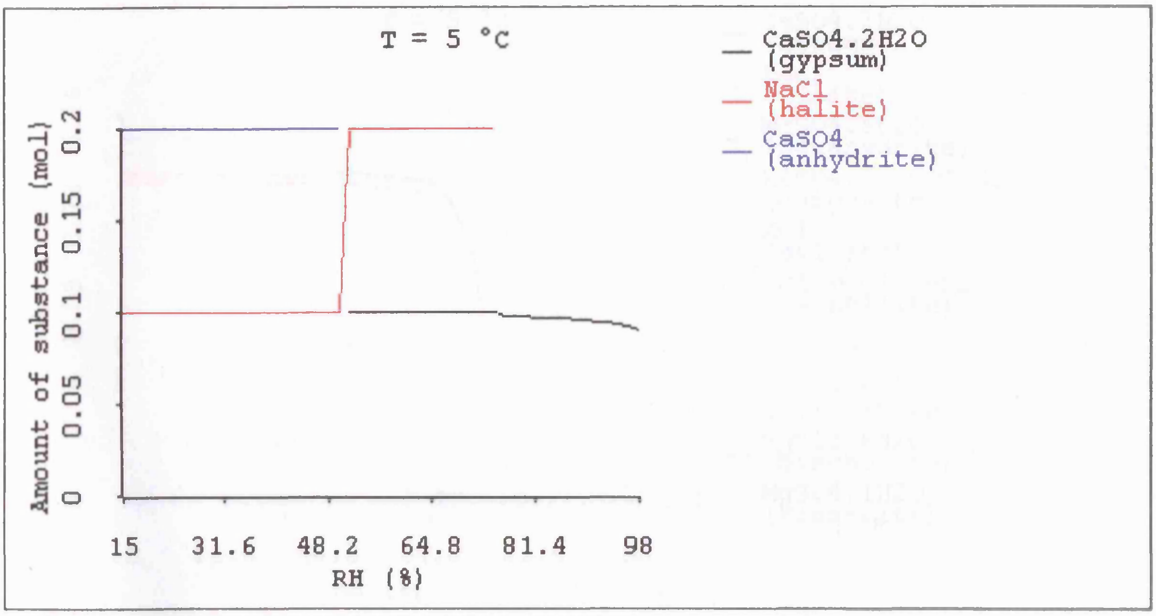


Chart 5 Na – Cl – Ca – SO_4

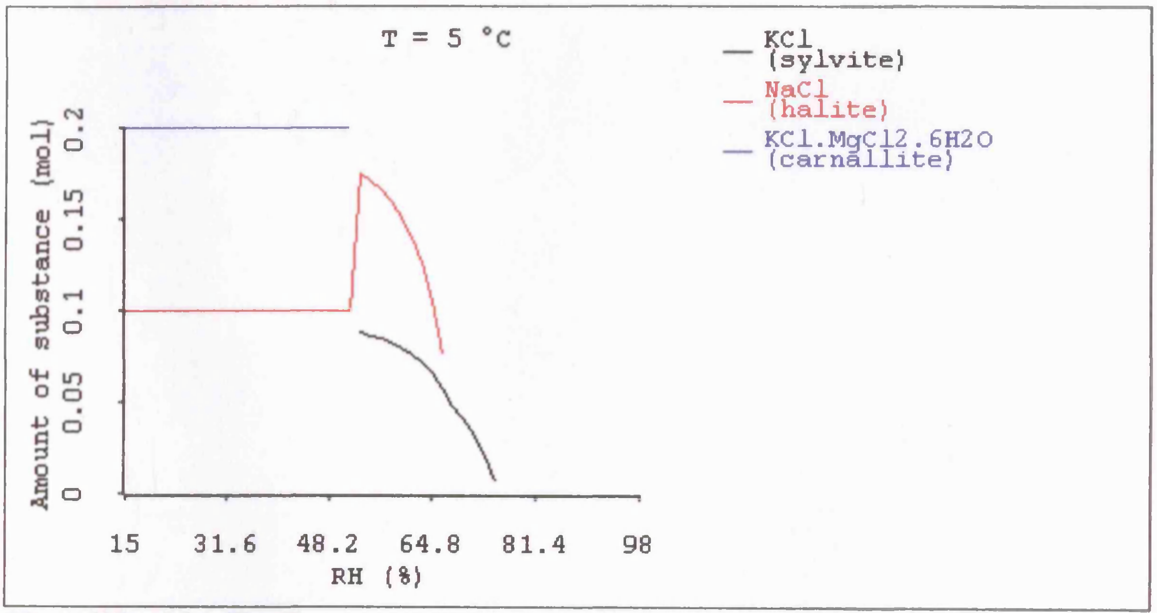


Chart 6 Na – Mg – K – Cl

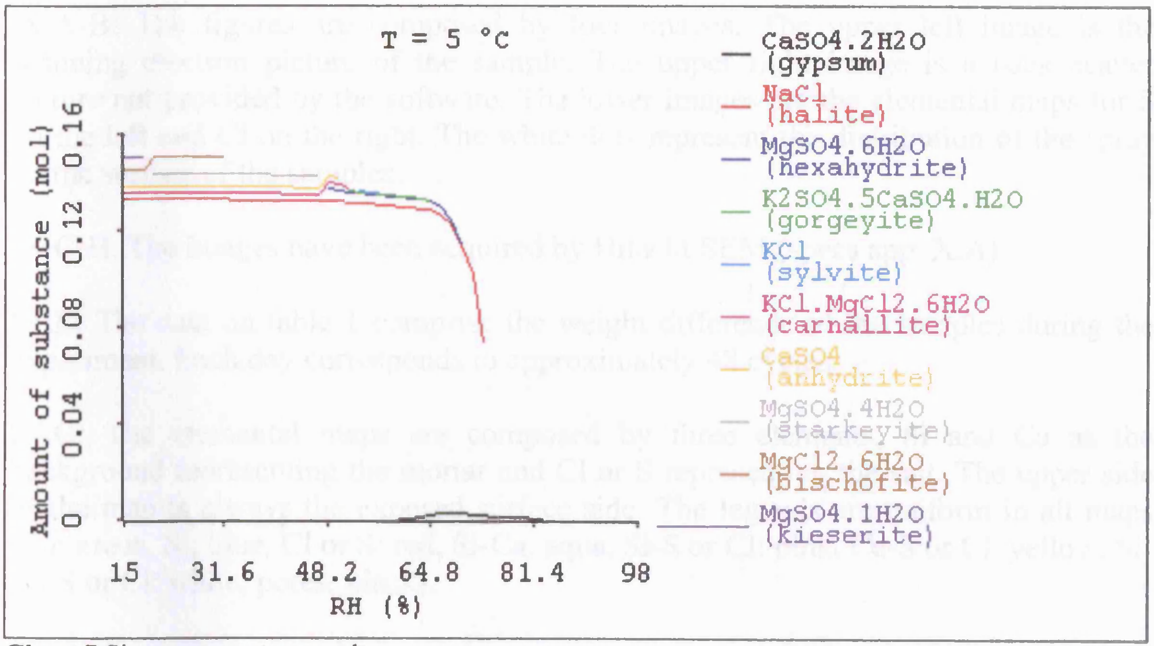


Chart 7 Six components sea salt

Appendix IX: Weathering simulation

IX.A-B: The figures are composed by four images. The upper left image is the scanning electron picture of the sample. The upper right image is a back scatter picture not provided by the software. The lower images are the elemental maps for S on the left and Cl on the right. The white dots represent the distribution of the spray on the surface of the samples.

IX.C-H: The images have been acquired by Hitachi SEM (specs app. X.A).

IX.E: The data on table 1 comprise the weight difference of the samples during the experiment. Each day corresponds to approximately 48 cycles.

IX.G: The elemental maps are composed by three elements, Si and Ca as the background representing the mortar and Cl or S representing the salt. The upper side of the map is always the exposed surface side. The legends are uniform in all maps (Ca: green, Si: blue, Cl or S: red, Si-Ca: aqua, Si-S or Cl: pink, Ca-S or Cl: yellow, Si-Ca-S or Cl: white, pores: black).

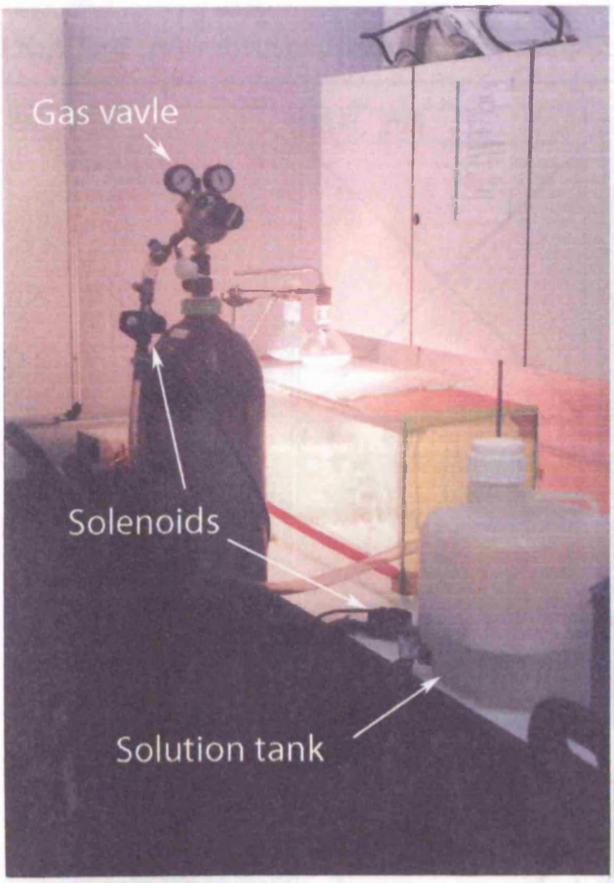


Fig. 1 Weathering chamber and tanks

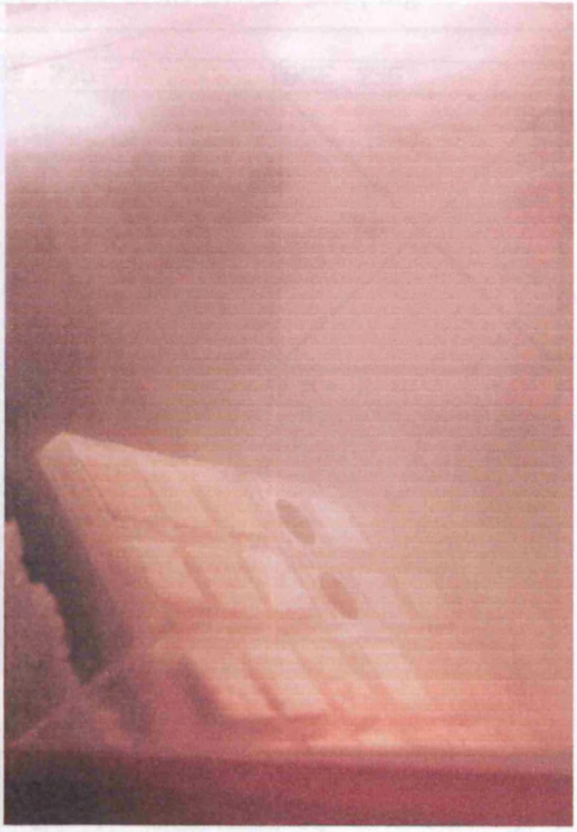


Fig. 2 Samples on holder during spraying

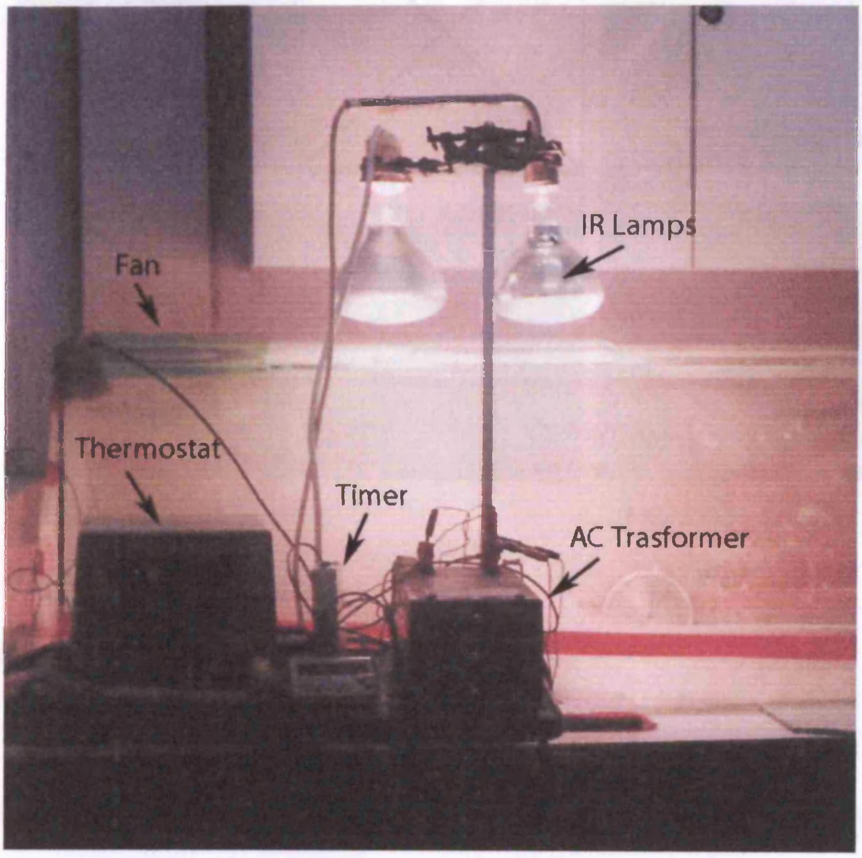


Fig.3 Electrical equipment

IX.A Salt spray distribution on mortar samples type A. SEM-EDAX mapping

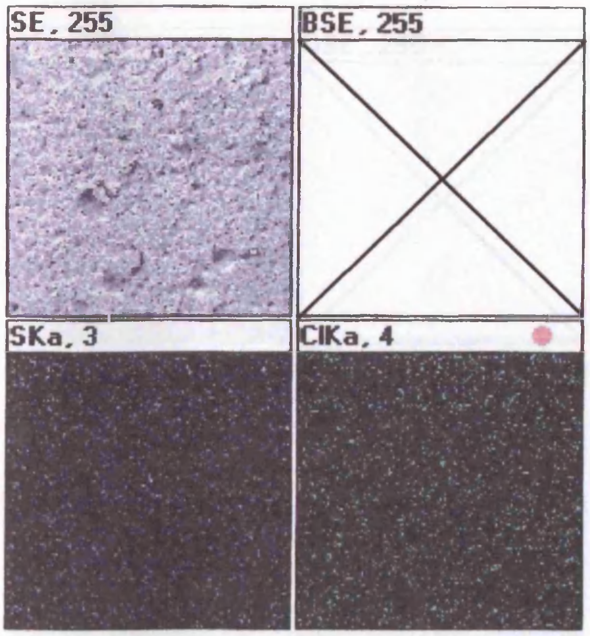


Fig. 4 Sample sdA1

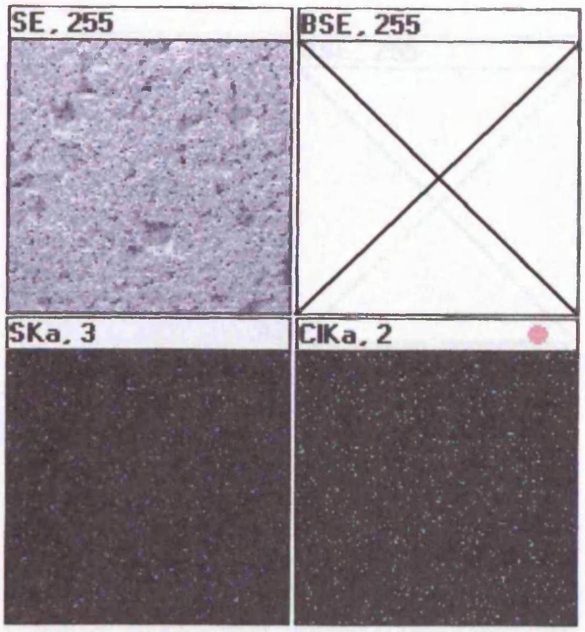


Fig. 5 Sample sdA2

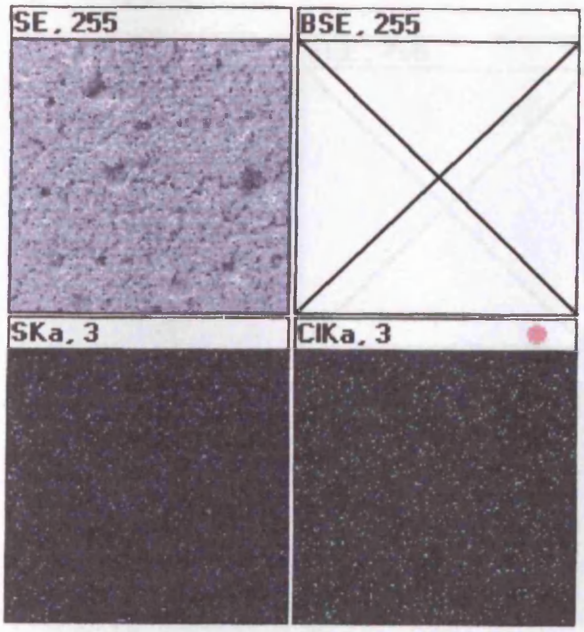


Fig. 6 Sample sdA3

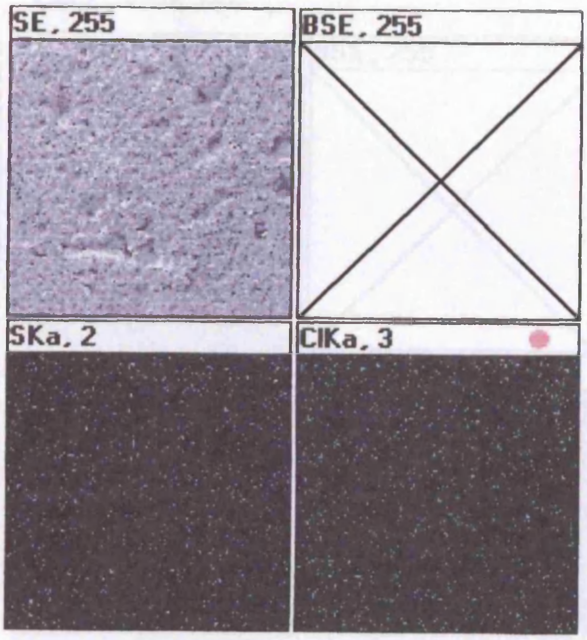


Fig. 7 Sample sdA4

IX.B Salt spray distribution on mortar samples type B. SEM-EDAX mapping

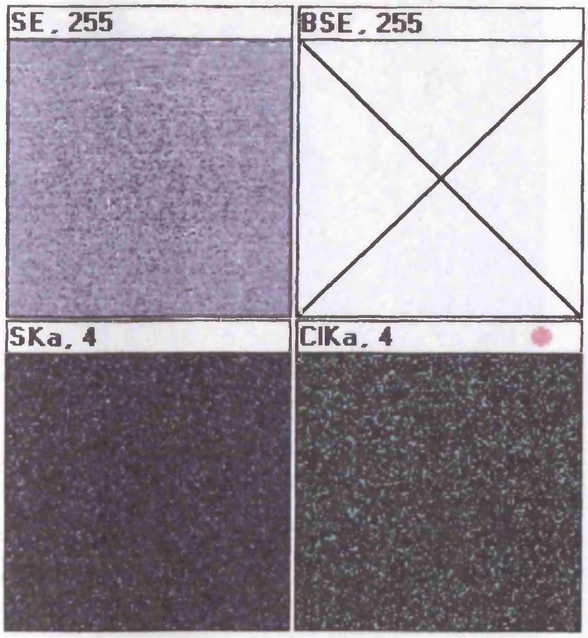


Fig. 8 Sample sdB1

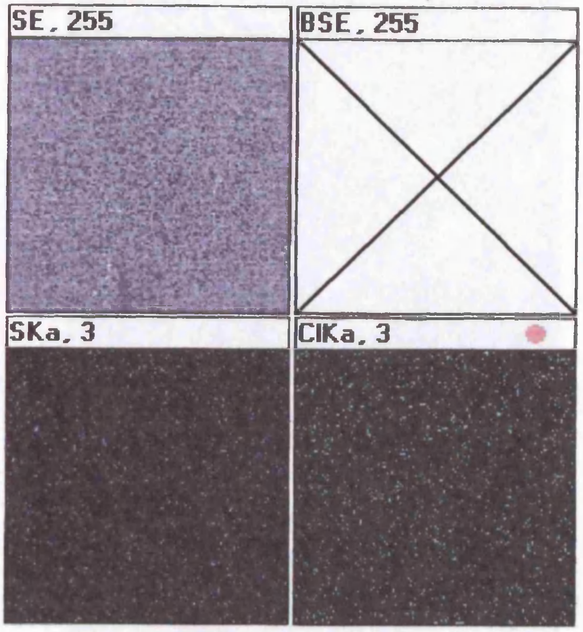


Fig. 9 Sample sdB2

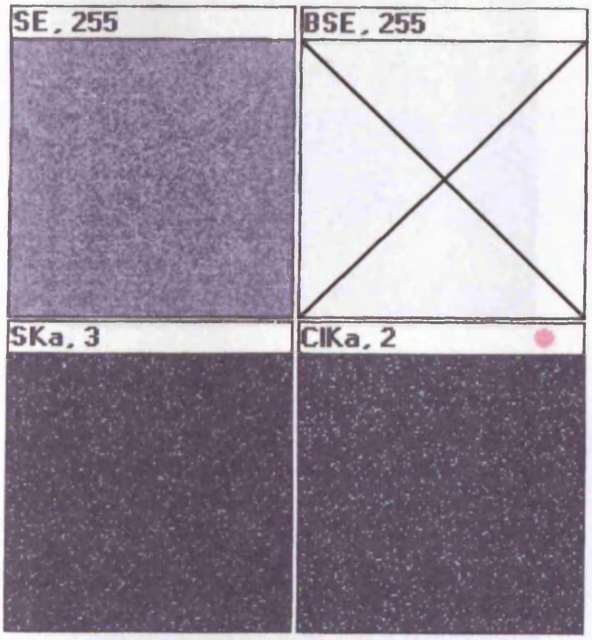


Fig. 10 Sample sdB3

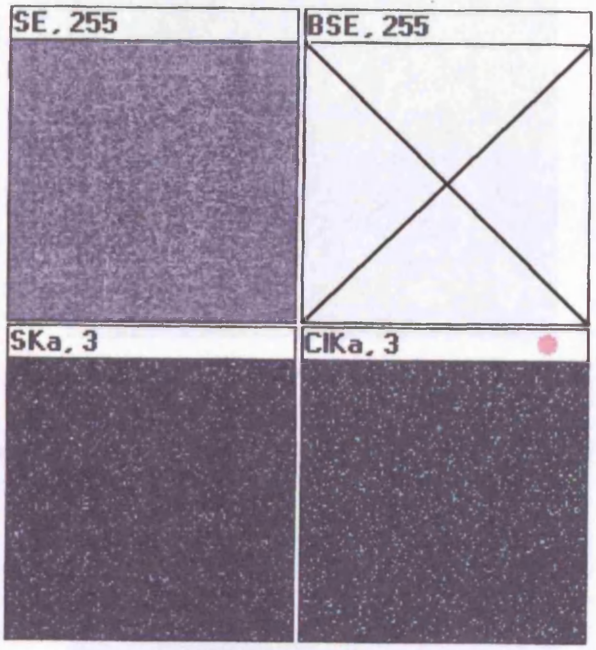


Fig. 11 Sample sdB4

IX.C Salt spray distribution on adhesive samples. SEM images

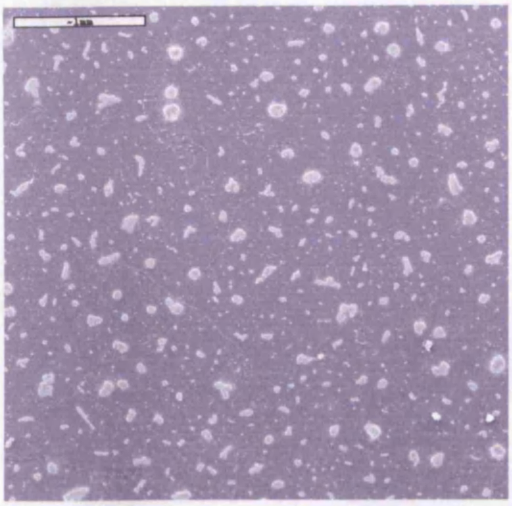


Fig. 12 Sample SP1 (sc.1mm)

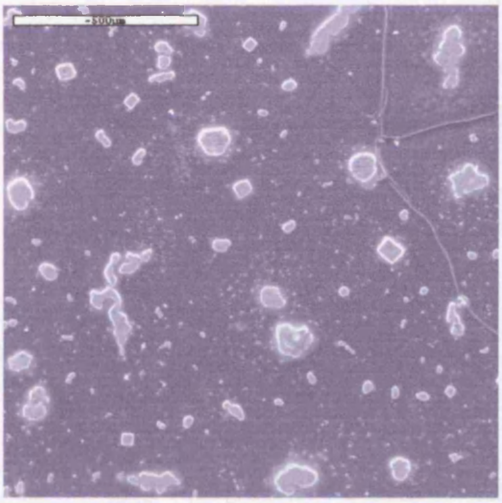


Fig. 13 Detail of SP1 (sc. 0.5mm)

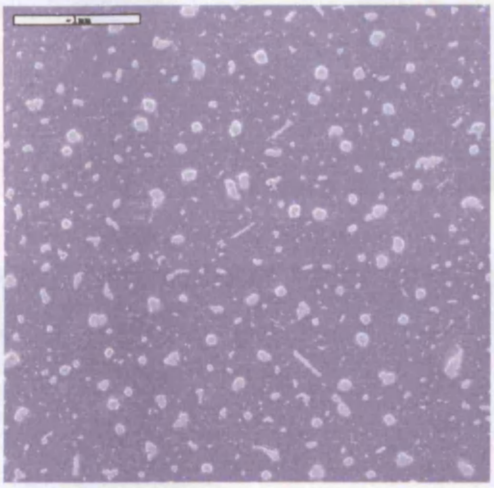


Fig. 14 Sample SP2 (sc.1mm)

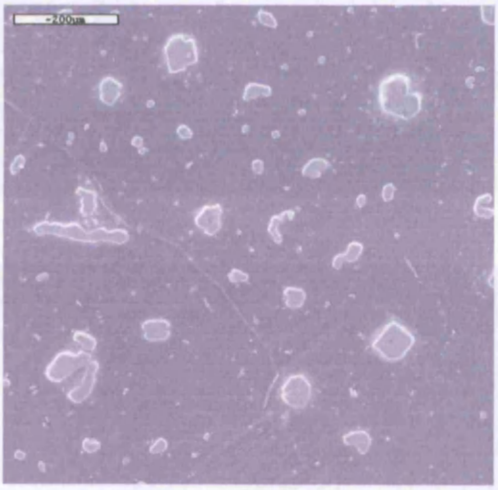


Fig. 15 Detail of SP2 (sc. 0.2mm)

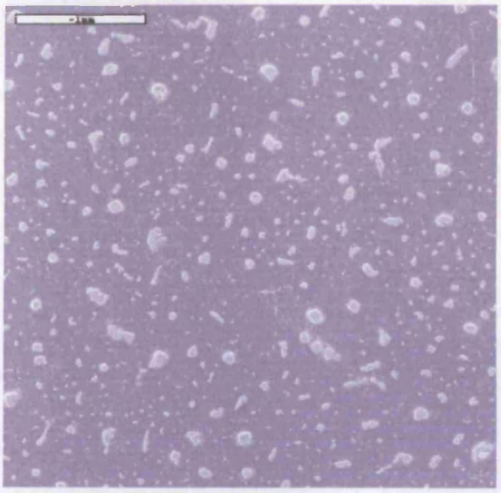


Fig. 16 Sample SP3 (sc.1mm)

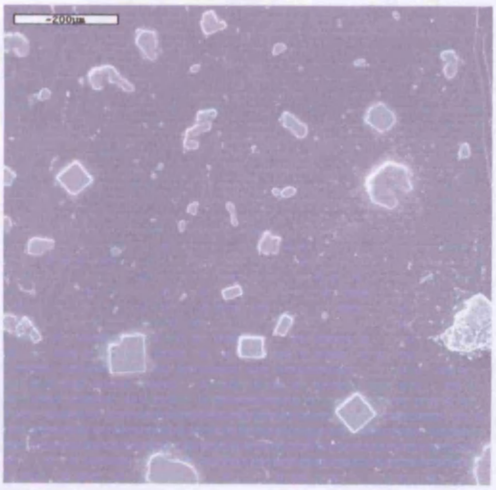


Fig. 17 Detail of SP3 (sc. 0.2mm)

IX.D Visual observations

Fig. 18 Visible swellings on type A samples

Fig. 19 Collapsed swelling of type a sample (up-right corner) and crusts on type B samples

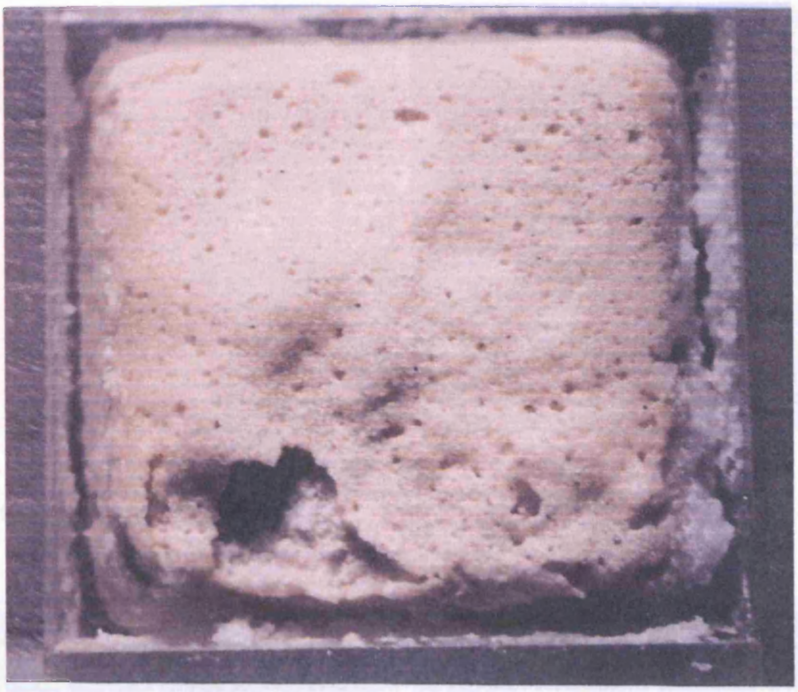
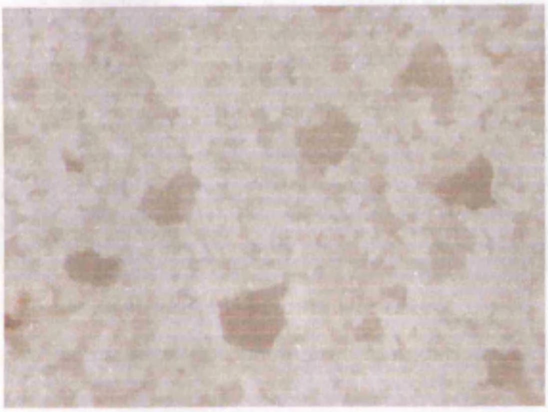


Fig. 20 Collapsed swelling



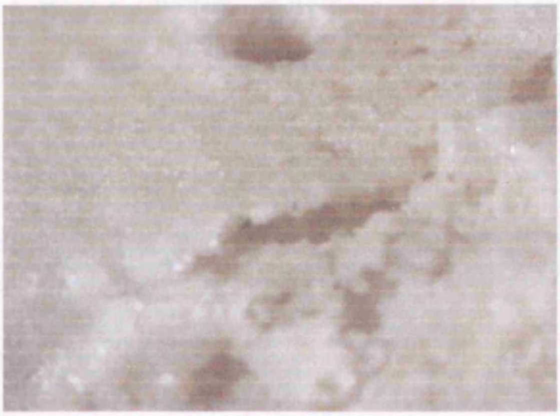


Fig. 21 The pores of type A sample are not filled with salts

Fig. 22 Start of swelling and superficial flake detachment

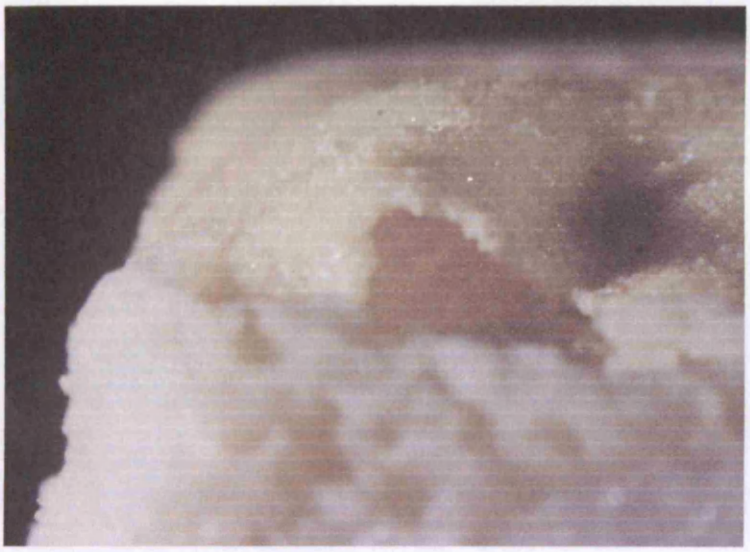
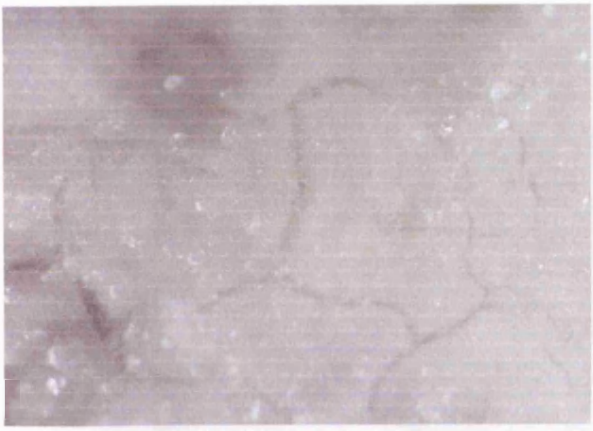


Fig. 23 Advanced swelling



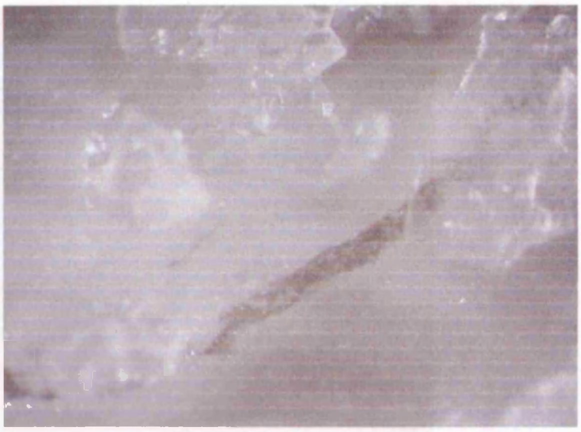
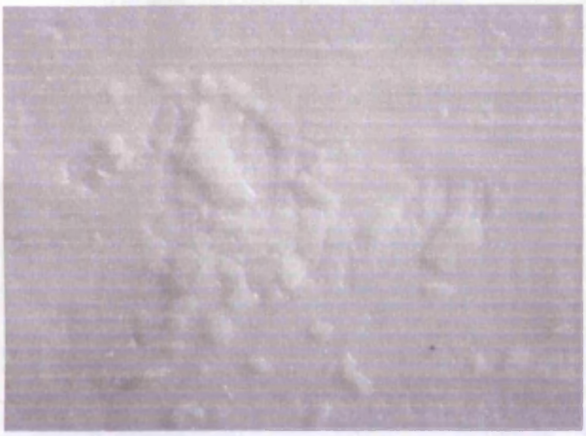


Fig. 24 Cracks on the lime wash layer under the salt crust

Fig. 25 Visible salt crystals and crack



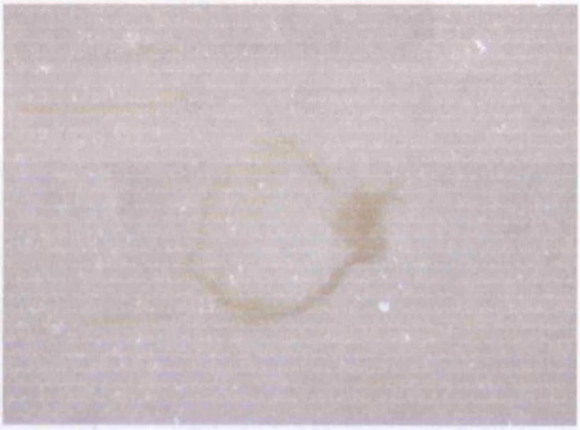


Fig. 26 Minor flaking of the lime wash layer

Fig. 27 Round crack, probably around underlying pore

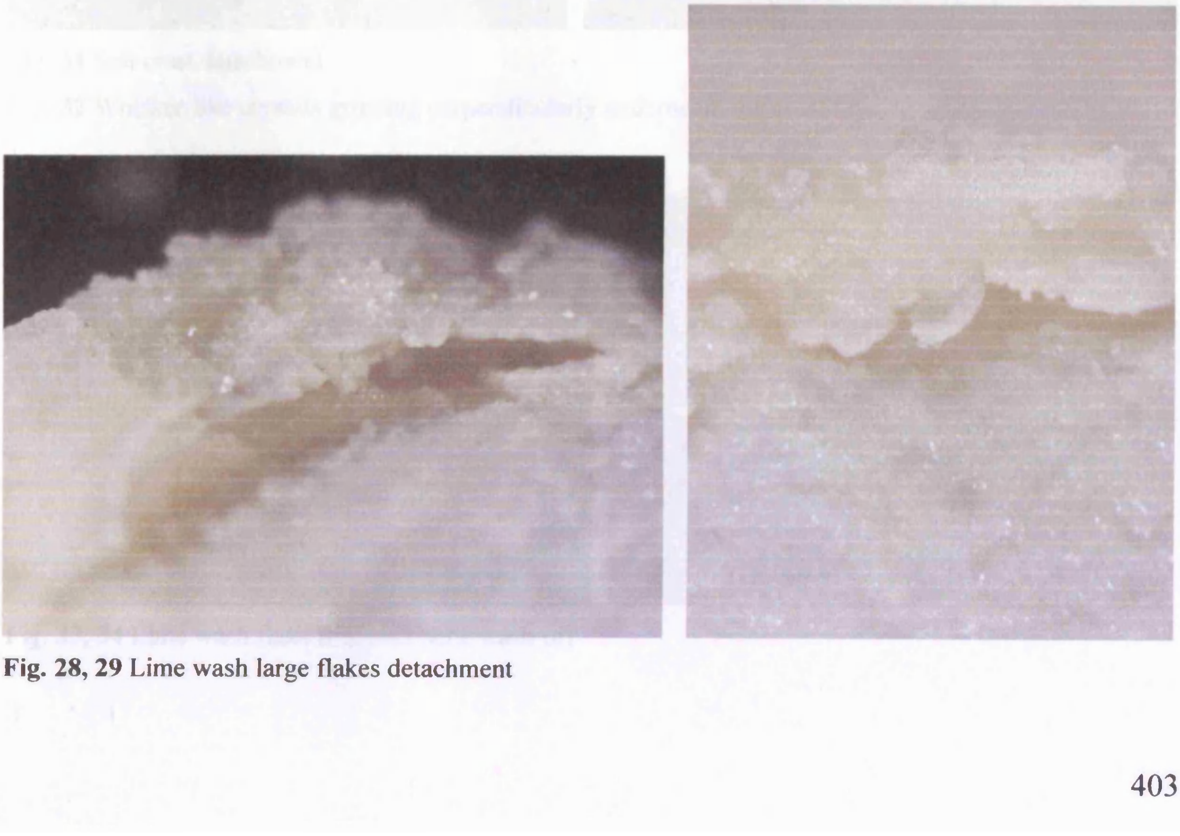


Fig. 28, 29 Lime wash large flakes detachment

Fig. 30 Lime wash flake detachment

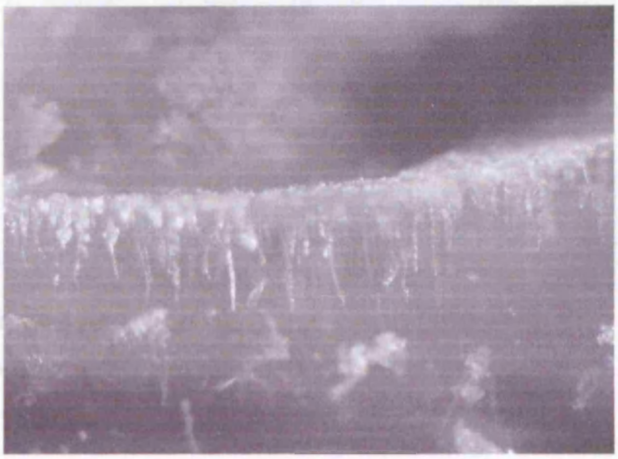


Fig. 31 Salt crust detachment

Fig. 32 Whisker-like crystals growing perpendicularly underneath the crust

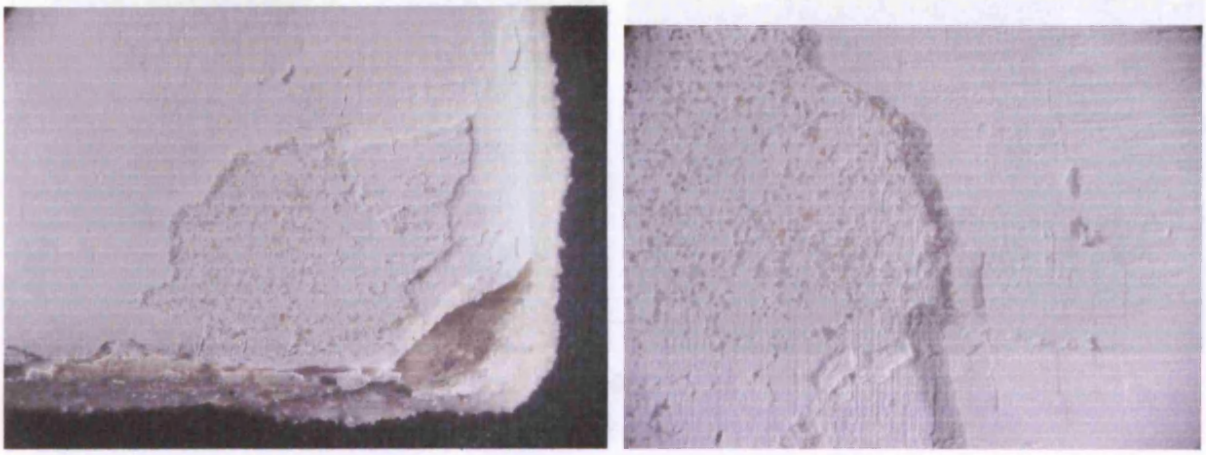


Fig. 33, 34 Lime wash flake loss after salts wash-off

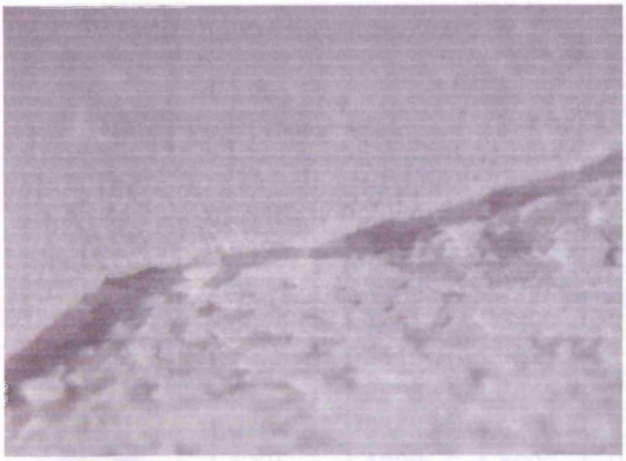
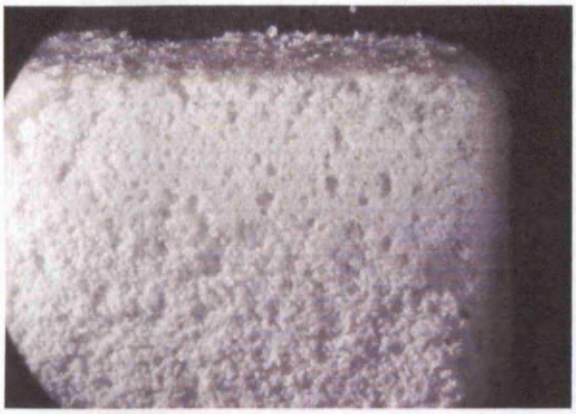


Fig. 35 Detached lime wash layer (after wash-off)

Fig. 36 Minor flaking (after wash-off)



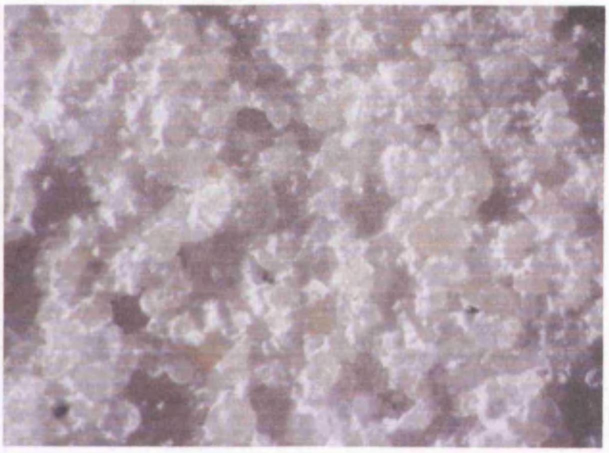
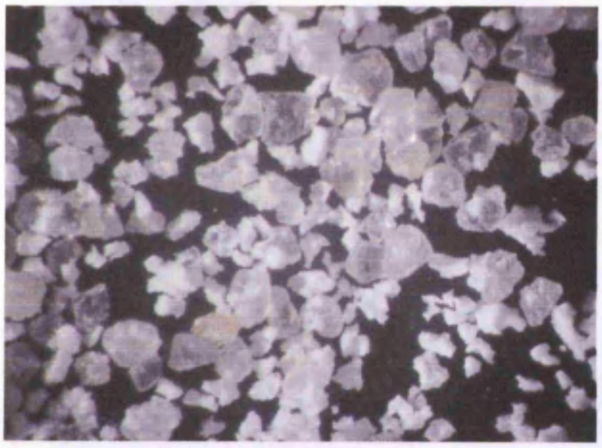


Fig. 37 Only the upper right corner maintained the original surface on this A type sample (after wash-off)

Fig. 38 The surface of A type samples after the removal of debris and salts. The pore structure has collapsed and the lime matrix has lost its continuity



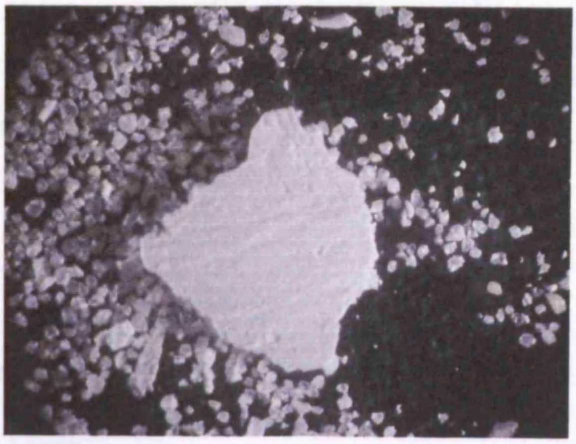


Fig. 39 Sand and lime debris washed off from A sample

Fig. 40 Large lime wash flake detached after wash-off

IX.E Weight change measurements

Table 1 Weight change (g)

Day	1A	2B	3A	4B	5A	6B	average
1	0.2518	0.7254	1.2218	0.8695	1.8030	1.9324	1.1340
2	0.5999	1.0082	1.3094	1.5842	2.1468	1.9887	1.4395
3	1.6614	1.5459	1.6692	1.8599	2.0951	2.1956	1.8379
4	1.5814	1.6291	1.8299	2.0400	2.2496	2.4738	1.9673
5	1.1936	1.3119	1.6871	1.8375	2.0520	2.3886	1.7451
6	1.0443	1.2965	1.7445	2.0225	2.1583	2.5609	1.8045
7	1.0704	1.3505	1.8206	2.0977	2.3290	2.7047	1.8955
8	1.1225	1.4092	1.8925	2.1945	2.5012	2.8783	1.9997
9	1.4567	1.6935	2.2422	2.4453	2.7487	3.2096	2.2993
10	1.4649	1.8066	2.3691	2.5947	2.9898	3.6469	2.4787
11	1.5006	1.9251	2.4861	2.7003	2.8995	3.6021	2.5190
12	1.4541	1.8945	2.4489	2.6932	2.9302	3.6132	2.5057
13	1.5146	2.0274	2.6067	2.8470	3.1635	3.7352	2.6491
14	1.5920	2.2365	2.9607	3.0591	3.3795	3.9527	2.8634
15	1.7589	2.3091	3.0900	3.2063	3.6710	4.3120	3.0579
16	1.8522	2.4833	3.1670	3.4526	3.9746	4.6855	3.2692
17	2.1360	2.6610	3.2367	3.2502	4.1839	4.4821	3.3250
18	2.4190	2.7872	3.4190	3.1030	4.1002	4.5222	3.3918
19	2.5540	2.8335	3.6168	3.2093	4.0340	4.5832	3.4718
20	2.6804	2.9134	3.6731	3.2789	3.9384	4.6590	3.5239
21	2.9619	3.1913	4.1224	3.3807	3.8947	4.8084	3.7266

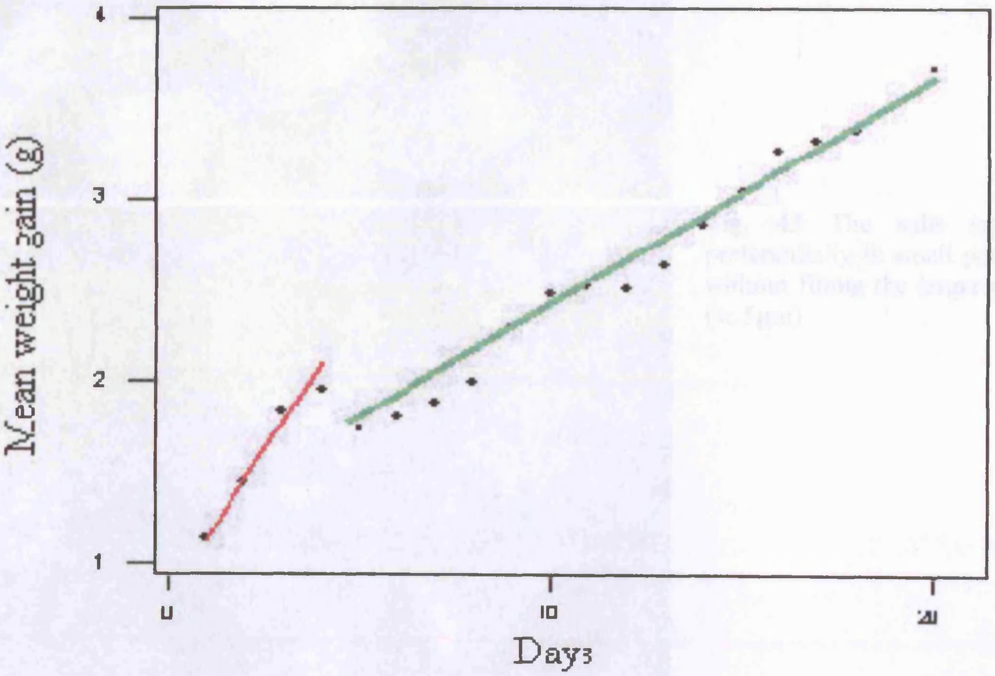


Chart 1 Fitted line plot of average weight gain

IX.F Thin sections – Optical microscopy

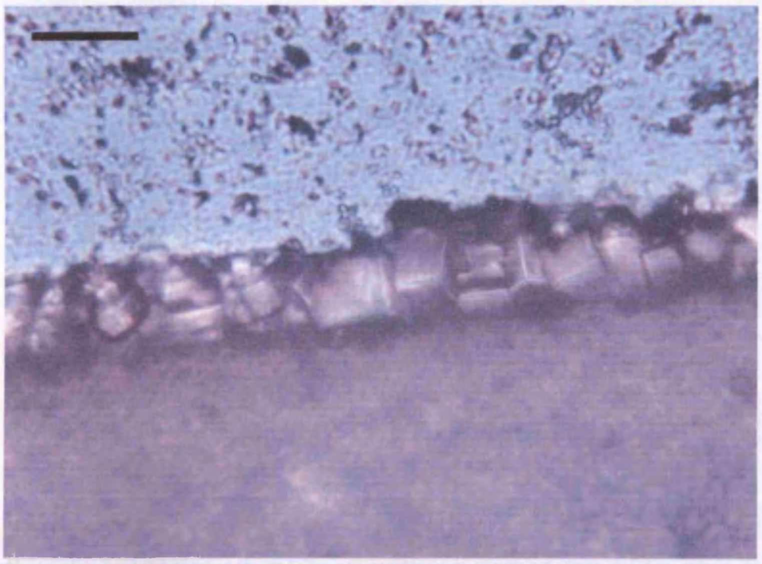


Fig. 41 Salt crust developed on the surface of samples type B early in the experiment. The crystals maintained their cubic habit (sc. 5μm)

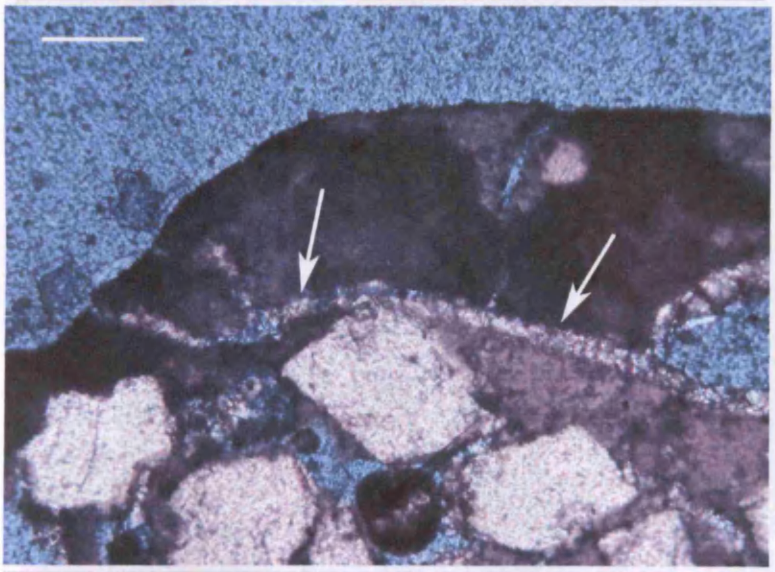


Fig. 42 The fine capillaries are filled with salts while the larger pores are empty. The arrows indicate a fine capillary near the surface. The pore space on the right presents some efflorescence on the walls. (sc. 30μm)

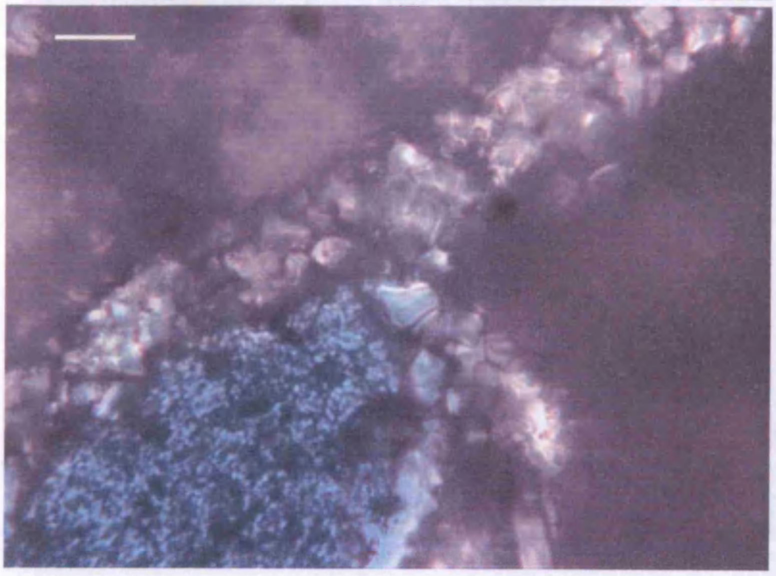


Fig. 43 The salts crystallized preferentially in small pore throats without filling the larger chambers (sc.5μm)

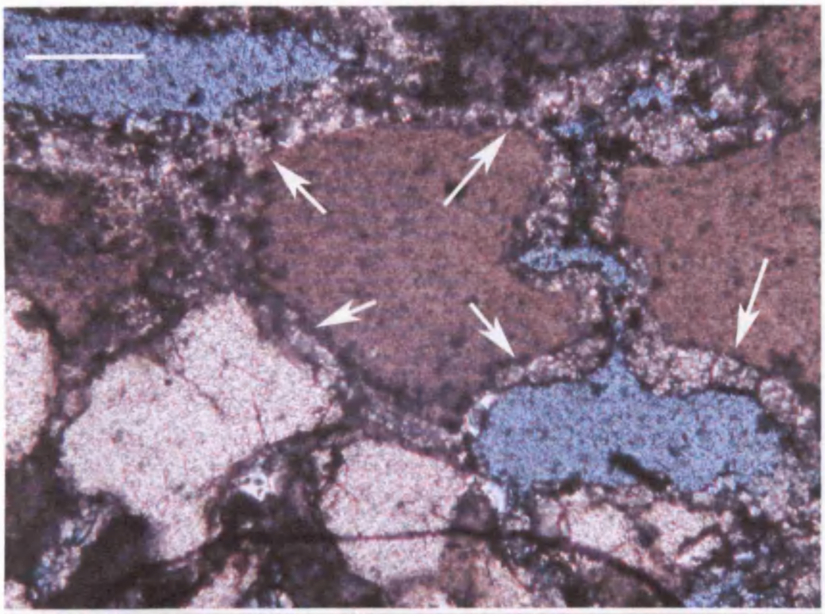


Fig. 44 The arrows indicate salt efflorescence on the walls of large pores and small pore throats (sc.20μm)

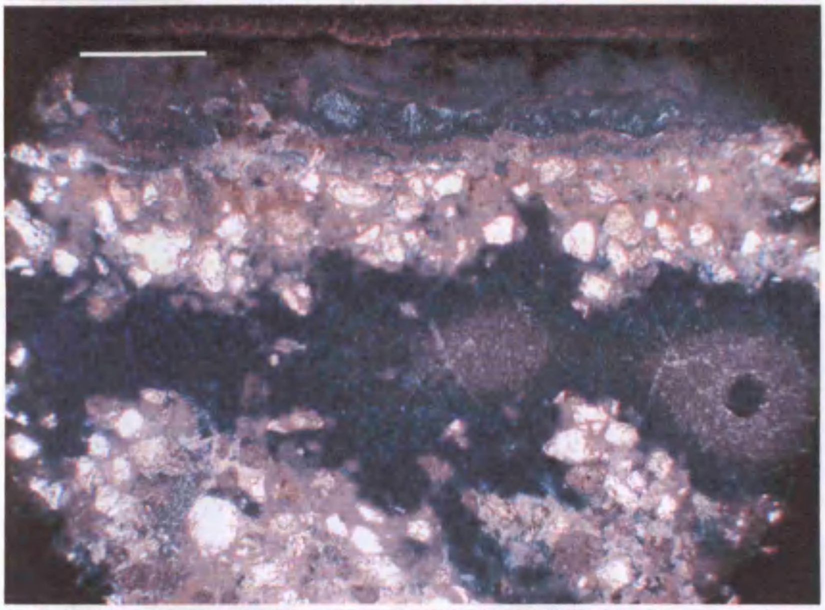


Fig. 45 The pore matrix collapsed near the surface of samples type A. The surface material formed a flake of pulverized material which appeared externally as swelling (sc.200μm)

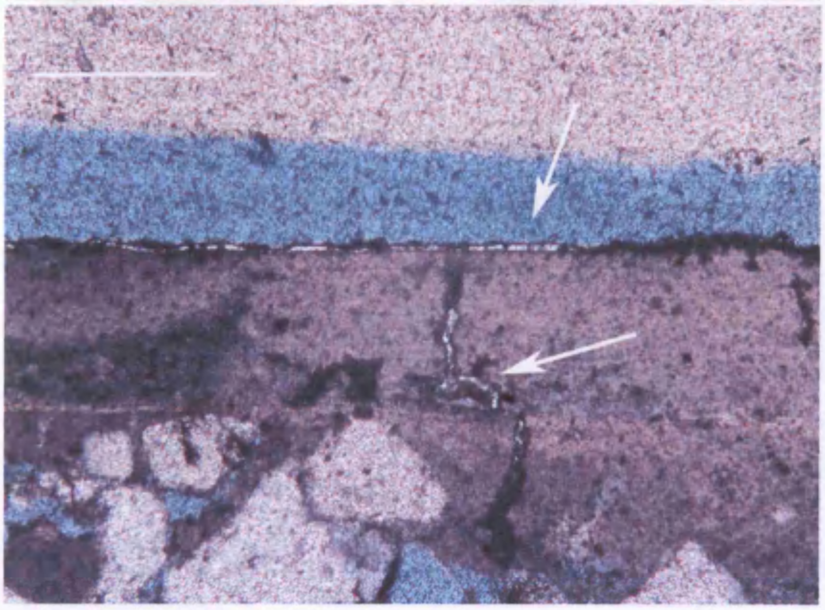


Fig. 46 The small perpendicular capillaries of samples type B supply slowly the solution allowing the formation of a crust on the surface (sc.50μm)

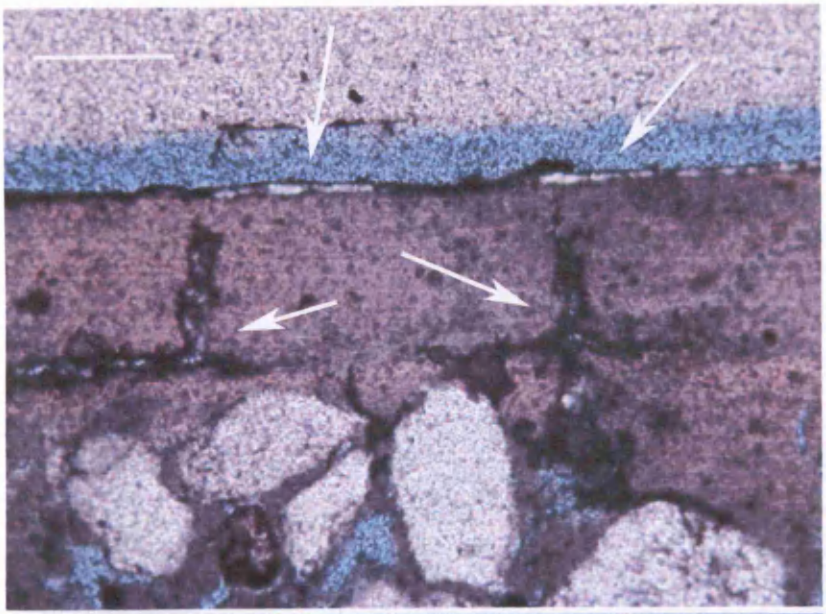


Fig. 47 Small gaps at the interface are filled with salt supplied by the perpendicular capillaries (sc.50μm)

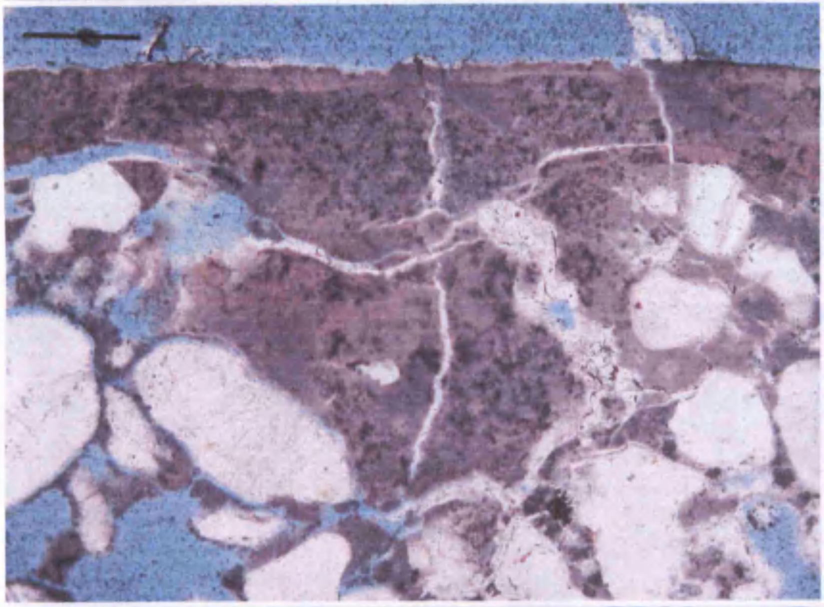


Fig. 48 Selective crystallization in small capillaries (sc.50μm)

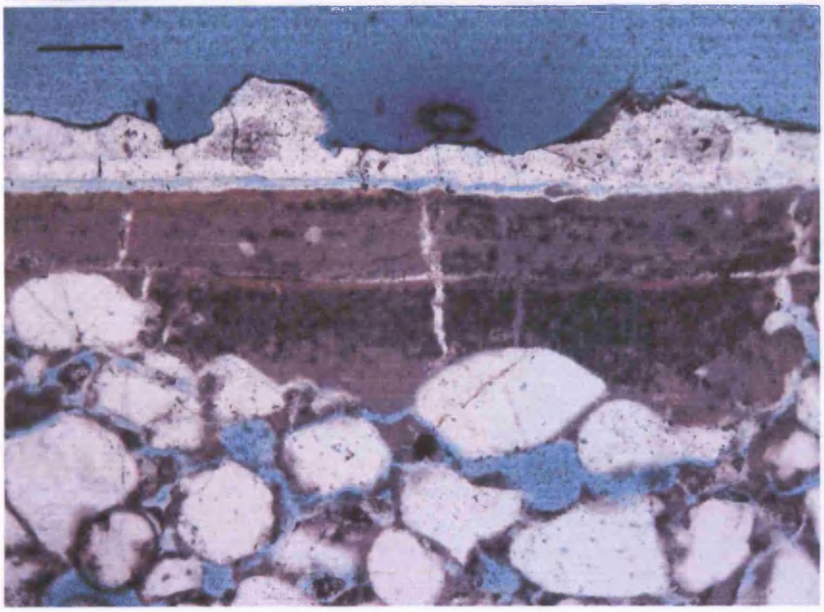


Fig. 49 The external crust has grown considerably but the pores are still empty. The salt begins to accumulate clearly at the interface (sc.50μm)

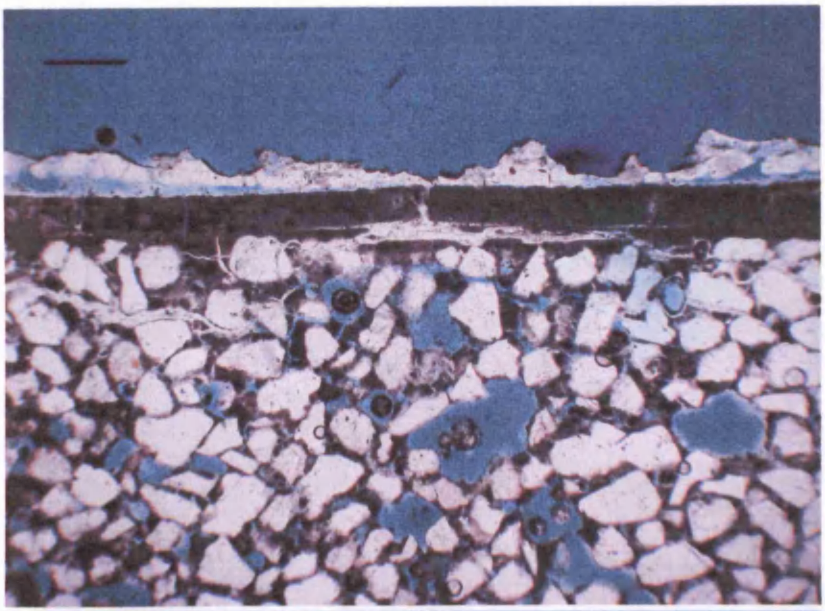


Fig. 50 Crystallisation at the interface (sc.50μm)

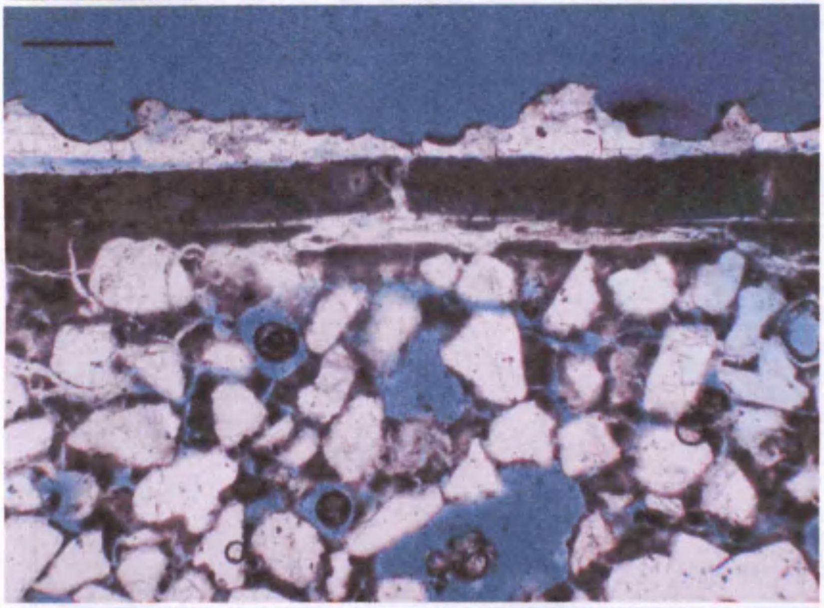


Fig. 51 Detail of fig. 51(sc.90μm)

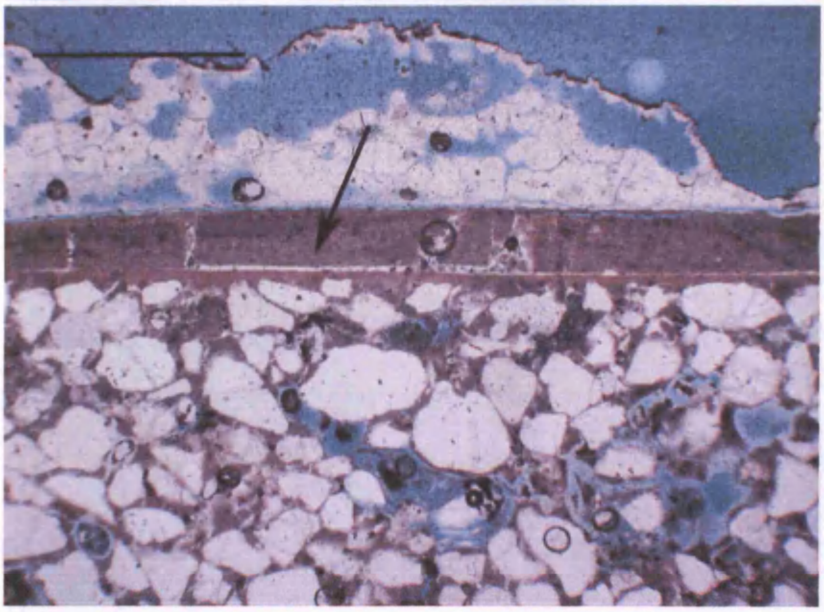


Fig. 52 the interface is filled with salts. The gap widens detaching the lime wash layer (sc.100μm)

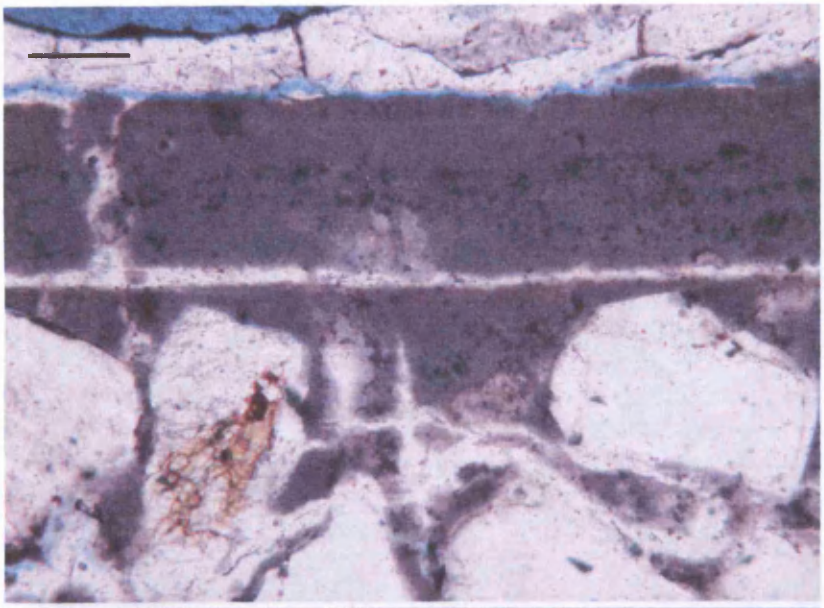


Fig. 53 Detail of detachment (fig.51). The interface is filled with salt (sc.20µm)

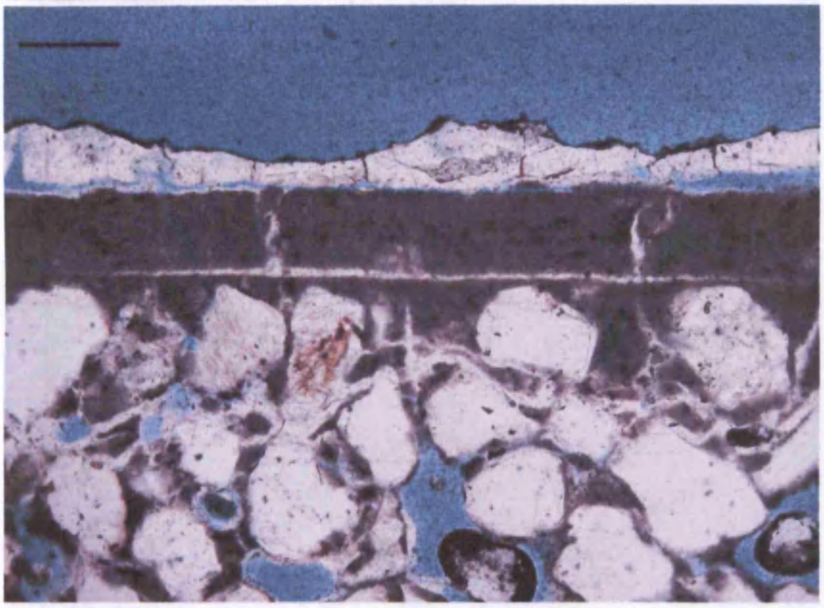


Fig. 54 The larger pores are still not filled with salts (sc.50µm)

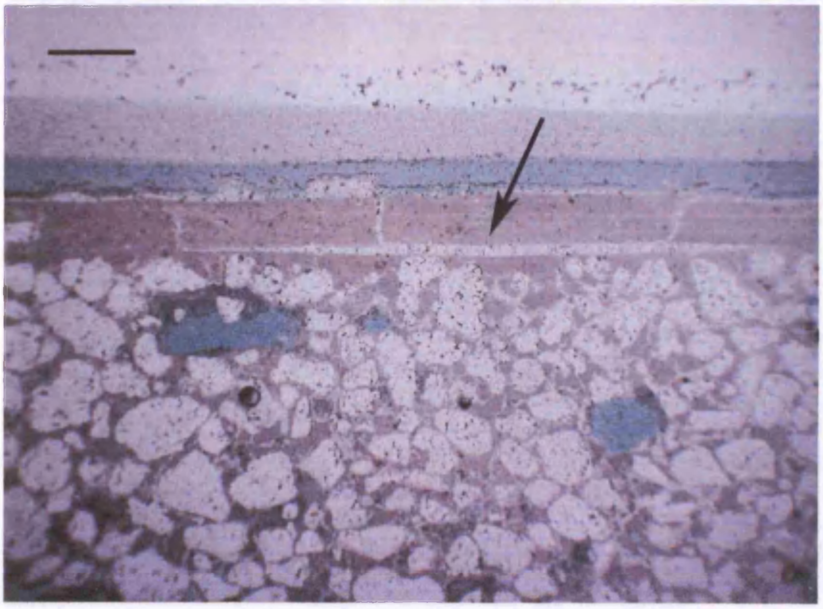


Fig. 55 Clear detachment of lime wash layer (sc.100µm)

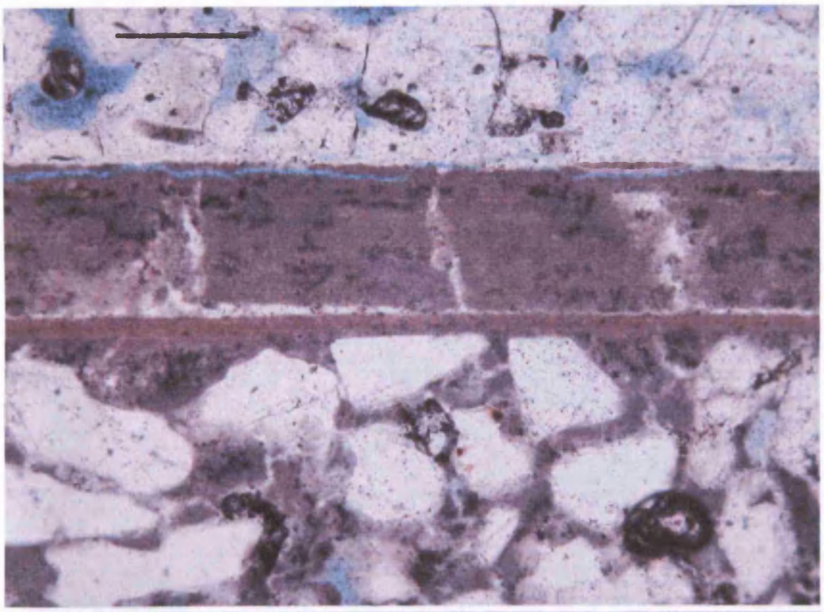


Fig. 56 Detached external flakes corresponding to figures IX.25,35 (sc.50μm)

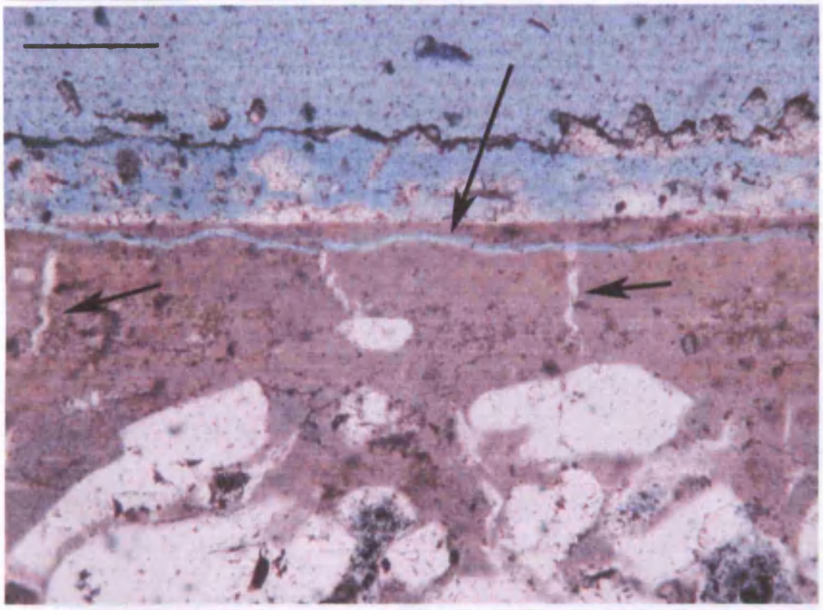


Fig. 57 Thin flakes of the lime wash layer before the accumulation of salt at the interface. The underlying capillaries are filled with salt (sc 50μm)

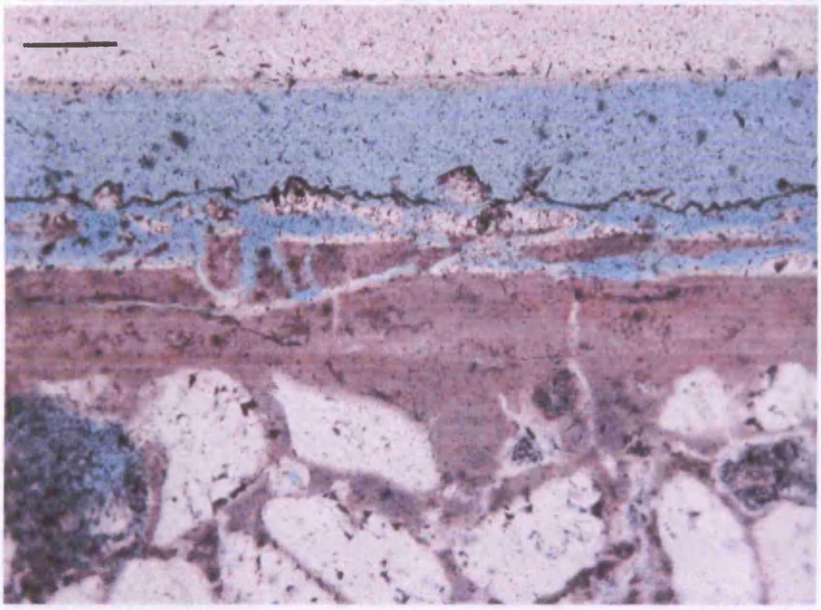


Fig. 58 As above (sc.50μm)

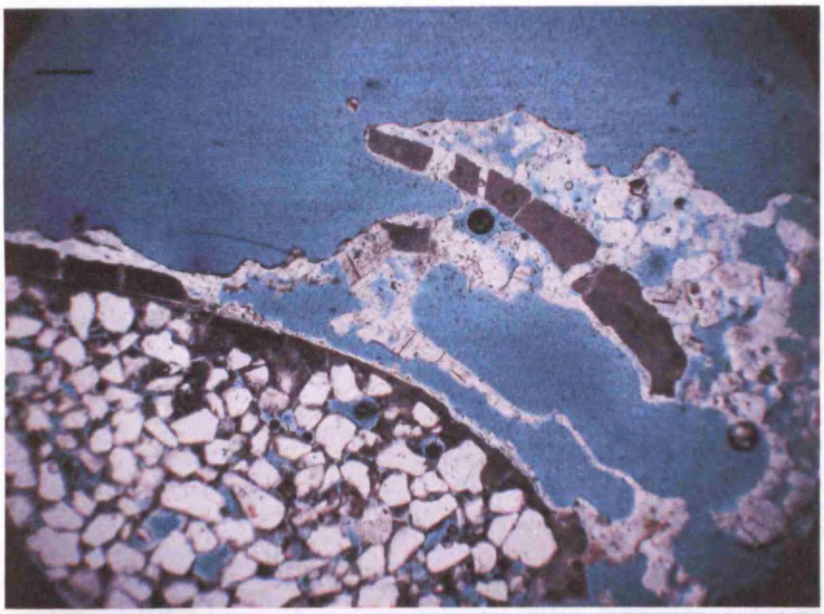


Fig. 59 The detached lime wash flake is incorporated in the salt crust (sc.50μm)

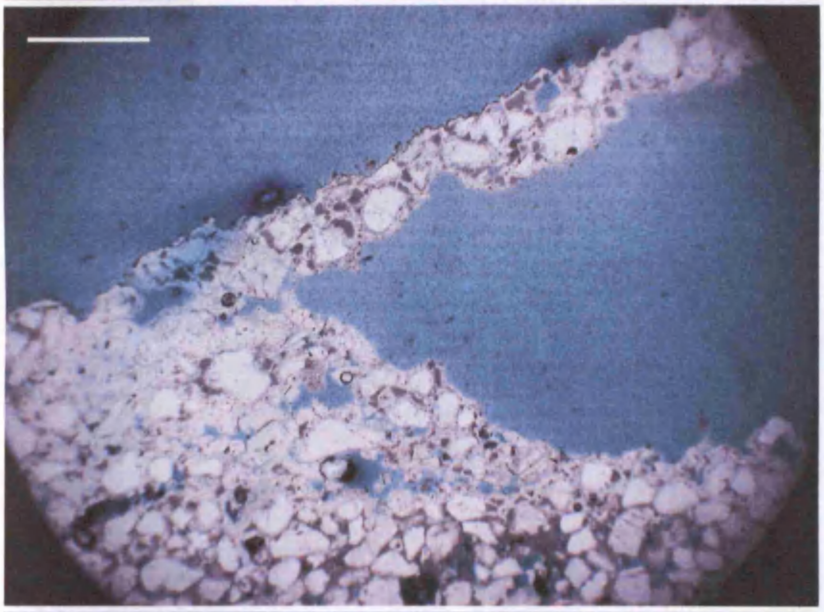


Fig. 60 Area of large swelling on type A sample. The flake-like detachment is comprised by pulverized material cemented by salts. The superficial area on the left presents the same status (sc.1mm)

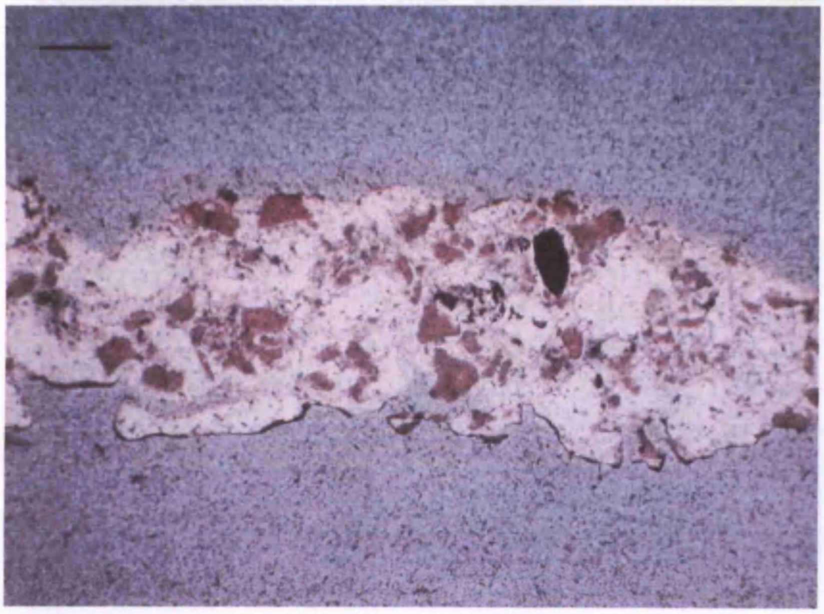


Fig. 61 Detail of swelling. The lime matrix (brown) has lost its continuity (sc100μm)

Fig. 62 The salt accumulates at the interface creating a complete detachment of the lime wash layer (sc.100μm)

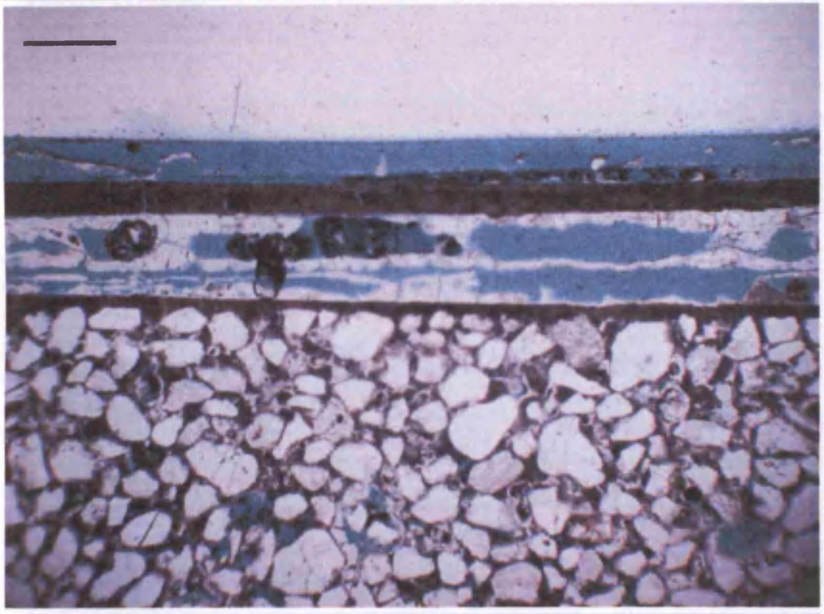


Fig. 63 As above (sc.100μm)

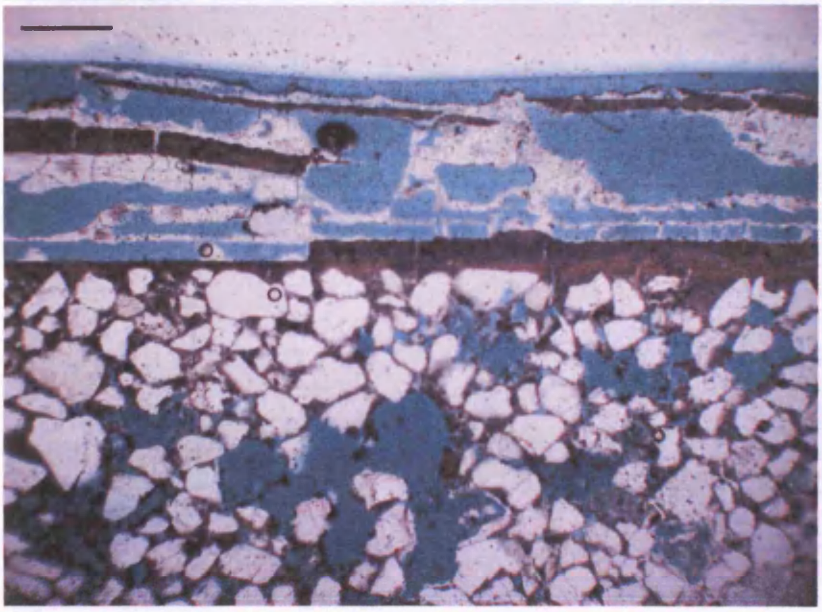


Fig. 64 Multiple flakes attached to the salt crust (sc.100μm)

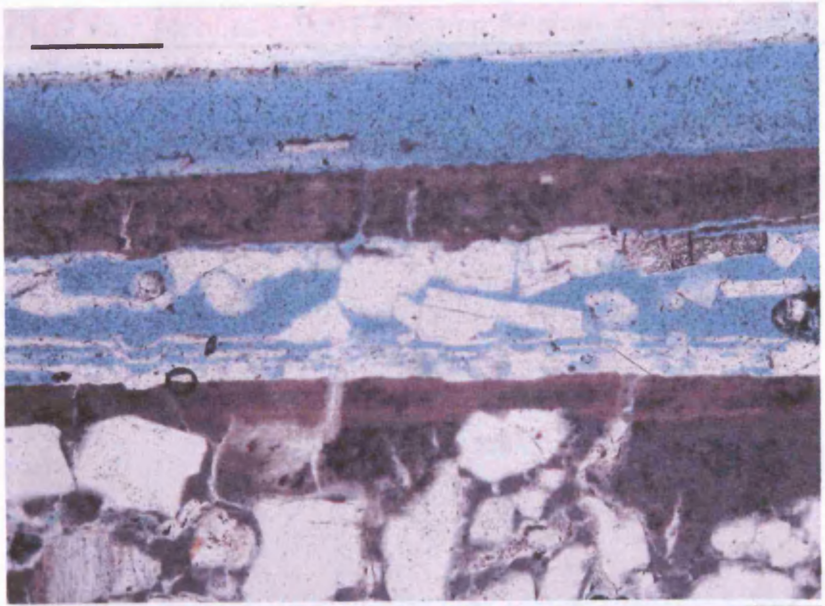


Fig. 65 Detail of detachment (sc.50μm)

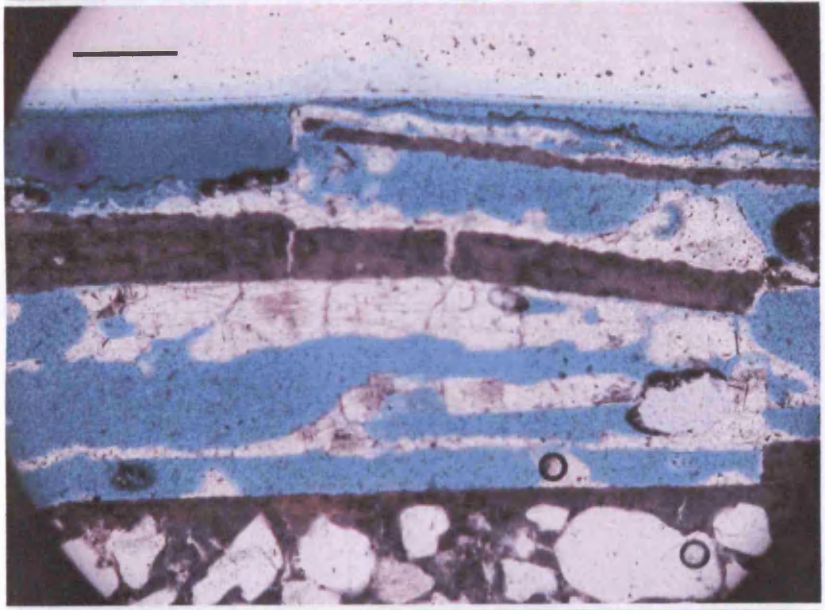


Fig. 66 Detail of fig. IX 64 (sc.50μm)

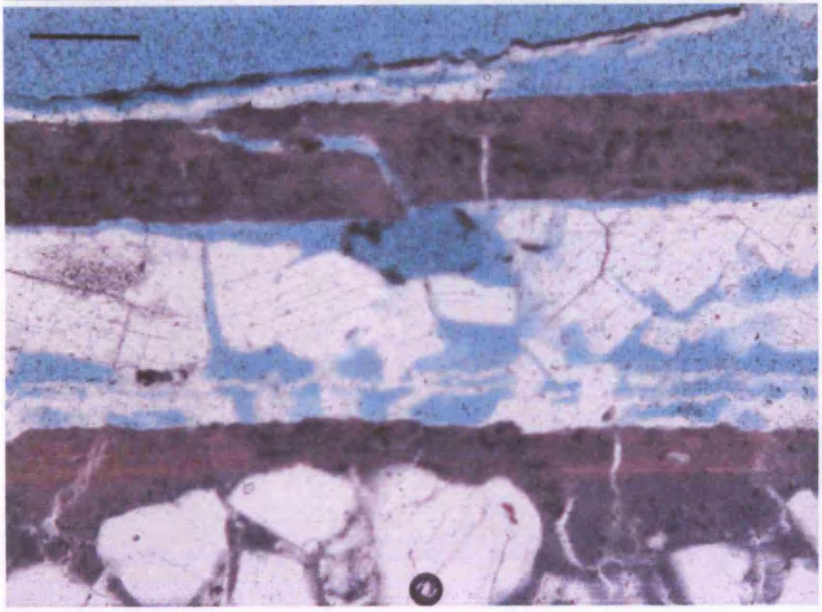


Fig. 67 Detail of detachment (sc.30μm)

IX.G Thin sections – WDS Microprobe elemental mapping

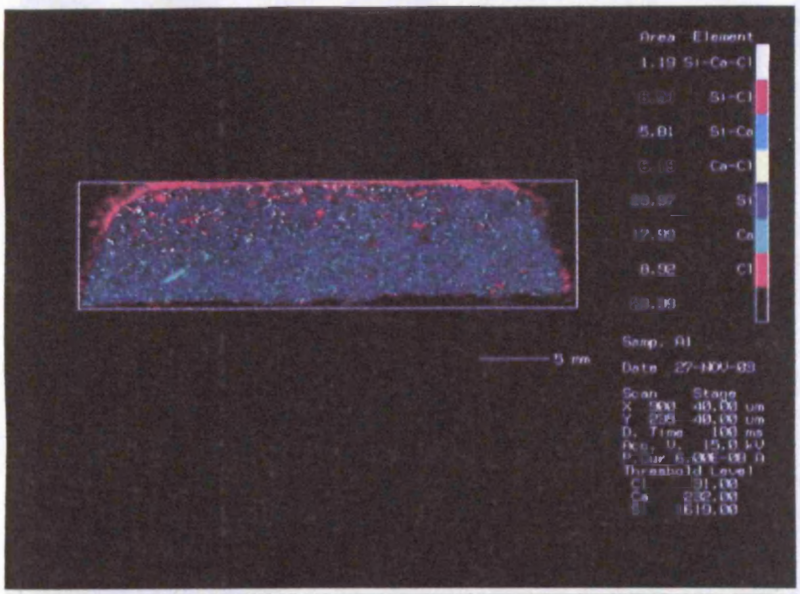


Fig. 68 Sample A type extracted on the 2nd day indicates a clear distribution of Cl near the exposed surface although there are traces down to half the sample's depth

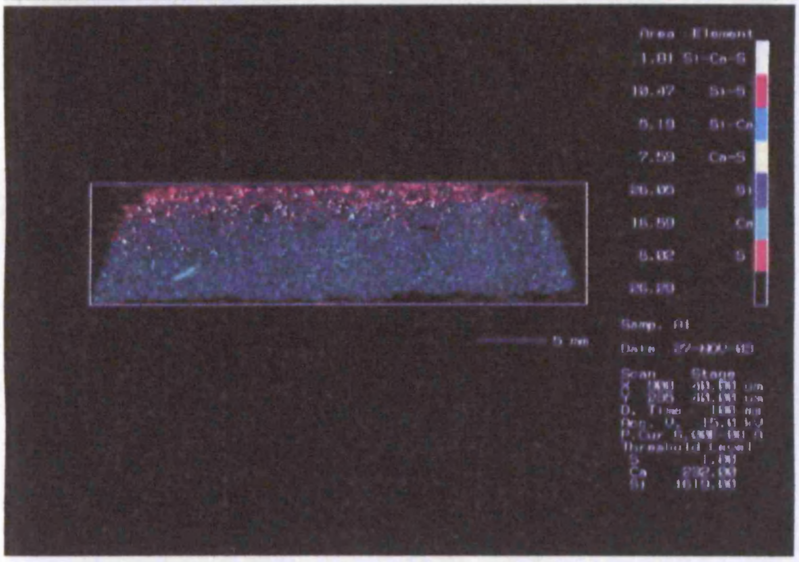


Fig. 69 The distribution of S presents a similar trend to Cl but with a stronger accumulation near the surface

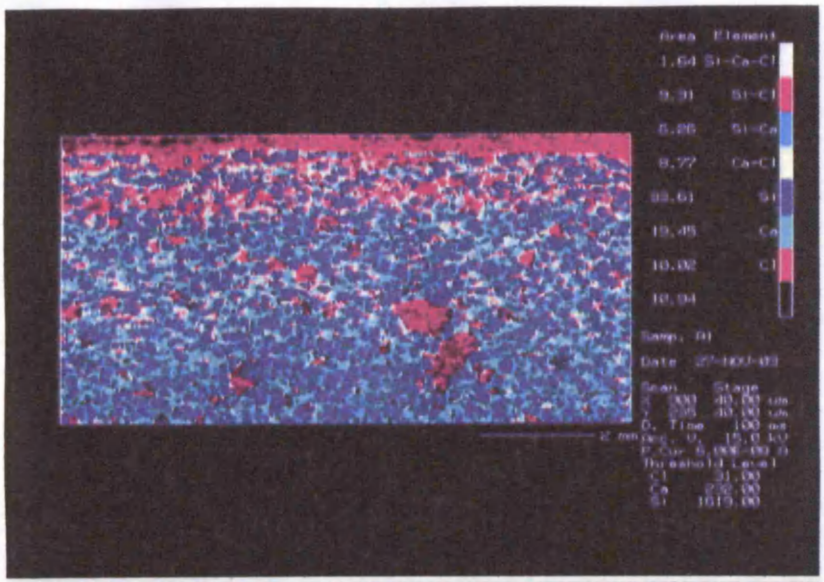


Fig. 70 Detail of fig. IX.69 The larger pores seem filled with salt at around 2mm from the surface

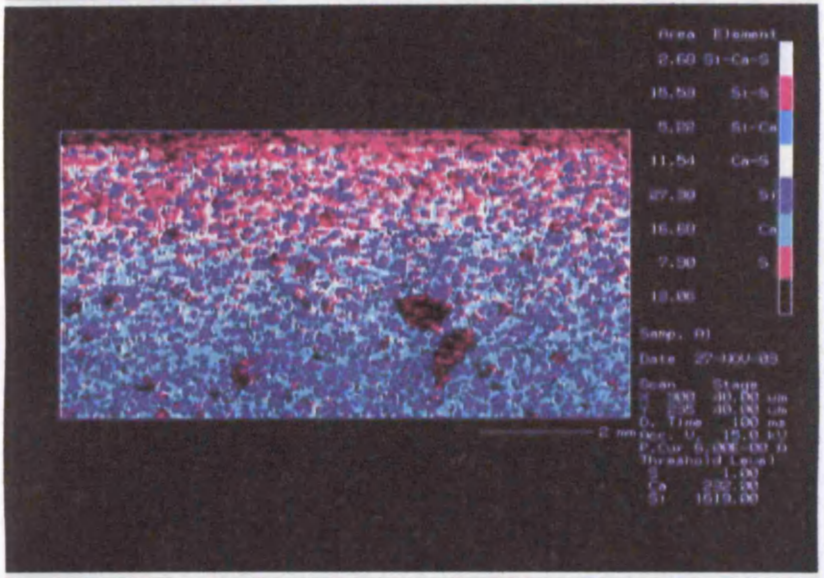


Fig. 71 Detail of fig. IX.68 Clearly S accumulates near the surface while there is a strong correlation to Ca (yellow)

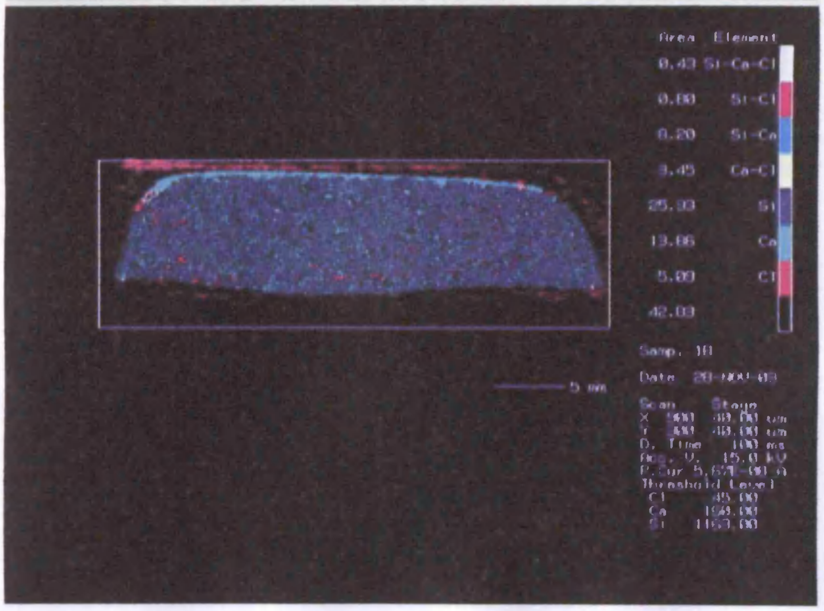


Fig. 72 Samples B type extracted on the 2nd day have not permitted a corresponding penetration to A type samples. The lime wash layer (green) restricts contamination and forces the salts to crystallize on the surface

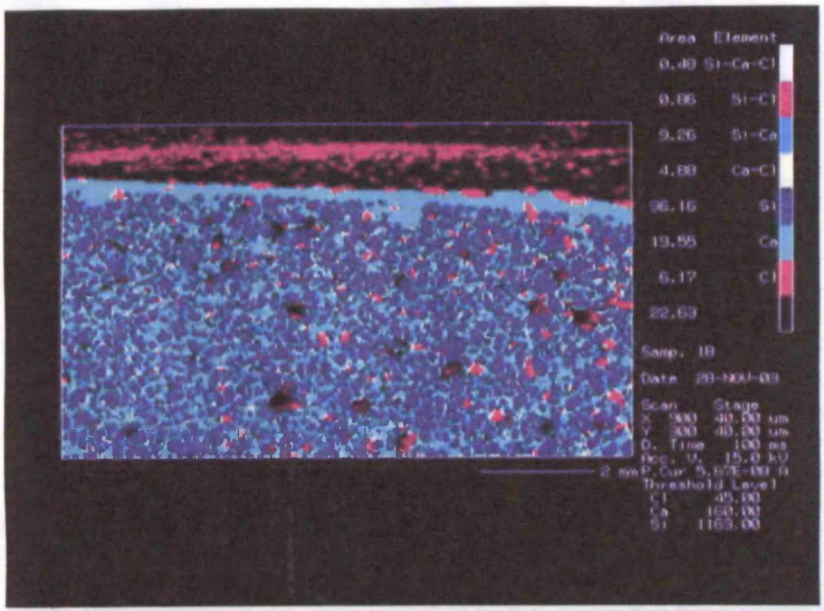


Fig. 73 Detail of fig. IX.72. There are Cl traces at a considerable depth indicating that the lime wash surface permits a certain degree of penetration but the concentration is obviously much smaller. The larger pores seem empty

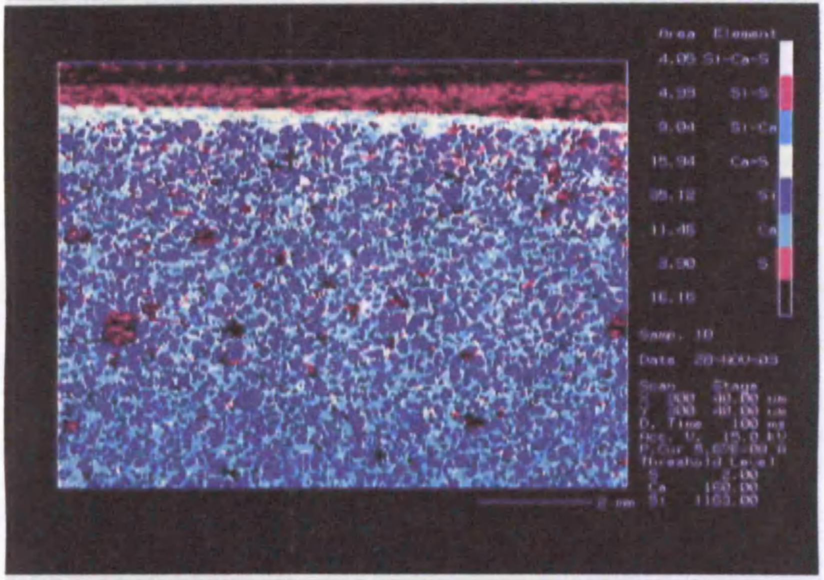


Fig. 74 The distribution of S presents a similar trend to Cl although there is a stronger accumulation near the surface and a particular correlation to Ca around the lime wash layer

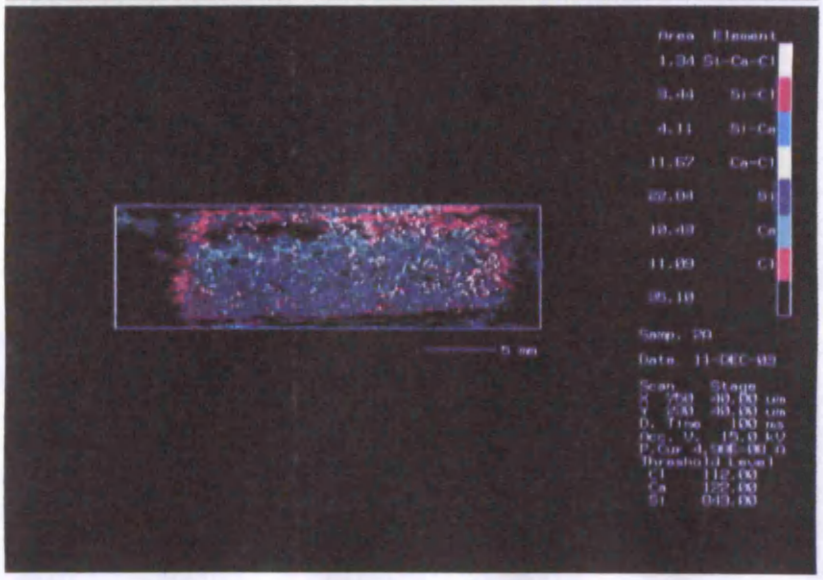


Fig. 75 Sample A type extracted on the 6th day presented already extended weathering in the form of a parallel to the surface fissure. The pore matrix collapsed at a depth of around 2mm leaving a superficial flake of disintegrated material cemented by the salt crust. The deformation was visible macroscopically on the surface. The undisturbed area of the sample (right) presented a strong concentration of salt at the same depth with the fissuring

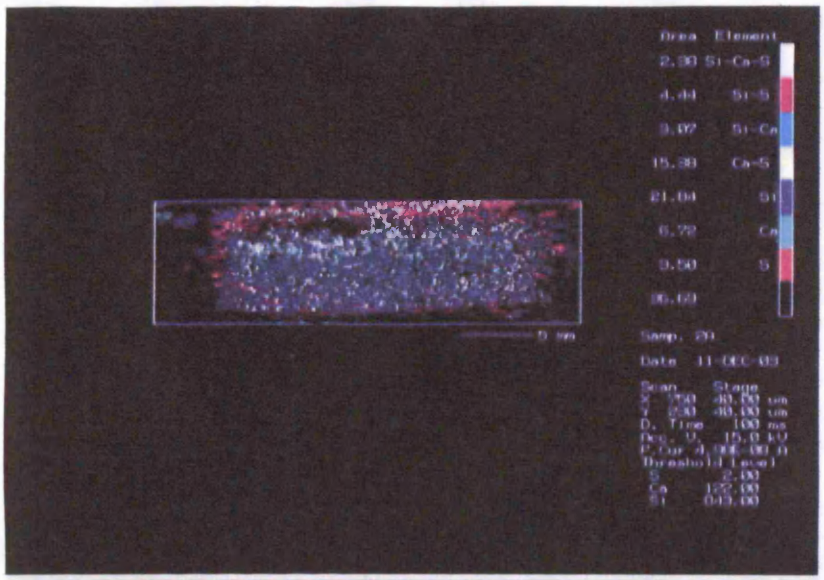


Fig. 76 The distribution of S is more likely

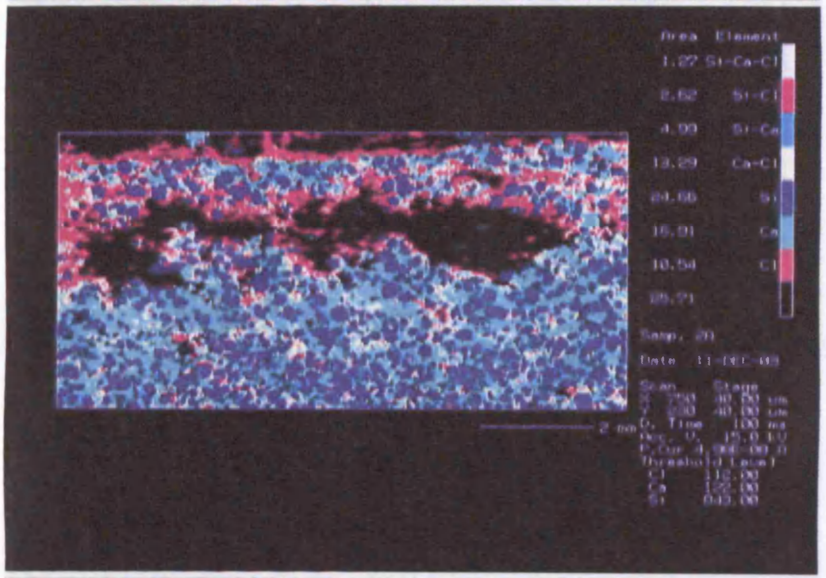


Fig. 77 Clear accumulation of salt around the fissure. The flake (up) maintains a certain continuity of the lime matrix. Although the deformation is visible to the naked eye, the surface is not as swelled as on other samples

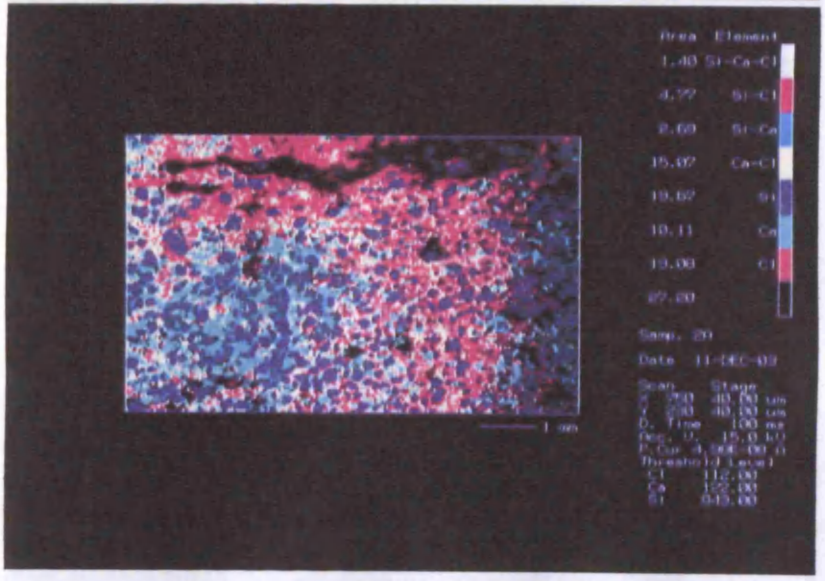


Fig. 78 (As above)

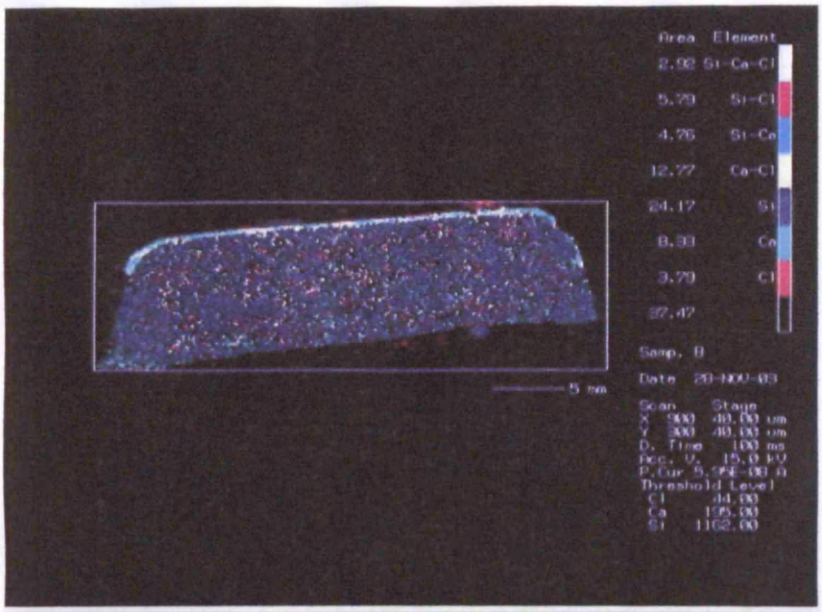


Fig. 79 The concentration of salt has increased on the samples type B extracted on the 6th day but still it is lower than the concentration of samples A type extracted earlier. The even distribution is indicative of slow solution supply which does permit the generation of a concentration gradient

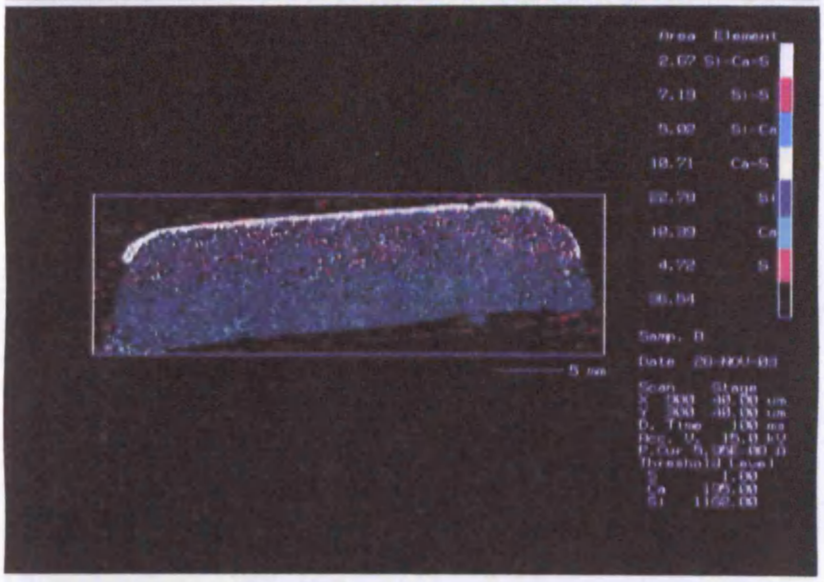


Fig. 80 The distribution of S though is not even. We observe a clear accumulation at the upper half of the sample. Obviously there is a species fractionation

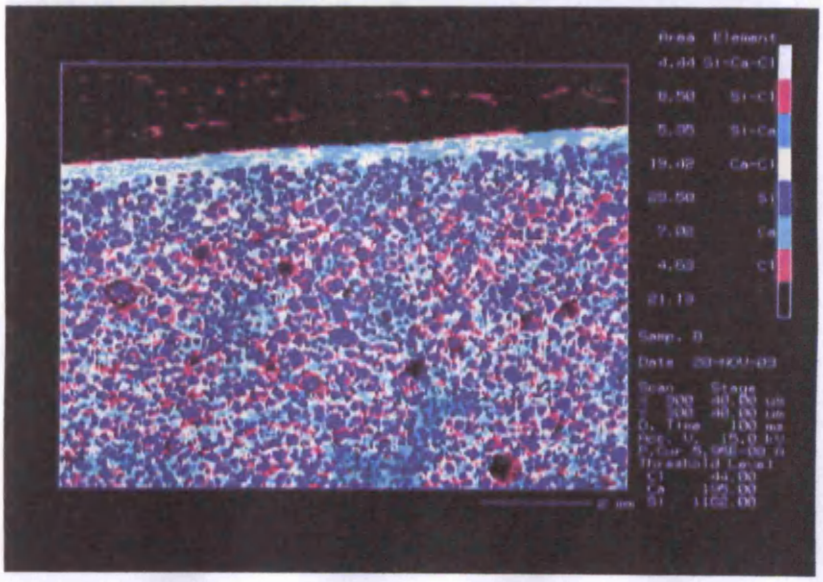


Fig. 81 The porosity is still undisturbed on samples B type. The larger pores are still not filled with salts (detail of fig. IX.79)

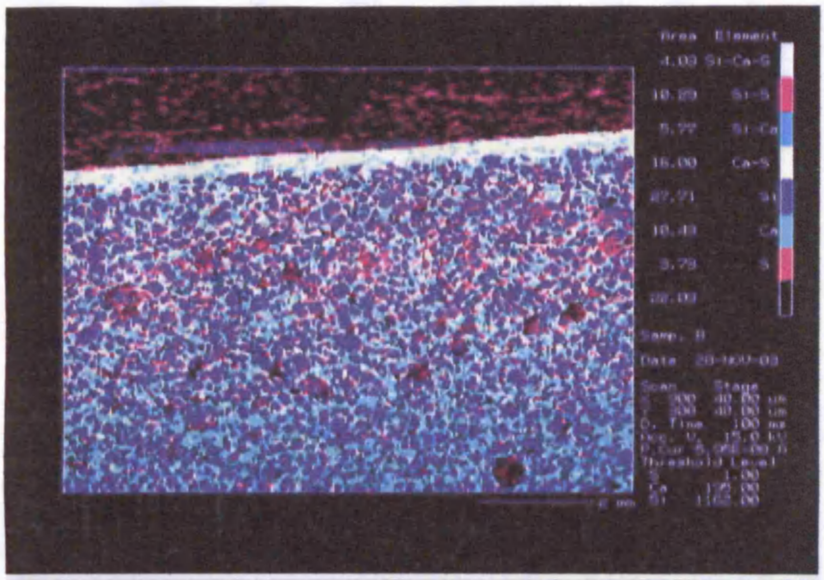


Fig. 82 The accumulation of S near the surface is more evident in this detail of fig. IX.76. We also observe a strong correlation to Ca on the lime wash layer (yellow)

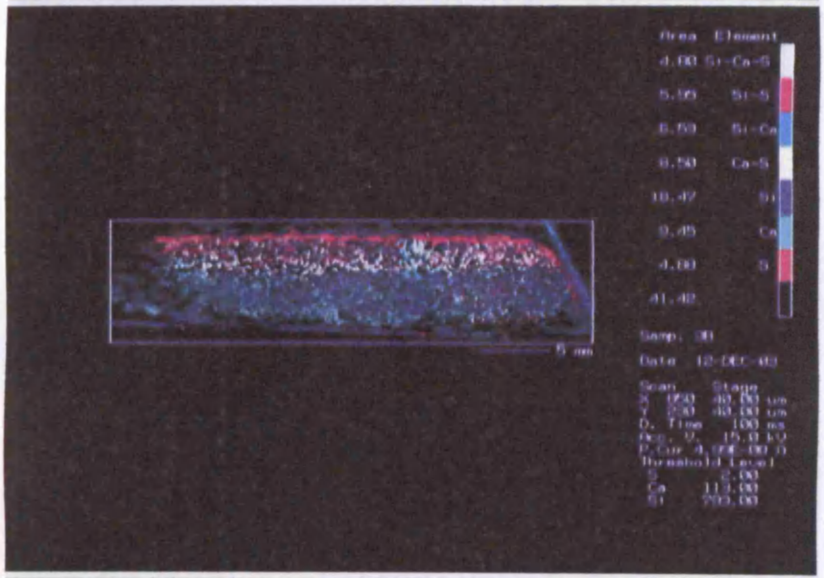


Fig. 83 A second sample type A extracted on the 6th day with no visible deformations revealed the same distribution trend with a particular accumulation at around 2mm from the surface. It is a strong indication that parallel fissuring and the resulting swelling originate from a concentration gradient at a certain depth

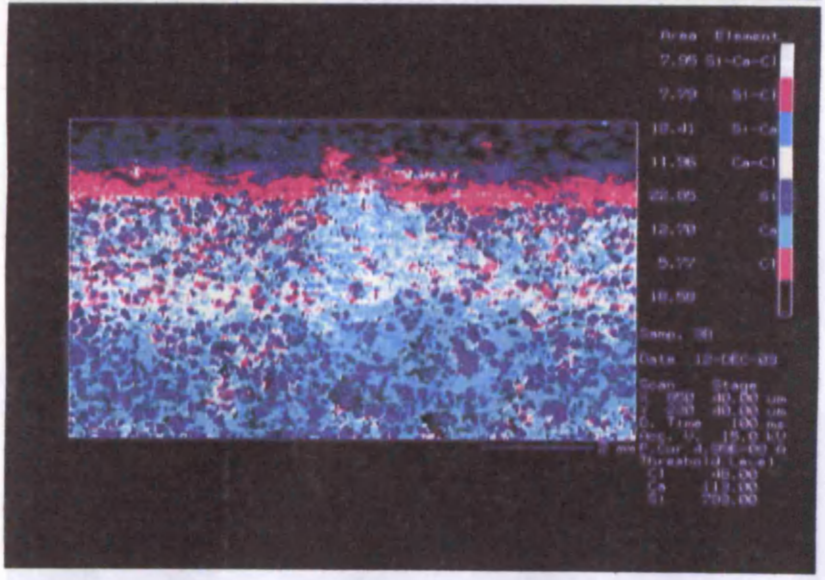


Fig. 84 Detail of fig. IX.83

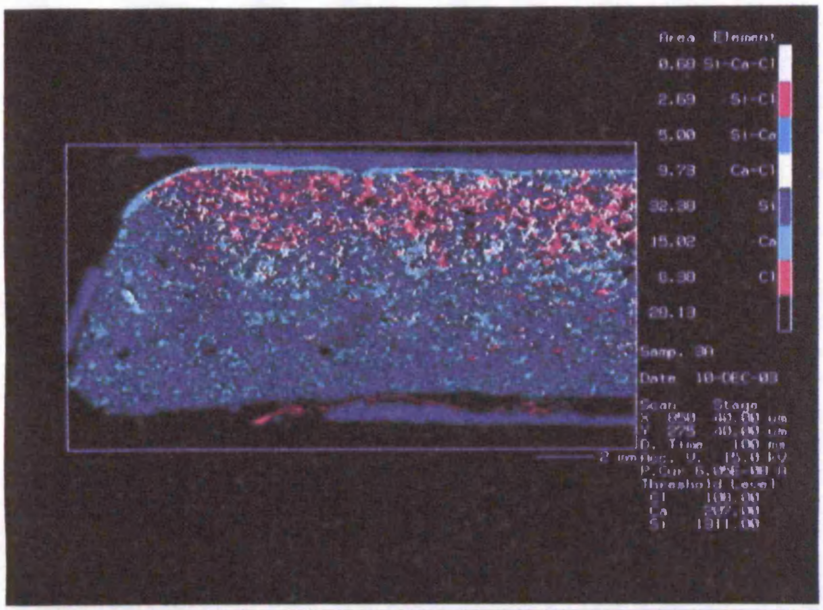


Fig. 85 The concentration has increased significantly in samples type B extracted on the 10th day. Still the matrix is undisturbed. We can observe that the distribution increases towards the surface creating a significant gradient

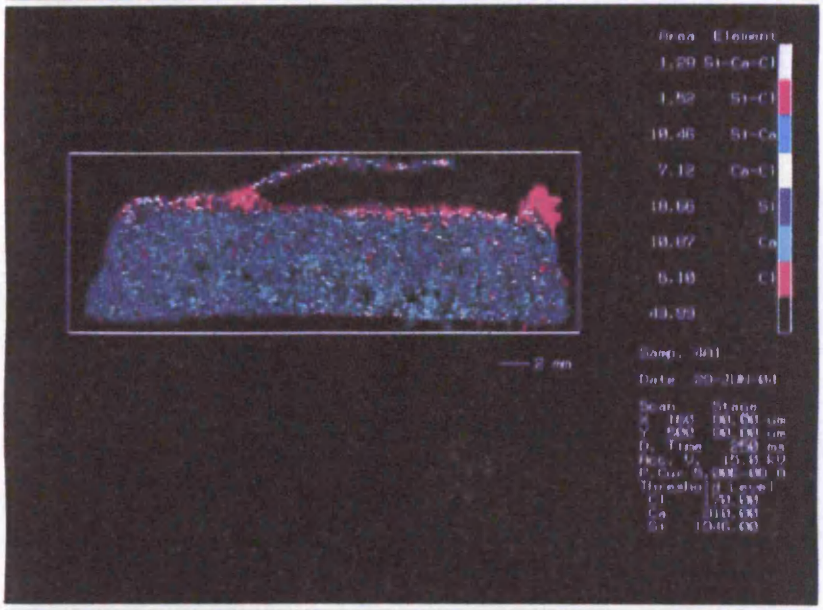


Fig. 86 The large swelling of type A sample extracted on the 10th day is actually a detached flake of cemented debris from the surface of the material. We observe a strong accumulation underneath the fake

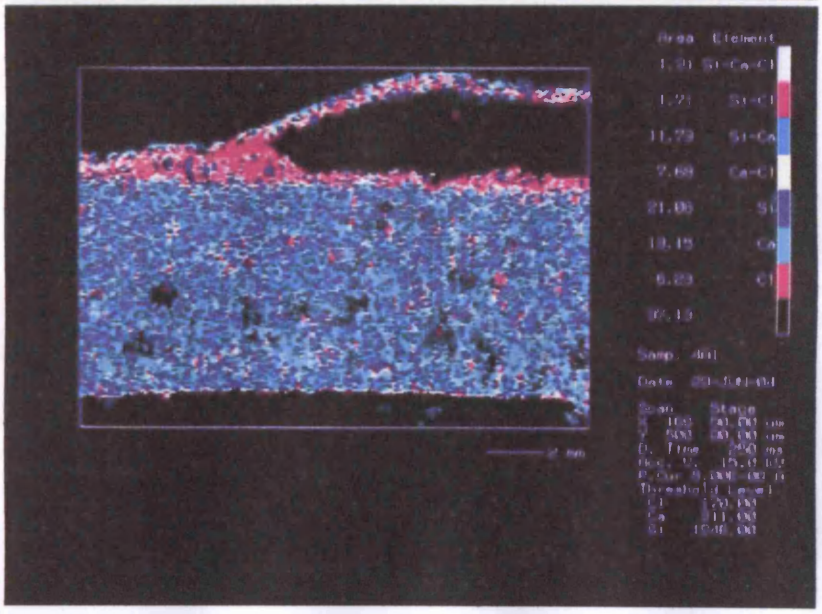


Fig. 87 The flake presents a very high concentration of Cl

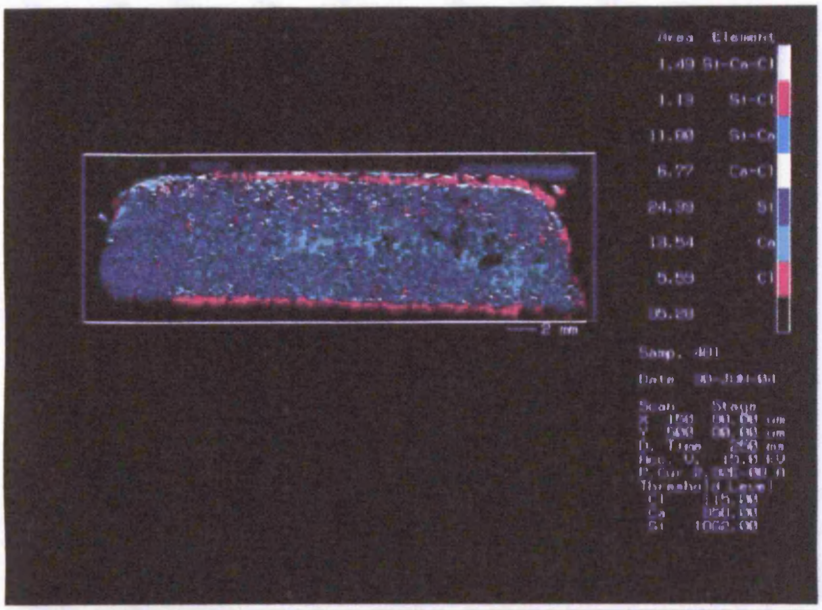


Fig. 88 The salt concentration at the interface is clearly depicted at the samples type B extracted on the 14th day

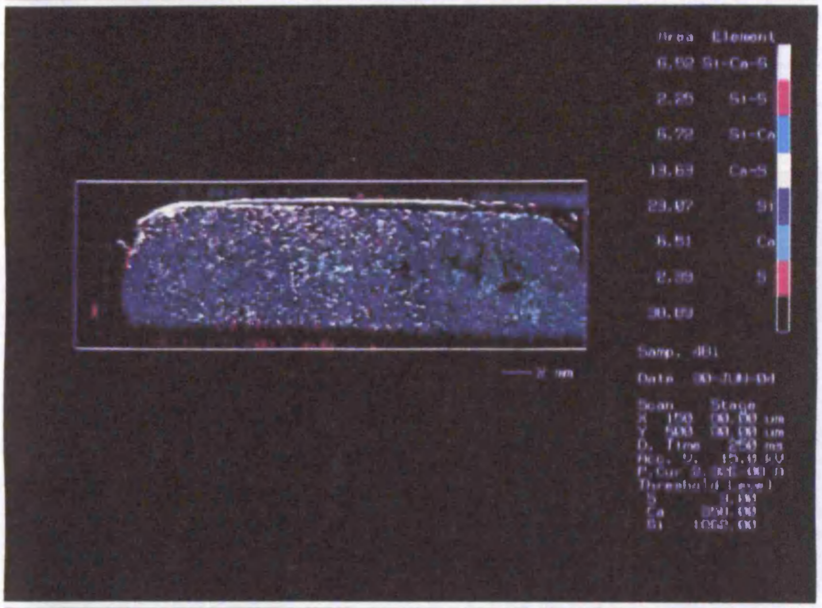


Fig. 89 The concentration of S is stronger on the lime wash flake and not at the interface. We also observe a correlation to Ca

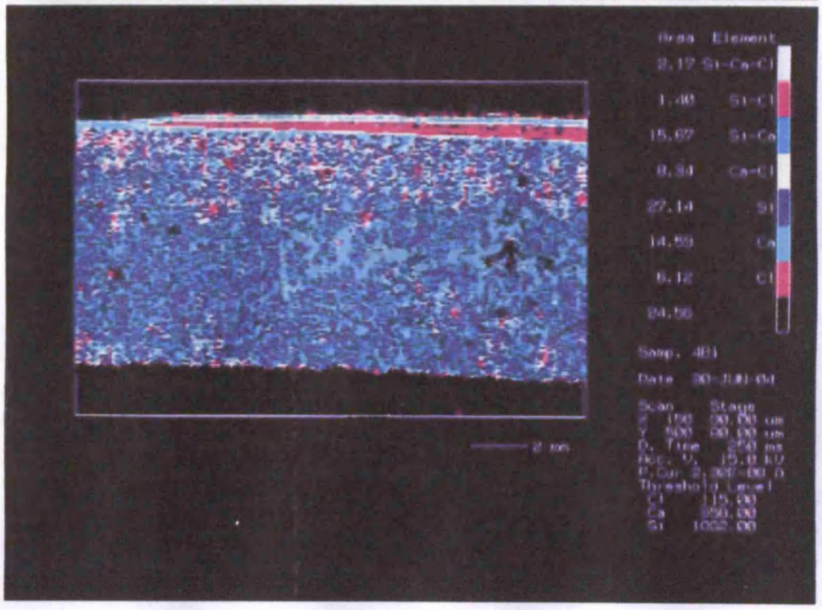


Fig. 90 Detail of fig. IX.88

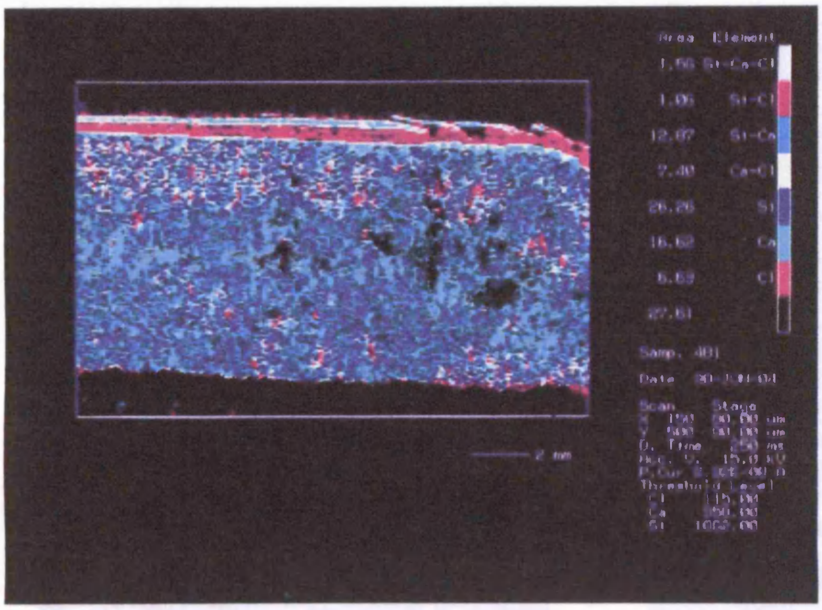


Fig. 91 Detail of fig. IX.88

IX.H Crystal morphology - SEM

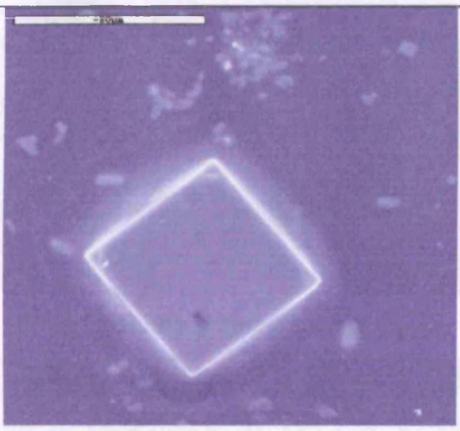


Fig. 92 Halite cubic crystal

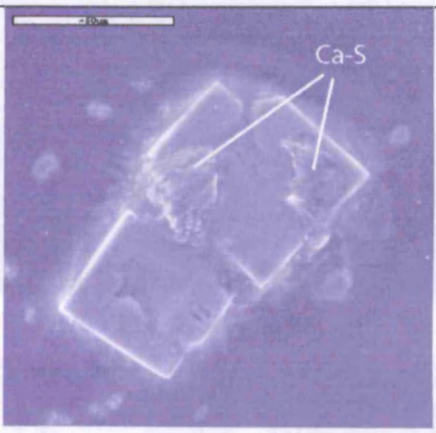


Fig. 93 Gypsum rods on halite

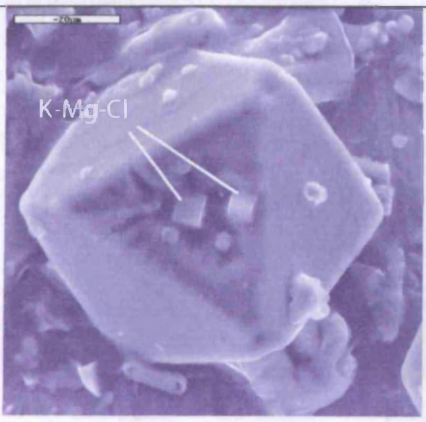


Fig. 94 K-Mg-Cl crystals on halite

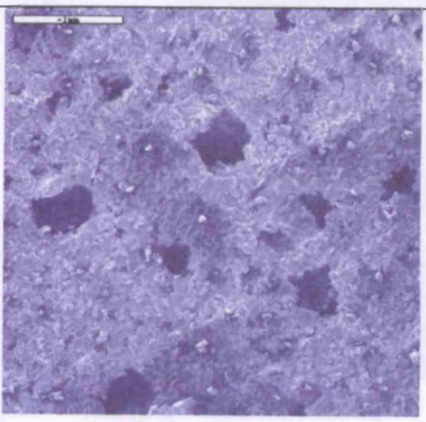


Fig. 95 The surface of A type weathered sample

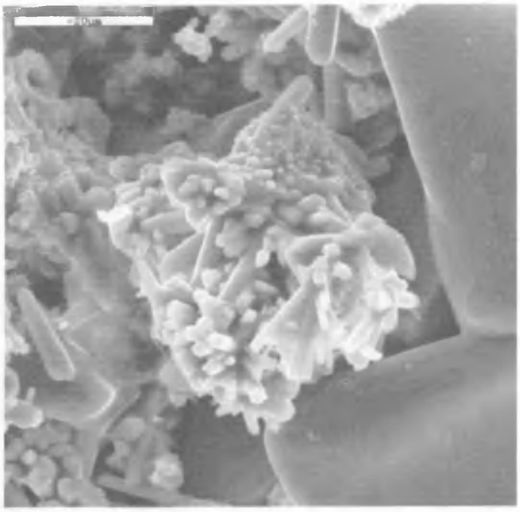


Fig. 96 Gypsum acicular crystals

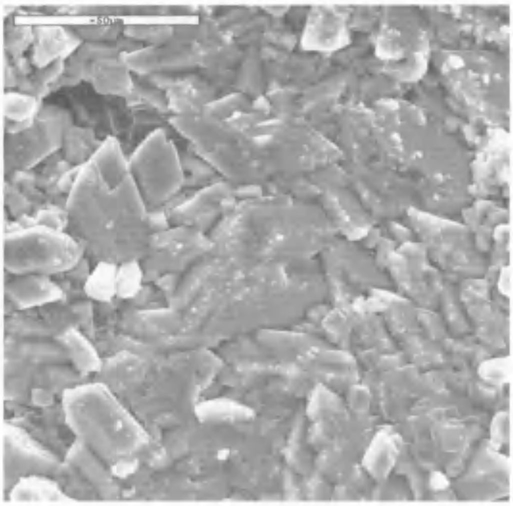


Fig. 97 Gypsum tabular crystals

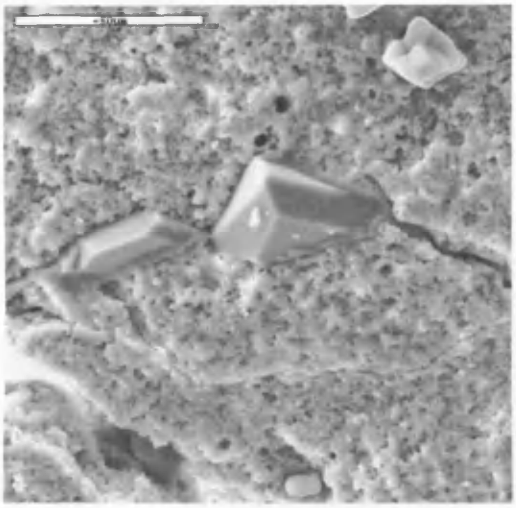


Fig. 98 Halite growing against crack

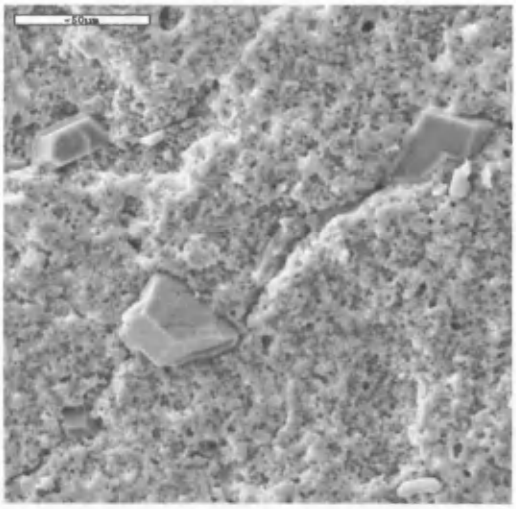


Fig. 99 (As fig.98)

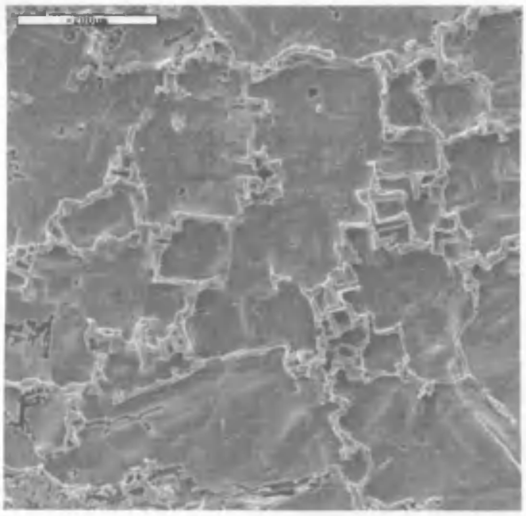


Fig. 100 Salt crust on B type sample

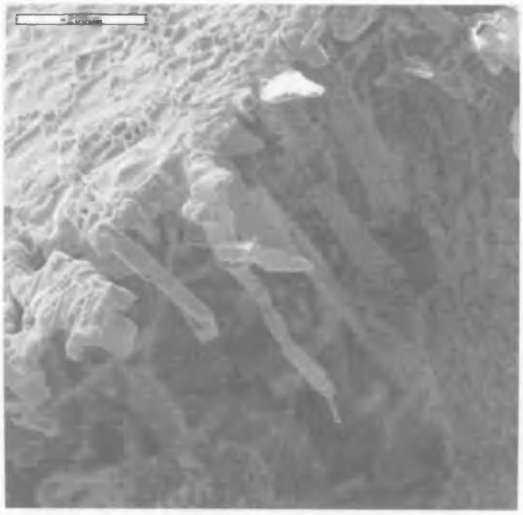


Fig. 101 Whiskers growing underneath the crust

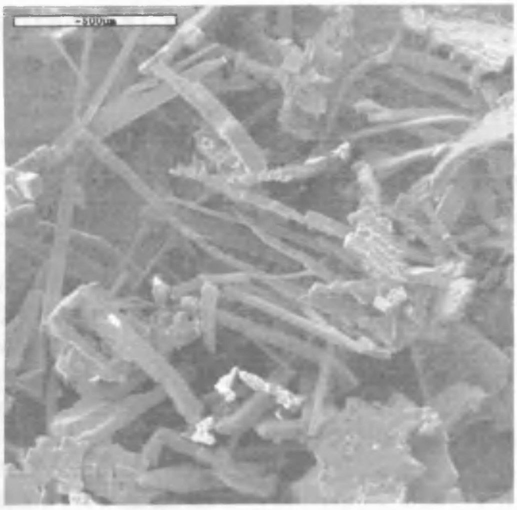


Fig. 102 Halite whiskers

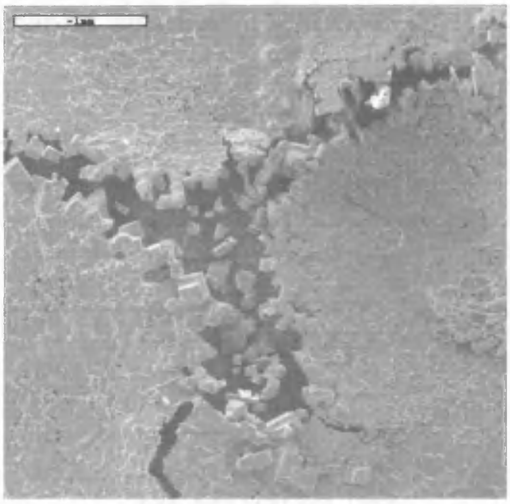


Fig. 103 Salt crust disruption and detachement

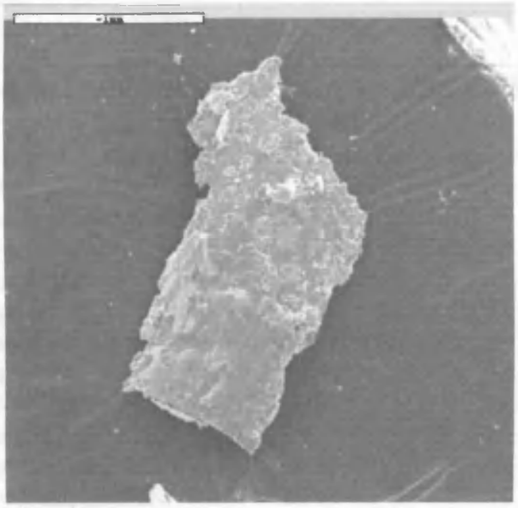


Fig. 104 Lime wash flake (sc.1mm)

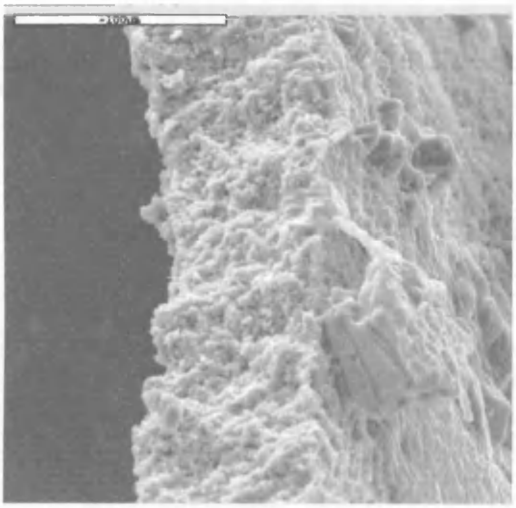


Fig. 105 Flake cross section (sc.200 μm)

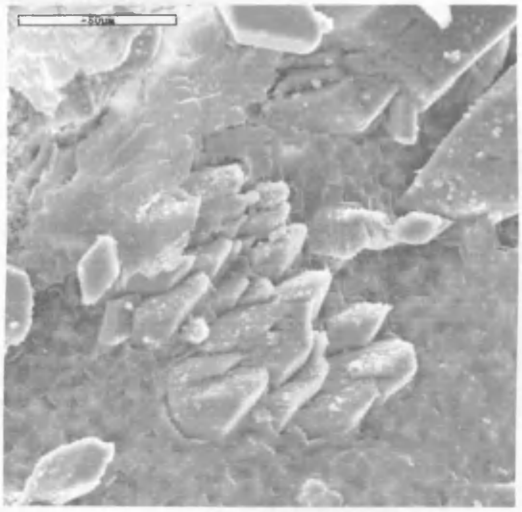


Fig. 106 Gypsum growing at the inner side of the flake (interface)

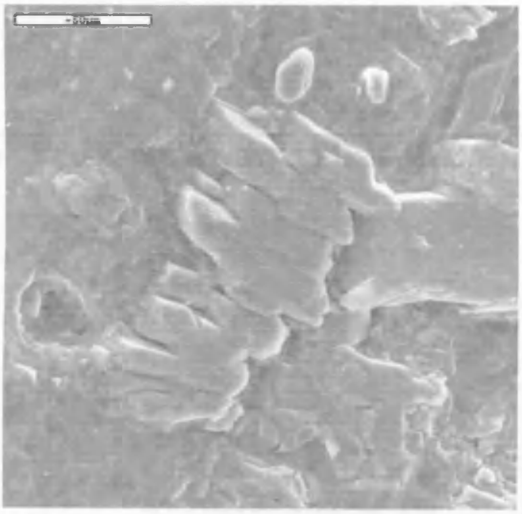


Fig. 107 Sulphation?

Appendix X: Specifications – Equipment, consumables, suppliers

X.A Analytical instruments and microscopes

Ion Chromatography (IC)

Dionex DX 100

AS14A anion column
AMMS II anion micromembrane suppressor
Eluant: 1.8 mM carbonate/1.7 mM bicarbonate
Regenerant: 0.05M H2SO4
Detection: Bipolar heated conductivity cell, digital signal processing over the range of 0-500 µS
Software: PeakNet-IA

Dionex (UK) Ltd. - Leeds Office
6 Pavilion Business Park
Royds Hall Road
LS12 6AJ
Leeds United Kingdom
Phone: 44 (113) 279 8579
Fax: 44 (113) 231 1597
e-mail: info@dionex.co.uk

Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES)

Perkin Elmer Optima 3300RL

Segmented array Charge-coupled-device Detector

Subarrays	235
Pixels per subarray	20 - 80
Injector tube (quartz)	1.50 mm id
Plasma power	0.8–1.2 kW
Coolant argon flow	11.0–15.0 l min21
Nebulizer argon pressure	280 kPa (40 psi)
Sample uptake	1.0 ml min21
Autosampler	AS91
Sample positions	98
Sample read delay	60 s
Autosampler wash delay	20 s
Integration time	3 s
Number of integration	3

PerkinElmer LAS (UK) Ltd
Chalfont Road
Seer Green
Beaconsfield
Bucks HP9 2FX
Tel. 0800-89 60 46
Fax 0800-89 17 14
http://uk.instruments.perkinelmer.com

Scanning Electron Microscopy – Energy Dispersive X-ray Analysis (SEM-EDAX)

Hitachi S-570 (ultra high resolution)

Electron gun: Lanthanum Hexaboride
Resolution: 3,5 nm
Magnification: 20 - 200.000 x
Accelerating voltage: 0,5 - 30 Kv
Secondary electron detector
Backscattered electron detector
LINK ExL II EDX microanalysis

Hitachi High - Technologies
Corporation (London)
Craven House
40, Uxbridge Road
Ealing
London
W5 2BS
Tel: +44 (0) 207 306 7979
Fax: +44 (0) 208 579 2683
www.hitachi-hitec-uk.com

Wave Dispersive Spectrometry Electron Microprobe (WDS-EPMA)

Jeol Superprobe JXA 8600

Detectable element range 5B to 92U (4Be to 92U)
Detectable wavelength range 0.087 to 9.3nm
Number of WDS X-ray spectrometers 3 (1 to 5 selectable)
Number of crystals: 6 (2 Lith; 2 Pet; 1 stearate;1 Tap)
Specimen size (maximum) 100mm × 100mm × 50mm (H)
Specimen stage drive speed 15mm/s
Accelerating voltage 0.2 to 30kV (0.1kV steps)
Probe current range 10-12 to 10-5 A
Probe current (Ip) stability ±0.5 × 10-3/h, ±3 × 10-3/12h
Secondary electron image (SEI) resolution 6nm (WD11mm, 30kV)
Backscattered electron image (BEI) Topography and composition image
Scanning image magnification × 40 to 300,000 (WD11mm)
Workstation (Sun Ultra 10 series)
Disk 20GB
Color monitor 21-inch display (For host computer)
17-inch display (For SEM)
Application software EPMA operation, qualitative, expert qualitative, semi-quantitative, quantitative, calibration curve, line, area, automated continuous, combination map, initial setting, file search, utility
Operating system Solaris (UNIX)
Language C

JEOL (U.K.) LTD.
JEOL House, Silver Court,
Watchmead,
Welwyn Garden City,
Herts AL7 ILT.
England
Phone: +44 (0) 1707 37 71 17
Fax: +44 (0) 1707 37 32 54
Email: uk.sales@jeoleuro.com

Environmental Scanning Electron Microscopy (ESEM)

Philips XL 30

Resolution: 2 nm
Accelerating voltage: 0.2 to 30 kV
Electron gun: Field-Emission
Magnification: 15 to 500,000
Stage movements: Tilt -15° to +75°
Z 50 mm
X 50 mm
Y 50 mm
Image media: Digital storage
Detectors:
Wet Mode: Gaseous secondary electron detector
Set of environmental secondary detectors
Solid state backscattered electron detector
High Vacuum Mode:Everhart-Thornley secondary electron detector
Solid state backscattered electron
Digital EDS Prism X-ray detector with IMIX-PC system.
Peltier cooling stage
Specimen chamber CCD camera

FEI UK Ltd.
Cambridge Business Park
Cowley Road
CB4 0HF Cambridge
United Kingdom
Tel: +44 1223 468560
Fax: +44 1223 468599

Optical Microscopy

Leica DMLP

Polarizing transmitted light microscope
Built-in 12V/100W illumination system
Objective magnifications 1.6x - 250x
RL/TL polarizers
10x Pol-eyepieces (field of view 25mm)

Leica Microsystems (UK) Ltd
Davy Avenue
Knowlhill
MK5 8LB Bucks Milton Keynes
Tel.:+44 1 908 246 246
Fax.:+44 1 908 609992
www.leica-microsystems.com

Wild M8-M113

Low magnification stereoscope
Lamps ring exposure VOLPI 150 W
Oblique exposure LGA 20 W
Objective lenses 0,4 x - 1x - 1.6x
Oculars for observation 10 (2x) - 20 (2x) - foto 10x
Zoom 6 - 50x
Eyepiece: Wild 10x/21B

X.B Consumables

Slaked lime putty

Bleaklow Industries Ltd

Total calcium oxide CaO	96.03 %
Calcium carbonate CaCO	3 3.89 %
Silica SiO2	0.75 %
Magnesium oxide MgO	0.27 %
Aluminium oxide Al2O3	0.27 %
Iron oxide Fe2O3	0.05 %
Calcium hydroxide Ca(OH)	2 4.87 %
Loss on ignition	2.89 %
Neutralising value (as CaO)	96.31 %
Gradings	86% BS 200
Bulk density	1300-1400 kg/m
Specific gravity	1.3-1.6
Soluble in water	

Bleaklow Industries Ltd.,
Hassop Avenue,
Hassop,
Bakewell,
Derbyshire DE45 1NS.
Tel: 01246 582 284
Fax: 01246 583 192
www.bleaklow.co.uk

Sharp sand

Leighton Buzzard washed fine sand

Quartz	>98%
Grind	0.3-0.1mm

Garside Sands
Eastern Way
Heath & Reach
Leighton Buzzard
Bedfordshire
LU7 9LF
tel:01525 237911
fax:01525 237991
www.garside-sands.com

Liquid latex

Taranti 404-100

Pre-vulcanised air drying liquid latex

Alec Tiranti Ltd
27, Warren Street
London
W1T 5NB
Tel: 020 7636 8565
Fax: 020 7636 8565
www.tiranti.co.uk

Drills

SKF&Dormer A125

HSS extra length drill
Flute Geometry Standard Helix, Right Hand Spiral
Point Angle 118°
Surface Treatment Bright
ISO 3292 / BS 328
Length 80-125mm
Diameter: 1mm

Dormer Tools
294 Kifissias Avenue
152 32 Chalandri
Athens
Greece
Tel. 30210 6823604
Fax 30210 6823771
dormer.gr@dormertools.com

Salts

Calcium chloride dihydrate
Merck 102382
GR for analysis ACS, Reag. Ph Eur

Assay (complexometric) 99.0 - 102.0 %
Identity passes test
Clarity of solution passes test
insoluble matter ≤ 0.01 %
Acidity or alkalinity passes test
pH-value (5 %; water) 4.5 - 8.5
Sulphate (SO4) ≤ 0.005 %
Heavy metals (as Pb) ≤ 0.0005 %
Al (Aluminium) ≤ 0.0001 %
Ba (Barium) ≤ 0.003 %
Cu (Copper) ≤ 0.0005 %
Fe (Iron) ≤ 0.0003 %
K (Potassium) ≤ 0.01 %
Mg (Magnesium) ≤ 0.005 %
Na (Sodium) ≤ 0.01 %
NH4 (Ammonium) ≤ 0.005 %
Sr (Strontium) ≤ 0.05 %
Magnesium and alkali metals ≤ 0.5 %
Oxidizing substances (as NO3) ≤ 0.003 %

Merck Chemicals Ltd.
Merck House
Poole, Dorset
England
BH15 1TD
Phone 01202 661616
Fax 01202 664489
Information@merckchem.co.uk

Calcium sulfate dehydrate
Merck 102161
precipitated GR for analysis
Assay (complexometric) 99.0 - 102.0 %
Substances insoluble in hydrochloric acid ≤ 0.01 %
Carbonate (CO3) conforms
Chloride (Cl) ≤ 0.005 %
Nitrate(NO3) conforms
Heavy metals (as Pb) ≤ 0.002 %
Fe (Iron) ≤ 0.001 %
K (Potassium) ≤ 0.005 %
Mg (Magnesium) ≤ 0.01 %
Na (Sodium) ≤ 0.2 %
Sr (Strontium) ≤ 0.05 %

Calcium nitrate tetrahydrate
Merck 102121
GR for analysis ACS
Assay (complexometric) 99.0 - 103.0 %
Insoluble matter ≤ 0.005 %
pH-value (5 %; water; 25 °C) 5.0 - 7.0
Chloride (Cl) ≤ 0.005 %
Nitrite (NO2) ≤ 0.001 %
Sulphate (SO4) ≤ 0.002 %
Heavy metals (as Pb) ≤ 0.0005 %
Ba (Barium) ≤ 0.005 %
Cu (Copper) ≤ 0.0002 %
Fe (Iron) ≤ 0.0005 %
K (Potassium) ≤ 0.005 %
Mg (Magnesium) ≤ 0.01 %
Na (Sodium) ≤ 0.01 %
Sr (Strontium) ≤ 0.01 %

Magnesium chloride hexahydrite
Merck 105833
GR for analysis ACS, ISO, Reag. Ph Eur
Assay (complexometric) 99.0 - 101.0 %
Identity conforms
Appearance of solution passes test
insoluble matter ≤ 0.005 %
pH-value (5 %; water) 5.0 - 6.5
Acidity or alkalinity passes test
Bromide (Br) ≤ 0.05 %
Nitrate (NO3) < 0.001 %
Phosphate (PO4) ≤ 0.0005 %
Sulphate (SO4) ≤ 0.002 %
Total nitrogen (N) < 0.0002 %
Heavy metals (as Pb) < 0.0005 %
Al (Aluminium) ≤ 0.0002 %
As (Arsenic) ≤ 0.0002 %
Ba (Barium) ≤ 0.002 %
Ca (Calcium) ≤ 0.003 %
Cu (Copper) ≤ 0.0005 %
Fe (Iron) ≤ 0.0005 %
K (Potassium) ≤ 0.001 %
Mn (Manganese) ≤ 0.0005 %
Na (Sodium) ≤ 0.001 %
NH4 (Ammonium) ≤ 0.002 %
Pb (Lead) ≤ 0.0005 %
Sr (Strontium) ≤ 0.005 %
Water 51.0 - 55.0 %

Magnesium sulphate heptahydrate
Merck 105886
GR for analysis ACS, Reag. Ph Eur
Assay
- complexometric 98.0 - 102.0 %
- calculated on dried substance 99.0 - 100.5 %

Identity passes test
Appearance of solution passes test
Insoluble matter < 0.005 %
Acidity or alkalinity passes test
pH-value (5 %; water; 25 °C) 5.0 - 8.0
Chloride (Cl) ≤ 0.0003 %
Total nitrogen (N) ≤ 0.002 %
Nitrate (NO3) < 0.002 %
Heavy metals (as Pb) < 0.0005 %
As (Arsenic) ≤ 0.0002 %
Ca (Calcium) ≤ 0.005 %
Cu (Copper) ≤ 0.0001 %
Fe (Iron) ≤ 0.0001 %
K (Potassium) ≤ 0.001 %
Mn (Manganese) ≤ 0.0005 %
Na (Sodium) ≤ 0.001 %
NH4 (Ammonium) ≤ 0.002 %
Pb (Lead) ≤ 0.0001 %
Sr (Strontium) ≤ 0.005 %
Loss on drying (400 °C) 48.0 - 52.0 %

Potassium chloride
Merck104936
GR for analysis ACS, ISO, Reag. Ph Eur
Assay
- argentometric 99.5 - 100.5 %
- calculated on dried substance 99.0 - 100.5 %

Identity passes test
Clarity of solution passes test
insoluble matter ≤ 0.005 %
pH-value (5 %; water) 5.5 - 8.0
Acidity or alkalinity passes test

Sodium chloride
Merck 106404
GR for analysis ACS, ISO, Reag. Ph Eur
Assay
- argentometric ≥ 99.5 %
- calculated on dried substance 99.0 - 100.5 %

Identity passes test
Appearance of solution passes test
Acidity or alkalinity passes test
pH-value (5 %; water) 5.0 - 8.0
Insoluble matter ≤ 0.005 %

Bromide (Br) ≤ 0.005 %
Chlorate and Nitrate (as NO3) ≤ 0.003 %
Iodide (I) ≤ 0.002 %
Phosphate (PO4) ≤ 0.0005 %
Sulphate (SO4) ≤ 0.001 %
Total nitrogen (N) ≤ 0.001 %
Heavy metals (as Pb) ≤ 0.0005 %
Ba (Barium) passes test
Ca (Calcium) ≤ 0.001 %
Fe (Iron) ≤ 0.0002 %
Mg (Magnesium) ≤ 0.0005 %
Na (Sodium) ≤ 0.005 %
Magnesium and earth alkali metals (as Ca) ≤ 0.02 %
Loss on drying (105 °C) ≤ 1.0 %

Sodium nitrate
Merck 106537
GR for analysis ACS, ISO, Reag. Ph Eur

Assay (acidimetric) ≥ 99.5 %
Insoluble matter ≤ 0.005 %
pH-value (5 %; water; 25 °C) 5.5 - 8.0
Chloride (Cl) ≤ 0.0005 %
Iodate ≤ 0.0005 %
Nitrite (NO2) ≤ 0.001 %
Phosphate (PO4) ≤ 0.0005 %
Sulphate (SO4) ≤ 0.003 %
Heavy metals (as Pb) ≤ 0.0005 %
Ca (Calcium) ≤ 0.002 %
Fe (Iron) ≤ 0.0003 %
K (Potassium) ≤ 0.01 %
Mg (Magnesium) ≤ 0.002 %
NH4 (Ammonium) ≤ 0.002 %

Sodium sulphate decahydrate
Merck 106648
GR for analysis ACS, Reag. Ph Eur

Assay
- acidimetric ≥ 99.0 %
- calculated on dried substance 98.5 - 101.0 %

Identity passes test
Clarity of solution passes test
insoluble matter ≤ 0.01 %
pH-value (5 %; water; 25 °C) 5.2 - 8.0
Acidity or alkalinity passes test
Chloride (Cl) ≤ 0.0003 %
Phosphate (PO4) ≤ 0.0005 %
Total nitrogen (N) ≤ 0.0003 %
Heavy metals (as Pb) ≤ 0.0003 %
As (Arsenic) ≤ 0.0001 %
Ca (Calcium) ≤ 0.002 %
Fe (Iron) ≤ 0.0005 %
K (Potassium) ≤ 0.002 %
Mg (Magnesium) ≤ 0.001 %
Loss on drying (130 °C) 52.0 - 57.0 %

Bromide (Br) ≤ 0.005 %
Chlorate and Nitrate (as NO3) ≤ 0.003 %
Hexacyanoferrate II ≤ 0.0001 %
ferrocyanides passes test
Iodide (I)
- ≤ 0.001 %
- passes test

Nitrite (NO2) passes test
Phosphate (PO4) ≤ 0.0005 %
Sulphate (SO4) ≤ 0.001 %
Total nitrogen (N) ≤ 0.0005 %
Heavy metals (as Pb) ≤ 0.0005 %
As (Arsenic) ≤ 0.00004 %
Ba (Barium)
- passes test
- ≤ 0.001 %

Ca (Calcium) ≤ 0.002 %
Cu (Copper) ≤ 0.0002 %
Fe (Iron) ≤ 0.0001 %
K (Potassium) ≤ 0.005 %
Mg (Magnesium) ≤ 0.001 %
Calcium, Magnesium and R2O3-precipitate ≤ 0.005 %
Magnesium and earth alkali metals (as Ca) ≤ 0.01 %
Loss on drying (105 °C, 2 h) ≤ 0.5 %

Artificial sea salt

Element	ppm
CHLORINE	19,000
SODIUM	10,500
MAGNESIUM	1,290
CALCIUM	420
POTASSIUM	379
SULPHUR	895
BROMINE	66
CARBON	30
STRONTIUM	10
BORON	4.8
FLOURINE	1.4
SILICONE	0.5
ALUMINIUM	0.15
ANTIMONY	0.0002
ARSENIC	0.002
BARIUM	0.05
BERYLLIUM	trace
BISMUTH	0.0002
CADIUM	trace
CESIUM	0.002
CERIUM	trace
CHROMIUM	0.0003
COBALT	0.0001
COPPER	0.005
DYSPROSIUM	trace
ERBIUM	trace
EUROPIUM	trace
GADOLINIUM	trace
GALLIUM	trace
GERMANIUM	0.00004
GOLD	0.000004
HAFNIUM	trace
HOLMIUM	trace
INDIUM	0.004
IODINE	0.1
IRON	<0.002
LANTHANUM	0.0001
LEAD	0.002
LITHIUM	0.2
LUTETIUM	trace
MANGANESE	0.005
MERCURY	0.00001
MOLYBDENUM	0.002
NICKEL	0.0003
NIOBIUM	0.00001
NITROGEN	<0.25
PHOSPHORUS	<0.006
PLATINUM	trace
PRAESIDIUM	trace
PROTACTINIUM	trace
RADIUM	trace
RHENIUM	trace

Red Sea (UK) Ltd
Interpet
Vincent Lane,
Dorking, Surrey,
RH4 3YX,
Tel: 44 1306 743747
Fax: 44 1278 446155
redsea@interpet.co.uk

RUBIDIUM	0.12
RUTHENIUM	trace
SAMARIUM	trace
SCANDIUM	0.00003
SELENIUM	0.004
SILVER	0.0003
TANTALUM	trace
TERBIUM	trace
THALLIUM	<0.0001
THULIUM	trace
TIN	0.0025
TITANIUM	trace
TUNGSTEN	trace
URANIUM	0.0001
VANADIUM	0.0003
YTTERBIUM	trace
YTTRIUM	0.0004
ZINC	0.015
ZIRCONIUM	trace

X.C Climate monitoring

Meteorological station

Climart 92

- Central logging unit
  - Climart 92 datalogger
  - Channels 8 (4x2)
  - Resolution 8bit
  - Memory card ....
  - LCD monitor
- Temperature
  - Sensor: NTC
  - Range: -30 – 70C°
  - Accuracy: 0.1C° (0-70C°)
  - Reproducibility: 0.1C°
- Relative humidity
  - Sensor: Capacitive thin film
  - Range: 5-98% RH
  - Accuracy: 2%RH
  - Reproducibility: 1%RH
- Wind speed
  - Cap anemometer
  - Range: 0.8 – 60 m/s
  - Resolution: 0.1m/s
  - Accuracy: 0.6 m/s (4% measured value)
- Wind direction
  - Rotating wind vane
  - Range: 0-360°
  - Resolution: 1°
  - Dead zone: appr.5°
  - Accuracy: 5% measured value
- Solar radiation
  - Sensor: Star pyranometer
  - Measuring range: 0-1500 W/m^2
  - Spectral range: 0.3-30μm
  - Accuracy: cos effect <3%, azimuth effect <3%, temp. infl.<1%
  - Adjustment time: 25s
  - Linearity: <0.5%
  - Stability: 1%
- Software: WinMacli (win95,98)

R &C Scientifica S.r.l.
Via Piave 24
36077 – Altavilla
Italy
Tel: 0444/349040
Fax: 0444/349041

Dataloggers

Tinytag plus TGP-1500

- Temperature sensor: 10k NTC thermistor
  - Range: -30 – 50C°
  - Response time: 20min to 90%
  - Accuracy: 0.2 C° (0-50C°)
  - Resolution: 0.25°C at 0C°
- Relative humidity sensor: Capacitive
  - Range: 0-100%RH
  - Response time: 10sec to 90%
  - Accuracy: 3%RH at 25C°
  - Resolution: 0.5%RH
  - Low temperature dependency
- Case: IP68
- Memory: 32K
- Resolution: 8bit
- ISO 9002

Gemini Dataloggers UK Ltd
Scientific House
Terminus Road
Chichester
West Sussex
PO19 8UJ
United Kingdom
+44 1243 813000
+44 1243 531948
www.geminidataloggers.co.uk

X.D Salt spray weathering chamber

Air atomizing spray nozzle

Spraying systems 1/4J

Capacity: 0.13 - 72 gph (0.49 - 280 l/h).
Pressure: 10-60 psi (0.7 - 4.0 bar)
Material: nickel-plated brass
Internal mix
Diameter: ¼ in.
Cap no: (round spray)

Spraying Systems Limited
Farnham Business Park
Weydon Lane
Farnham, Surrey
GU9 8QT
England
Telephone: +44 (0) 1252 727200
Fax: +44 (0) 1252 712211
Email: info@spray-uk.co.uk

Fan

EBM PAPST 8414NGR High Humidity Protected

'R' rated >95% RH
DIN40040 group C (3.3)
24V
Air flow max. 69 M^3/h
Power input 2W
Noise level 32dBa

RS Components Ltd
Birchington Road,
Corby,
Northants,
NN17 9RS,
UK
Tel. 01536 444222
www.rs-components.co.uk

Solenoids

BURKERT CONTROMATIC 058796D

2-Way Water & Steam Valves
1/4in BSP
24Vdc
Power consumption: 35-40VA d.c. 10W(warm)
Constant 16VA/10W
Cycling frequency 600 c.p.m.
Viscosity 21mm2/s
Max. fluid temp. 180°C
Pressure range 0-6 bar d.c.
Kv Value (water) 0·5m3/h
Orifice size 4·0mm
Ambient temp. +55°C
Seal material PTFE
3-pin DIN connector rated to IP65

Timer switch

MERLIN GERIN 16067 Time Delay Relay

Analogue
Time delay range 0·1s to 100h
24V

IR Lamps

PHILIPS LIGHTING IR250C

Par38, infrared, heat, ES, blown frosted
250W

Thermometer

HANNA INSTRUMENTS NS920

Thermistor NS920
Pt 100 penetration probe

Thermostat
Scratch built by RC components
with **Pt100 probe**
PICO TECHNOLOGY SE012
Temperature range (Tip temp.) -50 to 250°C
Accuracy ±0·03 at 0°C (1/10th Class B**)
Connector MiniDIN 4 way male connector
Material (Stainless Steel) PTFE cable