

THE ROLE OF STRONG ACID IN SPELEO-INCEPTION AND SUBSEQUENT CAVERN DEVELOPMENT

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ABSTRACT

In this paper we examine alternatives to conventional views which suggest that carbonate speleogenesis is achieved by the single process of carbonic acid dissolution. Various dissolutional mechanisms, including those involving sulphuric acid, are discussed with particular emphasis upon their potential role during the earliest, inception, phase of speleogenesis. Minerals that can break down to produce sulphuric acid, with or without microbial mediation, occur as trace components in most carbonate sequences, but they are more concentrated at specific levels. These levels comprise beds of atypical lithology, together termed inception horizons, and are commonly associated with breaks between major depositional cycles. Examination of earlier results that have referred to 'special' cases of carbonate dissolution leads to the suggestion that these are better described as 'extreme' cases, and that the processes described are dominant during inception and ubiquitous during later speleogenesis. Selected studies outside mainstream cave research are re-examined and it is noted that processes and mechanisms active in non-carbonate rocks are equally likely to affect carbonate sequences.

INTRODUCTION

The chemical processes by which limestone is dissolved in water containing dissolved carbon dioxide are well understood and discussed in detail in many texts (eg Ford & Williams, 1989). These processes are of undoubted importance in the subaerial dissolution of limestone, in dissolution at the soil-limestone interface and in the development of surface and underground landforms. However, as Howard (1964) pointed out, caves ought not to form if carbonic acid dissolution alone drives speleogenesis, since infiltrating solutions will become saturated before they can penetrate sufficiently into the limestone. Later kinetic modelling by Dreybrodt (1990) and Groves & Howard (1994a, 1994b, 1995) suggests that at least in theory the effects of carbonic acid dissolution may penetrate further and persist longer than originally thought. However, the models still require the presence of primary voids through which initial water movement takes place and they do not explain the common phenomena whereby cave passages are concentrated at specific levels within most carbonate sequences.

In his earlier paper, Howard (1964) deduced that for speleogenesis to begin, acid must be generated in the rock mass and theorised that acid could be generated by inorganic or bacterial oxidation of rock sulphides or organic matter in groundwater, as suggested by Kaye (1957). Similar conclusions were drawn by Durov (1956; English translation 1979,

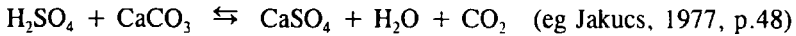
p.186) who stated: "During the evolution of karst features ... in carbonaceous [sic] rock (limestone and dolomite), the solvent is water containing carbonic acid. Generally no mention is made of any other agents promoting rapid solution of bedrock. However, A Saukov points to the particular significance of the products of oxidation of sulfides [sic; ?sulphides] and above all sulfuric acid in those regions where carbonaceous rocks (limestone) prevail. As Saukov has said, the resulting solutions 'pave themselves a way' in the calciferous rocks; during that time the karst process is abruptly reinforced, which promotes the rapid advance of the lower boundary of the zone of oxidation attaining in such cases a depth of 100 meters from the surface". Although later work, notably by Jakucs (1977), showed that carbonate dissolution by strong acids, especially sulphuric acid, is a sound theoretical possibility, those case studies that have provided evidence for alternatives to carbonic acid dissolution (eg Morehouse, 1968; Egemeier, 1981; Van Everingden and others, 1985; Hill, 1987) have been labelled as '*special*' or '*aberrant*' situations.

It is widely assumed that dissolution due to sulphuric acid is unimportant, because analyses of water from active underground drains rarely include significant amounts of anions such as 'sulphate'. An alternative explanation of the available evidence is that most anions in limited inception flows comprise sulphate, but this dominance decreases as conduits enlarge. Carbonic acid by-product levels increase significantly relative to those of sulphate after turbulent breakthrough. A still more significant jump occurs on transition from phreatic to vadose conditions. Sulphate (or other strong acid related anion) values in water from vadose and shallow phreatic systems are swamped by the bicarbonate ions. Flows from artesian or deep phreatic elements in multi-level systems contain significantly higher sulphate concentrations and relatively less bicarbonate (Worthington, 1991; Worthington & Ford, 1995).

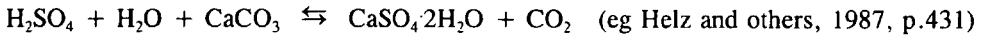
More contentious than potential sulphuric acid involvement in speleogenesis, are questions of its scale and importance. These questions have rarely been viewed objectively though the concept has been applied to '*special*' cases. We prefer to view the '*special*' cases of earlier workers as '*extreme*' examples of a widespread, possibly ubiquitous, aspect of speleogenesis and believe that the scale of strong acid effects has been misunderstood and their importance relegated to obscurity. We argue that in many carbonate sequences the earliest stage of conduit development, which we refer to as inception (Lowe, 1992), is likely to be dominated by sulphuric acid dissolution and related processes and that, as the conduits enlarge, this dominance decreases. Regrettably there have been relatively few analyses of sulphate ions in karst groundwaters, especially from inception situations, and hence, in this paper, we draw on published case studies and indirect evidence to support our arguments.

THE CHEMISTRY OF THE SULPHURIC ACID REACTION

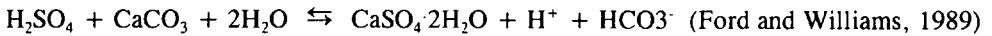
At the centre of many reactions suggested as contributory to the ultimate dissolutorial mechanism is the interaction of sulphuric acid and calcium carbonate to produce calcium sulphate, water and carbon dioxide:



This may be written in other ways, such as:



or:

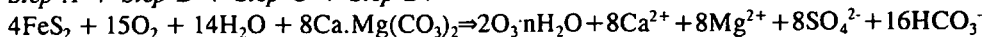
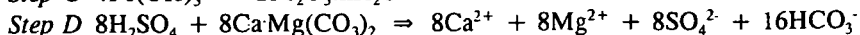
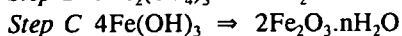
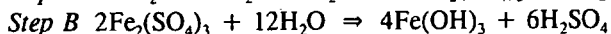
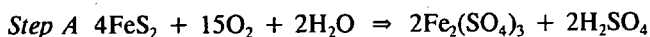


It might appear that the reaction is irreversible under temperature and pressure conditions in the cave environment, yet it can proceed from right to left. For example, Klimchouk (1986) found that in some Ukrainian gypsum caves, condensation water containing dissolved carbon dioxide dissolves gypsum roof or wall rock and precipitates calcium carbonate. In the context of normal carbonate speleogenesis, the left to right reaction is essentially irreversible, but in the reduction zone the reaction may be reversed, depending upon the prevailing Eh (Oral communication, Dr T K Ball, British Geological Survey, 1991). Carbon dioxide produced by the sulphuric acid reaction can react to dissolve more calcium carbonate, a potential for enhanced dissolution termed the '*doubled solvency effect*' by Ford and Williams (1989, p.75). Ball and Jones (1990, p.5) reported: "*When consideration is taken of the mass balances and of the different densities of the minerals, one volume of totally oxidised pyrite can result in the dissolution of a further six volumes of calcite.*".

CASE STUDIES OF SPELEOGENESIS BY STRONG ACIDS

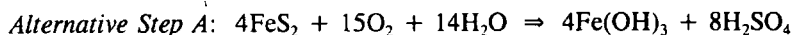
Level Crevice cave, Iowa, United States

Level Crevice Cave, Iowa, was opened to the surface by mining activity (Morehouse, 1968). It is unclear whether the absence of a surface connection was due to an impermeable cover or whether connections smaller than the anthropocentric limit (the limit of human accessibility) pre-existed. If the former, the point is significant as few earlier authors acknowledged that caves (other than isolated dissolutional chambers) could form without surface input and output points. The cave is formed in the Middle Ordovician Galena Formation and has three bedding-parallel levels or tiers. The bedrock is dolomite, and calcite, pyrite, marcasite, galena and limonite occur in the cave. Morehouse described the cave as "*joint controlled*", but stated: "*The cave passages also appear to have been controlled by development at favourable stratigraphic levels...*" (1968, p.2). This stratigraphic control, previously noted by Howard (1960), was linked to differential bedrock fracturing or brecciation, and uneven solubility due to varied porosity and chemical composition. Water analyses showed that: "*...sulfate ion is present in the cave waters in fairly large concentrations.*" (1968, p.7), and Morehouse concluded that sulphuric acid dissolution was dominant in the cave. The reaction chain deduced by Morehouse is:



Morehouse pointed out that the stoichiometry of the sulphuric acid reaction should produce a sulphate ion concentration half that of the bicarbonate ion and his analytical results agreed with this ideal ratio within 4%. Other observations supported the view that sulphuric acid dissolution dominates in the cave. Massive and disseminated pyrite and marcasite occur in the wall rocks and Morehouse (1968, p.10) stated: "...it does not take much sulfuric acid (or, therefore, much pyrite or much marcasite) to significantly affect cave development.". The cave waters were saturated in dissolved oxygen at all times. Limonite ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) was present within the dolomite wall rocks in amounts between 0.9 and 2.3%. No sulphate concentrations exist near the cave to account for high sulphate values in the analyses. Lack of seasonal fluctuation in analytical data suggests that dissolution is independent of carbon dioxide levels in overlying soils. Finally, 'valley bars', where passages narrow beneath surface valleys, are reciprocal to expectation if carbonic acid dissolution were dominant. In the latter case dissolution should be greater where percolation passes through less bedrock and has less opportunity to achieve saturation. Larger passages would be expected at these points. In the case of the sulphuric acid reaction, downward percolating water is acidified in passing through the overlying rock, being theoretically less acidic where the rock is thinnest, beneath valley floors. The validity of this argument is uncertain, as laterally moving water must contribute to development, and vertically descending water must constantly be reacting with carbonate in penetrating the bedrock.

As an alternative to Step A, Morehouse suggested that iron bacteria (*Crenothrix* and *Gallionella*), common in the cave, gain energy by oxidising ferrous to ferric iron:

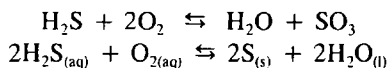


Ferric hydroxide excreted by the bacteria rearranges as in Step C of the inorganic mechanism. Morehouse noted that equal numbers of moles of pyrite/marcasite, oxygen and water are used in the inorganic and bacterial reactions and that the same number of moles of sulphuric acid are produced. Whichever mechanism operates, the result is the same. Morehouse concluded that the primary development [inception] of the cave was achieved by the sulphuric acid reaction under artesian conditions, as outlined by Howard (1964). He reasoned that artesian conditions developed because the Galena Formation was sealed beneath the Maquoketa Shale, except where relatively few, steep valleys, such as those cut by glacial meltwater, had incised the carbonate sequence. This supports the proposed chemistry, as percolation reaching the cave level would have reached equilibrium with

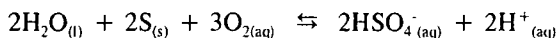
respect to the carbonic acid reaction, but still be saturated with oxygen. The general reasoning and proposed reactions remain basically sound, but it is no longer certain that the inferred linking of inception to Quaternary time (by reference to downcutting by glacial streams) is realistic (Lowe, 1992). The cave was drained by mining, so at least part of the system had not reacted to surface downcutting by that time. Inception by the Howard (1964) mechanism could long have been active before breakthrough to turbulent flow conditions and before the cave acquired its present dimensions.

Cave development by thermal waters

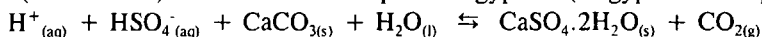
(Egemeier, 1973, 1981), studied cave development by thermal waters and 'replacement solution', in the Big Horn Basin of Wyoming, where much underground drainage penetrates a confined carbonate aquifer, the Madison Limestone. The broadly synclinal basin includes local anticlines, some cut by surface river canyons. Water from recharge areas (Absaroka and Big Horn mountains) around the basin, traverses the confined aquifer under artesian conditions, discharging from non-thermal springs near the mountains, or warm springs where canyons cut anticlines within the basin. Deep flow, up to 2000 m beneath the surface in the main axial area, and commonly 1000 m down across much of the basin, is responsible for the temperatures of the thermal springs. Artesian springs discharge thermal water containing dissolved hydrogen sulphide into open caves. Though not specified by Egemeier, presumably the water issues from conduits extending to great depth within adjacent synclines. The artesian head is provided by the greater elevation of remote, synclinal limbs in the mountainous recharge areas. Egemeier did not identify the origin of the hydrogen sulphide but, by implication, it derives from gypsum in the Madison Limestone. Elevated temperature and pressure enable supersaturation, and degassing is inevitable as spring water encounters cave air. Some hydrogen sulphide reacts with oxygen as the spring water dissolves cave air, generating sulphuric acid. This attacks calcium carbonate in the stream bed. Hydrogen sulphide escaping into the cave air redissolves in oxygen-rich water on cave walls and ceiling, forming sulphur and sulphuric acid. Airborne fallout of sulphuric acid is probably formed, as described by Van Everingden and others (1985), but this was not noted by Egemeier.



Elemental sulphur is oxidised further, with or without mediation by bacteria such as *Thiobacillus* spp and *Sulphobus* spp (Ehrlich, 1981), generating additional sulphuric acid:



Limestone (or dolomite) is then attacked to produce gypsum (or gypsum and epsomite):



Solid gypsum (or gypsum and epsomite) begins to redissolve in cave water immediately, if the two are in contact. Crystal crusts formed above water level on passage walls and ceilings eventually fall, due to increasing weight, and cave streams dissolve them or carry them away. This basic chemistry agrees well with processes described by other workers, and with more general reactions described by Ehrlich (1981).

Egemeier (1981, p.39) noted that: "*The Madison contains breccias that may represent a previous karst cycle of erosion. They are, however, cemented into solid rock today. Where they are cut by the caves there is no evidence of influence on the cavern passage.*". As there are no known abandoned passages associated with the spring, Egemeier described the Big Horn caves as '*one cycle*', referring back to the theories of W M Davis (1930). Egemeier studied accessible caves carrying water to springs, or '*dead*' caves, assumed to be of similar origin but there was no consideration of the guidance of, or processes involved in, cave inception. Describing a second aquifer, the Tensleep Sandstone, Egemeier concluded that the Madison Limestone is the better aquifer because its hydraulic gradient is more favourable than that in the sandstone. However, he did not question whether this was always so, or if it reflects cavernization in the limestone.

We argue that it is invalid to assume that the Madison Limestone always provided a ready pathway for underground drainage. If speleogenesis depended solely upon input to and output from an artesian system imposed after formation of the Big Horn Basin, how did water initially enter the aquifer in the recharge areas? Was the Madison Limestone permeable or impermeable when the aquifer was exhumed from beneath shale caprock in the recharge areas? Was there already a secondary, joint or fault linked, permeability? It is unrealistic to assume tacitly that, after caprock erosion in the recharge areas, water simply entered the Madison Limestone, worked its way down-dip to great depth in the synclinal core and then rose again towards the crests of unroofed anticlines, **at which time and at which locations** speleogenesis due to strong acid dissolution began. Egemeier may have been misled in asserting that relict karst features are not implicated in current cavern development, as Sando (1988) subsequently described an extensive palaeokarst suite within the Madison Limestone. Sando (1988, p.264) considered that: "*The geometry of later caves was undoubtedly overprinted on these ancient features.*" He also refers to "*a significant paleohydrological conduit*" in an evaporite [gypsum] zone at the base of a component member of the Madison Limestone, and to a zone of evaporite leaching at the base of a higher member. Though not stated explicitly, potential links can be deduced between palaeokarst features in the Madison Limestone, palaeo-conduits and, in view of the crucial involvement of evaporite minerals in Egemeier's dissolution mechanism, current speleogenetic activity.

Concatenation of Egemeier's dissolution mechanism and Sando's observations of Madison Limestone palaeokarsts suggests that the speleogenetic history is longer and more complex than Egemeier supposed. Speleogenesis affected parts of the Madison Limestone during its deposition, and caves existed before folding produced the basin. Whether open

voids remained when deformation began, or whether all were filled by younger deposits is unknown; leaning to Egemeier's viewpoint the latter must be assumed. Nevertheless, infill would offer potential drainage routes if possessing less hydraulic resistance than the primary rock. Sando's comment that cave geometry is superimposed upon ancient features, suggests regeneration of earlier routes. Supposed links between palaeo-hydraulic routes and evaporitic horizons (Sando, 1988) suggest other theoretical connections. The possibility that hydrogen sulphide required by Egemeier's (1981) reaction is formed by reduction of evaporites cannot be ignored. Sulphate reduction by bacteria (*Desulfovibrio* spp, *Desulfotomaculum* spp and *Desulfuromonas* spp) is common in anaerobic conditions (Ehrlich, 1981). Its possible importance to inception in the pre-folding Madison Limestone, cannot be disregarded, particularly as dissolved hydrogen sulphide is itself acidic. Microbial reduction (or equivalent inorganic reactions) in the 'pre-cave' rock mass is unconfirmed, but with physical dissolution of evaporites as the only alternative, the possibility must be noted. Hydrogen sulphide generation in the anaerobic deep phreatic zone after inception is a still more attractive possibility.

Cave formation in travertine

Studies in the Banff National Park, Canada, led to recognition of an unusual example of sulphuric acid speleogenesis. Van Everingden and others (1985) described cave formation due to travertine corrosion by airborne sulphuric acid. This process was not linked into a more general consideration of speleogenesis, but the chemistry described, if not the actual development mechanism, is similar to ideas developed by Egemeier (1981). Dissolved sulphates are reduced by bacteria to form hydrogen sulphide in solution. Gaseous hydrogen sulphide escapes from the water surface and is oxidised and hydrolysed to produce sulphuric acid and sulphur dioxide. The airborne acid attacks calcium carbonate to produce calcium sulphate and carbon dioxide. Much of the authors' reasoning involved detailed study of oxygen and sulphur isotopes in various components (Figure 1). This allowed them to state, with reasonable certainty, that airborne acid fallout is currently involved in dissolving exposed carbonate, and the dissolved calcium sulphate, upon which the process depends, originated as primary marine evaporite. From the present viewpoint the conditions and type of speleogenesis encountered at this locality must be considered a special case, but similar chemistry, with or without microbial mediation, may be more widely applicable. Sulphate occurs, even if only in trace quantities, in most marine limestones. More sulphate is expected in parts of carbonate successions deposited under the hypersaline conditions commonly associated with cycle boundaries (*sensu lato*) or, more locally, in lagoons, isolated from marine influence by reefs or sand bars. Such deposits, perhaps containing only limited evaporite, probably occur in most carbonate sequences. In the speleo-inception context, traces of 'impurity' provide atypical chemistry at inception horizons. The mechanism described by Van Everingden and others, utilizing strong acid derived from sulphate rather than from sulphide, may be viable at these stratigraphical levels.

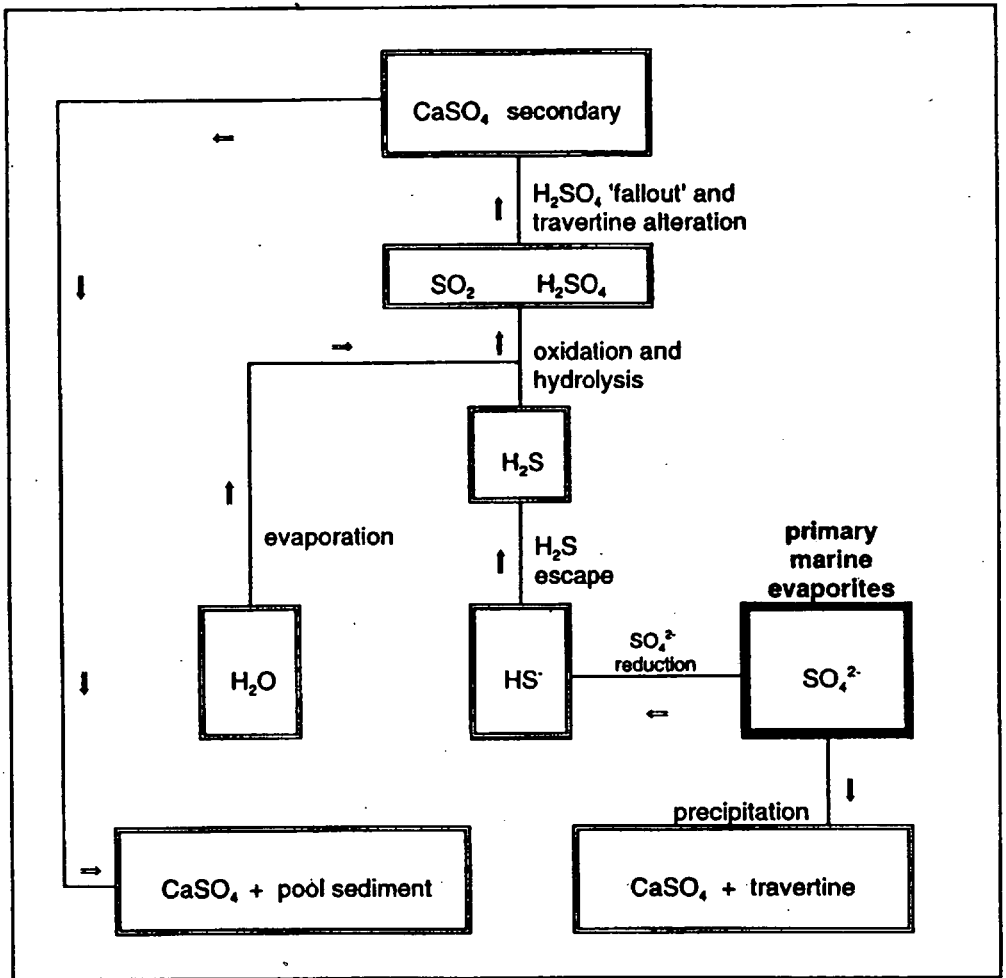
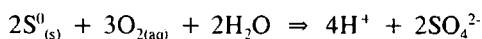
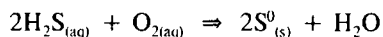


Figure 1 Diagrammatic representation of the interactions involved in fallout dissolution. Primary marine evaporites provide the starting point for the processes (after Van Everingden and others, 1985)

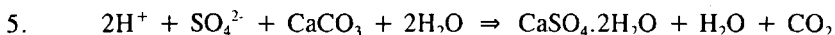
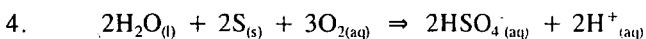
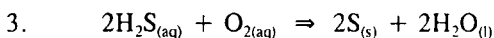
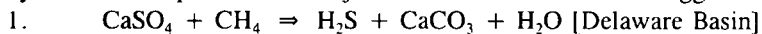
Another cave in Quaternary travertine, Cesspool Cave in Virginia, owes its development to hydrogen sulphide hydration and oxidation and carbon dioxide hydration (Hubbard, Herman and Bell, 1986). Water entering the cave contains hydrogen sulphide, some of which is oxidised, probably partly by colourless bacteria (eg *Thiothrix* sp, *Beggiatoa* sp and *Achromatium* sp) in the cave water, to produce sulphuric acid via a sulphur intermediary:



Hydrogen sulphide outgassing from cave water redissolves in film water on cave ceiling and walls and is oxidised by dissolved oxygen. Dissolution of wall and ceiling calcite proceeds in parallel with gypsum precipitation. The mechanism is identical to that proposed by Egemeier (1973, 1981) and replicates part of that deduced by Van Everingden and others (1985) for "fallout" dissolution. Three possible sources for the hydrogen sulphide are suggested. Local spring water shows high sulphate concentrations, and bacterial reduction of sulphate to sulphide could occur in the subsurface water supply. The travertine is underlain by black shales containing metastable iron minerals such as greigite (Fe_3S_4) and mackinawite (FeS) that can decompose to generate hydrogen sulphide. Finally, hydrogen sulphide could be derived from hydrocarbons in the black shale or adjacent Helderberg Limestone, the gas moving up dip to the cave area.

Caves in the Guadalupe Mountains, New Mexico

A major publication (Hill, 1987) describing cave development in the Capitan Reef of the Guadalupe Mountains, New Mexico consolidated ideas from earlier short papers (Hill, 1981, 1985, 1986). A multistage history of speleogenesis was described, including a major phase of dissolution due to sulphuric acid, by a mechanism previously proposed by D.G. Davis (1979, 1981) and resembling that described by Egemeier (above). Within a history that included three stages of dissolution, Hill considered that only Stage III was dominated to sulphuric acid, formed from hydrogen sulphide derived biogenically from hydrocarbon deposits in the adjacent Delaware Basin. The suggested reactions are:



Hill's basic model for these processes is very well supported by analytical results and by observations in the caves and has been further developed in subsequent papers (eg Hill 1990, 1995). As Hill stated (1995, p.16): "*The Delaware Basin...is probably the best example of sulfuric acid karst anywhere in the world.*". However, the Hill model for sulphuric acid speleogenesis during Stage III relies to some degree upon earlier speleogenetic activity in Stages I and II, deduced by Hill (1987) to have commenced soon after deposition and diagenesis of the Capitan Reef and associated fore- and backreef deposits during the Permian. In contrast to the 'special' case of the Stage III sulphuric acid dissolution, Hill's explanation of the earlier stages relies upon more traditional ideas of speleogenesis, in particular upon the Ford-Ewers (1978) model.

We have no first-hand knowledge of the Guadalupe caves, but would make several related points in the context of Hill's research and earlier cave development models proposed for the area. Firstly we suggest that in a speleogenetic history that began soon after the deposition of the host rocks in a reefal environment, the probable development and preservation of conduit permeability by dissolution adjacent to a contemporary freshwater lens cannot be ignored. If accepted, it must also be accepted that a proportion of open or loosely-filled conduits would survive subsequent uplift, stacked at several levels, as described in the Trobriand Islands (Ollier, 1975) and Tonga (Lowe, 1989). Such conduits would provide preferred sites for later underground drainage and dissolution. Secondly, if the presence and preservation of stacked conduits is accepted then much of the argument for bathyphreatic flow based on the Ford-Ewers model is no longer necessary. Relationships between conduits in the forereef area and those in the stacked backreef deposits are potentially analogous to those observed in the reef hinterland of 'Eua Island, Tonga (Lowe and Gunn, 1986). Following from this, a possibility emerges that secondary conduit enlargement (Hill's Stage II) could be partly due to dissolution by sulphuric acid derived from the backreef Yates Formation, as suggested by Jagnow (1977) but dismissed by Hill as inadequate to have caused the Stage III passage growth.

INDIRECT EVIDENCE FOR THE ROLE OF STRONG ACIDS IN SPELEOGENESIS

Many authors noted 'in passing' the potential involvement of strong acid in speleogenesis; in this section we consider indirect evidence and ideas crucial to the theme of this paper.

Sulphates in Castleguard Cave

Chemical studies by Yonge and Krouse (1987) indicate a link between sulphur-bearing compounds and carbonate speleogenesis. Samples of gypsum, mirabilite (hydrated sodium sulphate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), adjacent carbonate bedrock and cave water were collected from Castleguard Cave in the Canadian Rocky Mountains. Water of crystallization (from the minerals) and the cave water samples were analyzed for deuterium and oxygen-18. The two mineral species were analyzed to determine sulphur and oxygen

isotope ratios, and bedrock samples were analyzed for trace sulphur species, using the method of Ueda and Sakai (1983). One of the formations analyzed, the Eldon Formation, was also studied by Gillott (1978; discussed below). Most sulphates in Castleguard Cave derive from sulphides in the host carbonates via pyrite oxidation (Yonge and Krouse, 1987); a minor proportion may derive directly from anhydrite in the rock mass. Discussing the acid forming process, Yonge and Krouse pointed out that each mole of oxidized pyrite can evolve 2 moles of sulphuric acid and that this reacts almost immediately with adjacent carbonate to produce sulphates and carbon dioxide that can dissolve to form another 2 moles of carbonic acid. They concluded that, "*The oxidation of pyrite as a source of the cave sulphates thus seems a likely mechanism in view of the isotopic and chemical evidence.*" (Yonge and Krouse, 1987, p.429).

Sulphates in Indiana spring waters

Hydrochemical and isotopic studies of spring waters by Krothe and Libra (1983) provided unequivocal quantitative pointers to the role of strong acid in speleo-inception in southern Indiana, where Pennsylvanian rocks overlie a Mississippian, mainly carbonate, sequence. The uppermost Mississippian formations are more varied lithologically than those below, probably resembling cyclothemic sequences of similar age in northern England. Underlying beds are more massive, particularly the St Louis Formation, similar to many Asbian and Holverian rocks in Britain. The St Louis Formation contains economic quantities of evaporite, the aspect of which passes from being interbedded, where preserved at depth, to occurring only as nodules closer to outcrop. Horizons that are highly evaporitic at depth are represented by brecciated rock at outcrop. Krothe and Libra deduced the presence of two flow systems. A shallow system carries meteoric water entering the system through open fractures and passing through traditionally and anthropocentrically defined cave passages; other waters utilize a deep, regional, system, recharged mainly by diffuse flow. Ion concentrations in the shallow system are highly variable; carbonic acid dissolution of calcite is the dominant process. Deep flow is characterized by limited ion concentration variation and high sulphate levels. A dissolution/precipitation interaction involving calcite, dolomite and gypsum dominates.

A possibility that currently observable 'shallow' systems elsewhere were conceived under conditions typical of Krothe and Libra's deep system cannot be ignored. Deep speleo-inception can begin before host carbonates are unroofed and before surface evolution provides viable conditions for 'normal' hydraulic flow. Evaporites occur within many deeply buried carbonate successions. After exhumation, the highest elements of incipient deep flow would transform into shallow flow systems, under conditions more normally associated with underground drainage. Early in the transformation residual evaporite would be removed from the rock mass, by speleogenesis (*sensu lato*) and by near surface weathering. Such changes explain the evaporite distribution in buried and outcrop elements of the St Louis Formation and may explain a lack of sulphate in near-outcrop shallow flow near recharge areas around the Big Horn Basin (Egemeier (1981; discussed above).

Sulphates in the English Dinantian

Tables 1 and 2 show extracts from whole rock analyses of major Dinantian formations in the Buxton and Settle areas, England. Most analyses are of unweathered borehole material, randomly sampled from each formation, rather than chosen to illustrate chemistry at different levels within depositional cycles. The values are for total sulphur content, expressed as SO_3 and therefore include sulphide as well as sulphate content. The values give a broad indication of sulphide/sulphate levels across typical Dinantian sequences.

Formation	Maximum SO_3 (%)	Minimum SO_3 (%)	Mean SO_3 %
Eyam Limestone	0.14	0.13	---
Monsal Dale Limestone	0.33	0.04	0.16
BEE LOW LIMESTONE			
Apron-reef facies	0.33	0.04	0.09
Miller's Dale Limestone	0.29	0.03	0.13
Chee Tor Rock	0.83	0.00	0.18
Undifferentiated	0.67	0.00	0.18
Woodale Limestone	0.62	0.00	0.17

Table 1 SO_3 content (see text for explanation) of the major carbonate units in the Buxton area, Derbyshire, England (after Harrison, 1981)

Additional information is provided by a deep borehole at Eyam in the Derbyshire Peak District (Dunham, 1973), which proved interbedded and disseminated anhydrite in deeply buried early Dinantian carbonates. The beds, which include crystals of calcium sulphate and calcite pseudomorphs after anhydrite, do not reach outcrop. It cannot be confirmed that exhumation and speleogenesis/weathering would remove evaporite, but T D Ford (1977) suggested that early groundwater movement could remove anhydrite, leading to increased permeability in the carbonate mass. Whether later Dinantian rocks at outcrop in Derbyshire included primary evaporites, deposited under sabhka conditions (Dunham, 1973) or as regressive elements of carbonate depositional cycles, is unknown. Little evidence of evaporites is recorded, yet widespread 'autobreccias' in the sequence could reflect evaporite removal, as described by Krothe and Libra (1983) in Indiana (discussed above). We suggest that primary evaporite is rarely preserved in relatively small outcrop and shallow subcrop areas, especially those of anticlinal aspect, such as those in the United Kingdom, due to dissolution. Only in zones of deep burial, such as proved at Eyam, or in much more extensive terrains, such as the Big Horn Basin and other North American examples, will evaporites survive uplift and dissolution across extended timespans.

Formation	Maximum SO ₃ (%)	Minimum SO ₃ (%)	Mean SO ₃ %
Unspecified dolomitised rocks	0.97	0.00	0.20
WENSLEYDALE GROUP			
Hardraw Scar Limestone	0.81	0.09	0.37
Grirvanella Beds, Upper Hawes Limestone and Gayle Limestone	0.95	0.07	0.38
Lower Hawes Limestone	1.45	0.04	0.23
MALHAM FORMATION			
Gordale Limestone	0.59	0.01	0.06
Cove Limestone	0.31	0.00	0.02
KILNSEY LIMESTONE			
Kilnsey Limestone	0.25	0.03	0.10
Kilnsey Limestone with Mudstone	1.42	0.21	0.74

Table 2 SO₃ content (see text for explanation) of the major carbonate units in the Settle/Malham area, Yorkshire, England (after Murray, 1983)

Exposure of limestone to coal leachates

Helz and others (1987) examined deleterious effects of coal leachates on the environment, confirming that: "When coal is exposed to atmospheric precipitation, strongly acidic leachates....are produced." (Helz and others, 1987, p.427) and: "These leachates....tend to be more acidic than acid mine drainage." (Helz and others, 1987, p.427). The main acid source was identified as oxidation of pyrite, catalyzed by bacteria. *Thiobacillus ferrooxidans* oxidizes ferrous to ferric iron, following which ferric ions rapidly oxidize pyrite by an abiotic mechanism that regenerates ferrous ions, propagating an ongoing reaction cycle. Adding dolomitic limestone to the stockpiles completely changed the leachate character, producing neutral solutions dominated by Ca²⁺, Mg²⁺ and SO₄²⁻ ions, with the sulphate yield controlled by gypsum solubility. These reactions are potentially analogous to those active at lithological junctions between sulphurous coal (or shale) and

carbonate rocks and calcium and magnesium sulphates rather than iron compounds dominated the leachate. Similar reactions proceed, more slowly, in less oxygenated conditions and at lower temperatures. The results confirm a commonplace chemical (and/or biochemical) mechanism, and provide several ancillary observations. Acid production in anoxic conditions is partially confirmed by observation that significant oxidation had occurred in fresh coal sampled at the mine, but whether this occurred *in situ* or when the coal was mined was not reported. The former possibility has far-reaching implications to speleogenesis; implications of the latter are only marginally less important. Acid generation in coal adjacent to voids or in contact with oxygenated groundwater in fracture zones appears inevitable rather than aberrant. Similar processes probably affect sulphurous rocks such as shale, mudstone and pyritic limestone.

In essentially carbonate-free conditions, distilled water passed through a coal stockpile acquired a pH of 3.2, decreasing gradually over 40 days to 1.8, then rising to 1.9 after 70 days. When 25% of dolomitic limestone was added to the stockpile acidic solutions were neutralised *in situ*. Starting at pH 7 the leachates were pH 6.4 after 14 days, dropping to 6.0 after 98 days, probably reflecting carbonate exhaustion. It is impossible to compare the effects of this 'strong acid' directly with the effects of carbonic acid, but clearly the sulphuric acid generated is a highly efficient remover of calcium (and magnesium) carbonate. Sulphuric acid generated *in-situ* removed carbonates forming 25% of the total solids in the stockpile in 98 days. Even if the test coal was exceptionally sulphurous and produced anomalously large volumes of acid, similar processes in less sulphurous coals or pyritic shales could produce less spectacular yet important speleogenetic effects. Carbonate sequences of different ages in different settings include, or lie adjacent to, beds of pyrite-rich shale, pyritic volcanic fallout or, more rarely, coal seams. If even a small proportion of their pyrite (or other sulphides) is oxidized to sulphuric acid, notable speleogenetic impact must be expected. Results from Vear and Curtis (below) confirm that significant volumes of sulphuric acid form even in slightly pyritic shales, and that this achieves appreciable carbonate dissolution. Such results, examined with so-called '*special cases*' (reviewed above), underline the potential importance of sulphuric acid, particularly to inception processes.

Chemical reactions in interbedded pyritic mudstones and carbonates

Two 'disasters' occurred during construction of the Carsington Dam and its associated aqueduct in Derbyshire, UK. In one incident workmen were asphyxiated by unexpectedly high carbon dioxide levels in a tunnel. In the second, less tragic, incident the dam collapsed. Subsequent detailed study of the geology, geomorphology and geochemistry near the dam was undertaken by the British Geological Survey (Aitkenhead and others, 1984), who concluded that the two incidents were potentially linked. The common factor was carbon dioxide, generated in undisturbed bedrock and, more critically, within compacted Namurian mudstone and limestone chippings comprising the dam body and drainage blankets. Carbon dioxide levels in gas drawn from the dam were far higher than

expected. After heavy rain the carbon dioxide concentration tended to rise, and that of oxygen to fall. Fluctuation was irregular and extreme values of more than 60% carbon dioxide and less than 1% oxygen were recorded. In an area of soil overlying bedrock, readings before rain were 0.52% carbon dioxide and 20% oxygen compared to levels of 3.5% and 17% after rain. Similar fluctuation occurred in disturbed or undisturbed ground, but disturbed ground values were more extreme. Gas bubbles rising through a water filled trench in a borrow pit included 8% carbon dioxide and negligible oxygen. Reactions within the dam were depleting oxygen and generating carbon dioxide. Relatively small volumes of carbon dioxide formed under equilibrium-weathering conditions in undisturbed rock are significant in the context of the present paper.

Highly weathered mudstone, overlain by shallow water, in a borrow pit contained up to 6% soluble sulphate and visible efflorescence indicated that mobile sulphates were common in the pit. Limestone drainage layers showed extensive alteration to gypsum and epsomite. Aitkenhead and others (1984) deduced complex oxidation of sulphide-bearing mudstones, involving some microbial mediation, the products including carbon dioxide and sulphuric acid. The latter immediately attacks adjacent rock to generate more carbon dioxide and dissolve other minerals, profoundly changing the rock, physically and chemically. Suggested carbon dioxide production mechanisms are: 1. Bacterial oxidation of sulphide to sulphate generates carbon dioxide as a metabolic by-product; 2. Acidic sulphate solutions react with disseminated or interbedded carbonate, or with the limestone drainage blankets; 3. Oxidation of organic matter within mudstones and carbonates. [This was not considered important in the Carsington context]. Mechanisms 1. and 2. generated at least 80% of the carbon dioxide produced in the disturbed materials of the dam. The processes deduced by Aitkenhead and others (1984) are illustrated in simplified form in *Figure 2*.

Work by Pye and Miller (1990) further explored chemical reactions in pyritic mudstones and interbedded carbonates. Their study included laboratory simulation of conditions established during embankment construction; overall the results agree closely with those of Aitkenhead and others (1984) and Vear and Curtis (1981). Several aspects are relevant to speleo-inception and the reaction chain deduced differs in detail from mechanisms discussed elsewhere in this paper. Elements of Pye and Miller's work crucial to speleogenesis are condensed in one paragraph: "...dilute sulphuric acid with an initial pH of 1.8 could dissolve virtually all the calcite present in the test specimens of Namurian marine mudstone within a period of two weeks. Dissolution of siderite and dolomite (where present) occurred at a slower rate. Carbonate dissolution can occur under either saturated or free-draining conditions, but in the field high rates of dissolution are likely to be favoured by a high acid flux. Under stagnant pore water conditions the rate of dissolution will be dependent primarily on the rate of ionic diffusion through the pore fluid." (Pye and Miller, 1990, p.378). The last sentence is particularly valuable, implying that oxidation and dissolution occur in situations where hydraulic flow would not be expected. The Inception Horizon Hypothesis (Lowe, 1992) assumes such motion as instrumental in the inception of primary voids in deep phreatic environments, remote from a surface landscape.

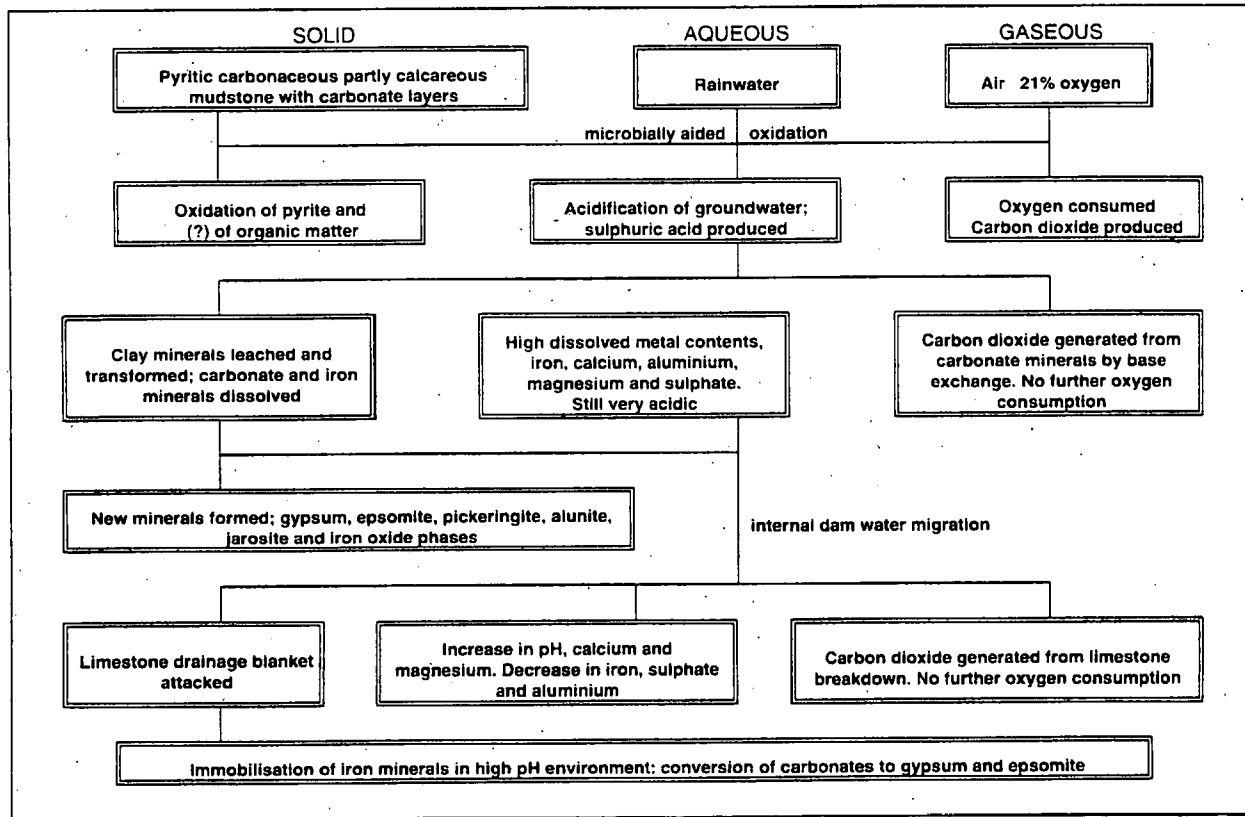
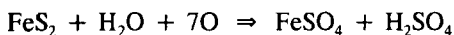


Figure 2 Organogram of chemical changes associated with the breakdown of Namurian mudstones (with minor carbonates) in the Carsington area (after Aitkenhead and others, 1984).

The dissolution rates described are of great importance. We consider that changes achieved rapidly under 'favourable' conditions can equally well be accomplished by similar processes acting under less favourable conditions during the far longer timespans of speleogenesis. The more important reactions listed by Pye and Miller (1990) are:

1. Pyrite dissolution in the presence of dissolved oxygen, forms ferrous sulphate and sulphuric acid:

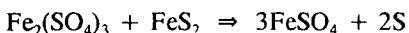


2. Ferrous sulphate reacts with oxygen and sulphuric acid, forming ferric sulphate:

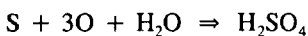


[This may be catalysed by *Thiobacillus* spp.]

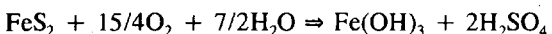
3. Ferric sulphate, a powerful oxidizing agent, can react with pyrite, producing ferrous sulphate and elemental sulphur:



4. Elemental sulphur in the presence of water and oxygen is converted to sulphuric acid, catalysed by *Thiobacillus ferrooxidans*:



5. If free oxygen is abundant, aqueous oxidation of pyrite produces ferric hydroxide and sulphuric acid:



Groundwater chemistry in Namurian rocks at Mam Tor, Derbyshire

Studying groundwater chemistry in Namurian rocks at Mam Tor, Derbyshire, Vear and Curtis (1981) demonstrated that shale pyrite was oxidising, producing sulphuric acid at an unprecedented rate. Oxygenated groundwater along a fault crush zone was breaking down 1.5g of pyrite per litre of water. More than 99% of the acid was consumed by clay-mineral transformations and carbonate dissolution. Many carbonate successions include pyritic clastic beds, coal seams or volcanic deposits, and dark carbonates adjacent to shale beds or in analogous positions represented by palaeokarstic surfaces are commonly pyritic. Groundwater within clastic rocks is not 'oxygenated' in the same sense as a fast-flowing stream, but it holds dissolved oxygen. Except for the host rock lithology, this water is analogous to shallow, oxygenated, phreatic zone water (cf Ball and Jones, 1990, figure 4) or 'vadose seeps' (Thraillkill, 1968) in carbonate aquifers. It appears unequivocal that sulphuric acid must form where pyrite-rich rocks are traversed by active shallow phreatic or vadose flow (cf Krothe and Libra (1983) discussed above).

Vear and Curtis analyzed what they term as 'karst' water from Peak Cavern resurgence. However, the actual sampling site was Peakshole Water downstream of the three resurgences which drain the Peak-Speedwell Cave System. Two of these, Slop Moll and Russet Well, receive significant allogenic recharge from streams sinking below Rushup Edge, west of Mam Tor while the third, the true Peak Cavern resurgence, is supplied solely by autogenic recharge from the limestone outcrop during normal conditions but functions as a flood overflow for the allogenic system (Gunn, 1991). In the allogenic catchment, precipitation, and drainage from minor springs on Namurian rocks similar to those of Mam Tor, descend an input system explored to a depth of 160 m, but with no passable link to the resurgences. Most of the flow must follow deep phreatic routes along joints, faults and veins (Ford, 1986). Over a ten-week sampling period Vear and Curtis found that the resurgent water chemistry responded relatively little to rainfall events. Fault crush zone drainage on Mam Tor showed a similar lack of chemical variation, though the overall chemistry was dissimilar. The similar behaviour suggests relatively lengthy residence times at depth for both waters although water tracing indicates more rapid flow-through times for the allogenic waters. Samples from surface runoff, shallow seepage and springs unrelated to the fault crush showed appreciable temporal variation. Many radicals included in Vear and Curtis's analyses (1981, p.193) are not relevant here, but selected figures (Table 3) are of interest.

Type of drainage	Calcium	Magnesium	Ferrous+ Ferric	Sulphate	pH
Surface runoff	21.0	7.9	3.0	105.0	5.2
Peak Cavern	78.0	2.9	2.6	90.0	6.4
Fault crush zone	385.0	178.0	111.0	2362.0	3.4
Mixture of surface and fault crush zone drainage	199.0	88.0	98.0	1156.0	3.2

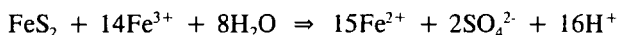
Table 3 Mean values of selected radicals (micrograms per millimetre) and pH from four types of water sampled during an eight-week period.

Note that the Peak Cavern samples were collected from Peakshole Water and include flows from Slop Moll and Russet Well. (after Vear and Curtis, 1981, Table II, p. 193)

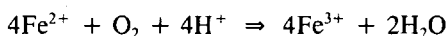
The pH of the Peakshole Water drainage is as expected in view of the projected residence times and the ready supply of calcium carbonate along the flow route to neutralise acids carried into the system or generated underground. The pH and sulphate content of

fault crush zone and karst waters present an interesting comparison, suggesting dilution effects and swamping by other processes. We assume that low calcium (and ?magnesium) values also mirror dilution within the bulk flow from the Peak-Speedwell system. The difference between the magnesium figures from the surface runoff and Peakshole Water analyses suggest an effective three-times dilution in the cave environment, though an obvious disparity of calcium values between the same two sets of analyses remains, due to environment differences.

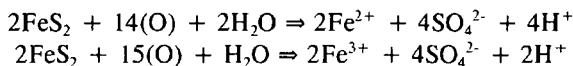
The pyrite decomposition mechanism suggested by Vear and Curtis resembles that proposed by Helz and others (1987, discussed above), the overall reaction being:



In near surface environments this is complemented by ferrous to ferric iron oxidation catalysed by *Thiobacillus ferrooxidans*:



Vear and Curtis suggested that the process is best described by two end-member reactions depending upon the degree of ferrous oxidation:



However, they also noted that the formulations fail to explain the full evolution of the waters analyzed, and discussed other processes, including hydrated ferric oxide precipitation, clay mineral alterations and carbonate dissolution. For every 1.4996g of pyrite destroyed, potentially 1.5684g of dolomite dissolves and 1.221g of limonite precipitates. If the products are removed by percolating water a "*massive increase in porosity*" (Vear and Curtis, 1981, p.196) occurs. Overall, Vear and Curtis concluded that the scale of chemical alteration is very great. More than 99% of the sulphuric acid formed at depth is consumed by silicate and carbonate reactions before reaching the surface. Of this 99%, 77% is involved in carbonate dissolution. These findings are potentially significant to speleogenesis. Figures deduced for sulphuric acid production in oxygenated phreatic environments indicate that, in some geological and hydrological conditions met in the context of speleogenesis, sulphuric acid could have great effect.

The effect of deicing agents and sulphate solutions on concrete aggregate

Although apparently unrelated to speleogenesis, evidence presented by Gillott (1978) indicates that factors other than acidic dissolution might play a previously unrecognised part in karst processes (*sensu lato*). Gillott studied quartzitic and carbonate aggregates, the carbonates ranging from almost pure dolomite to almost pure calcite. Measured rock cylinders were immersed in distilled water (as control) and in solutions of

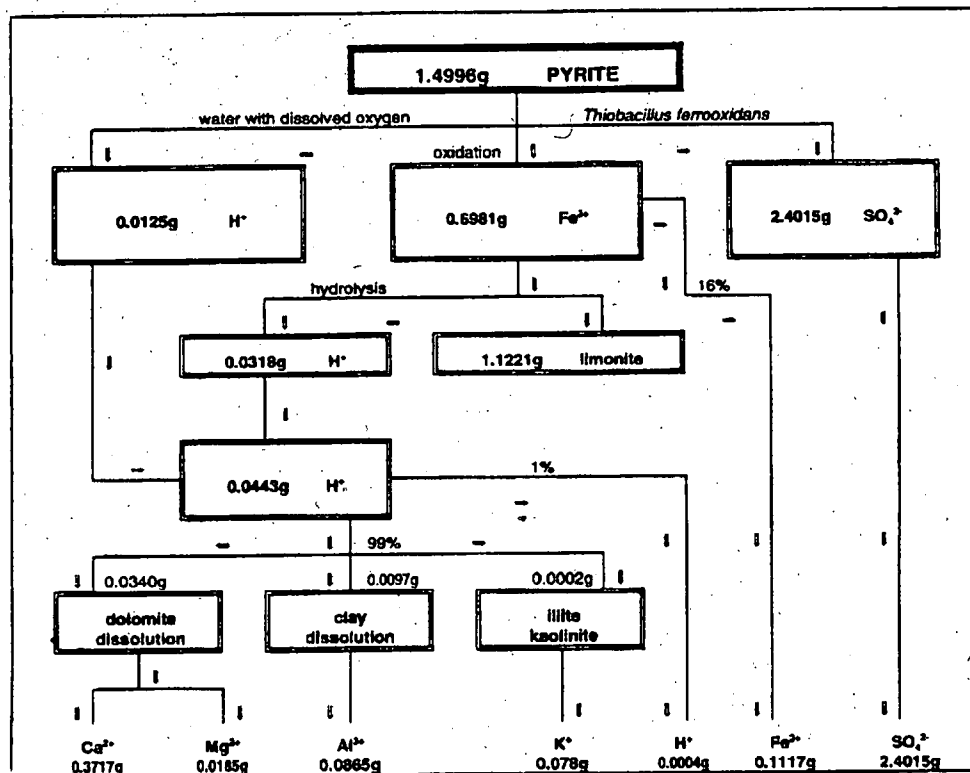


Figure 3

Chemical reactions affecting the water from a fault crush zone spring. Amounts shown refer to changes affected by the passage of 1 litre of water and the values balance when account is taken of molecular weights (after Vear and Curtis, 1981).

sodium and calcium chlorides (5% and saturated) and magnesium sulphate (4% and saturated) at a constant 20 °C. All cylinders were soaked in water for a week before testing, to ensure saturation of open pores, and were remeasured after three days and seven days, at weekly intervals for a month, and every month for more than two years. A broad picture of dimensional change emerged, related to carbonate lithology and salt solution chemistry/concentration. Samples of Eldon Limestone (calcite with minor dolomite) showed a dimensional decrease of 0.12% after immersion in saturated magnesium sulphate solution. This apparently trivial decrease is sufficient to allow the removal by sulphate action of 1.2mm in every 1m of carbonate, if the effects were concentrated along a bedding plane or joint. Gillott examined immersed carbonates using a scanning electron microscope. Most effects observed involved dissolutional removal of carbonate, plus or minus scaling off of crystalline sheets; a few involved deposition. Similar effects were noted on dolomitic and calcitic rocks.

Gillott's results, significant in a civil engineering context, also have a link to speleogenesis, suggesting that carbonate dissolution need not be due only to acids. If chloride and sulphate solutions cause dissolution in concrete aggregates, naturally occurring solutions could also affect porous or secondarily permeable carbonate bedrock. We suggest two potential situations. Sulphates and (less commonly) chlorides precipitate during regressive phases of cyclic carbonate deposition (eg Scoffin, 1987), and chlorides and other salts in sea-water are in contact with carbonate rocks in coastal situations. Some effects noted by Gillott relate to visible cleavage within the carbonate mineral fabric. Calcite's molecular/crystal structure presents a perfect cleavage on the microscopic scale, but it is unclear whether these planes are significant, or whether only the coarser, visible cleavage fabric is involved. If the latter, dissolution should be more marked where sulphate- and/or chloride-rich solutions can attack coarse, readily cleavable, crystalline rocks. 'Sparry limestone' should be more susceptible than 'micritic' rocks and shell-rich beds could be especially implicated. In regressive parts of 'perfect' depositional cycles, sulphate- and chloride-rich sediments and shelly build-ups occur close to superimposed 'sparry' carbonates. The potential links between hypersaline deposition, shell beds and secondary porosity due to dissolution of evaporites or their reaction with carbonate require further investigation.

Processes including evaporite dissolution and the effects of 'salt solutions' in corroding carbonates are deduced to affect cave inception in suitable environments. Subsidence into cavities in gypsum (eg Cooper, 1986) demonstrates that dissolution occurs deep in buried sequences with no initial potential for direct flow to surface risings and no viable hydraulic gradient, both seen by many workers as essential to trigger underground drainage and speleogenesis. Evidence from many fields supports the view that non-traditional dissolution occurs in buried rocks before surface downcutting establishes resurgences and local hydraulic gradients.

Microbial activity

Ehrlich (1981) described many bio-chemical interactions that may potentially affect speleogenesis. The full extent of Ehrlich's work cannot be examined here, but three basic reactions and their implications are summarized. Similar reactions, if not the microbial mediation, are discussed elsewhere in this paper, but the variety of organisms potentially involved is of interest:

- a. Sulphide oxidation to elemental sulphur, mediated by:

Thiobacillus spp

Purple sulphur bacteria

Green sulphur bacteria

Cyanobacteria

Beggiatoa spp

- b. Oxidation of elemental sulphur to sulphuric acid, mediated by:

Thiobacillus spp

Sulfolobus spp

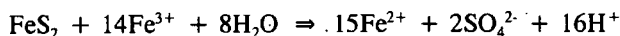
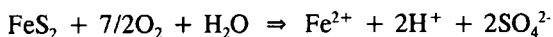
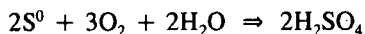
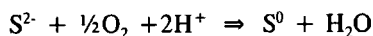
- c. Reduction of sulphates to hydrogen sulphide, mediated by:

Desulfovibrio spp

Desulfotomaculum spp

Desulfuromonas spp

Ehrlich also noted that elemental sulphur may be reduced to hydrogen sulphide by bacteria such as *Desulfuromonas acetoxidans*, in anaerobic conditions. Many processes described are rationalised into equations equivalent to those reproduced in this paper. The following are potentially important to speleogenesis, but the list is not exhaustive:



Ehrlich's equations to illustrate sulphate reduction reactions (Ehrlich, 1981, pp.263-265) comprise several steps, involving complex organic intermediaries, and are not repeated here. Optimum temperature and aeration conditions for bacterial activity described by Ehrlich indicate that organisms exist that can, and do, mediate in aerobic and anaerobic environments spanning the spectrum of hydrographic zones.

Reports by T.D. Ford (1965), of a link between microbial activity and rock breakdown were largely ignored, but the role of bacteria in speleogenesis, barely touched in the current paper, invites detailed study. Bottrell and others (1990) produced convincing evidence that acidity is generated by bacterial reduction of sulphates near the halocline at

the base of the freshwater/saltwater mixing zone. The sulphur species are re-oxidised at shallower depths, providing sulphuric acid whose contribution to wall rock dissolution is at least as great as that of freshwater/saltwater mixing, itself a highly effective process with a clear and fundamental importance to speleogenesis. Bosch and others (1989), provided further insight of activity within coastal carbonate aquifers, where ion exchange (cf Gillott, 1978; discussed above) was shown as potentially important in carbonate dissolution below the vadose zone. All water samples were depleted in sulphate following reduction to hydrogen sulphide, giving further evidence for the potential involvement of reduced/re-oxidized sulphur compounds in early speleogenesis. These results provide a valuable link between conventional views of carbonate dissolution, the more recently recognized process of mixing zone corrosion and sulphuric acid dissolution.

CONCLUSION

In this paper we have attempted to illustrate and emphasise the importance of sulphuric acid, plus or minus other non-traditional processes, to early speleogenesis, while acknowledging that carbonic acid dissolution is volumetrically more significant during later stages. It is important to recognise that analytical data from mature cave systems may obscure evidence for the vital role of sulphuric acid in cave inception. Regrettably, but not surprisingly, most data are from mature systems and shallow flow springs and there are relatively few data from 'deep' flow systems. Analyses of 'deep' flows in Derbyshire, including '*thermal springs*' (Edmunds, 1971), showed sulphate levels as high as 384 mg/litre suggesting that speleogenesis by sulphuric acid and/or calcium sulphate dissolution may be dominant at depth. In this context it is interesting to note that the role of sulphur-related redox processes in deep karst processes has recently begun to be accepted (Palmer, 1995). In addition, Worthington (1991) suggested that much dissolution by '*underflow*' water is of calcium sulphate rather than calcium carbonate. This may indicate physical, dissolution of primary mineral in the rock mass, a potential inception horizon function, although Worthington suggested that sulphate could form *in situ* as a product of calcium carbonate dissolution by sulphuric acid. Much of Worthington's work was quantitative and his results underline the importance of strong acid dissolution, as deduced qualitatively and reported here. Worthington's recognition of the significance of calcium sulphate removal may be crucial to the future development of cave formational theories, but his ideas do not relate directly to inception horizons or other forms of chemical zonation in carbonate successions.

Increasing evidence points directly or indirectly to the importance of sulphuric acid in speleogenesis. We suggest that sulphuric acid dissolution, and other 'aberrant' mechanisms, affect all stages of speleogenesis, but their greatest importance, instrumentally and volumetrically, is during inception and the subsequent phase of laminar flow, prior to turbulent breakthrough, which we term gestation. We cannot yet show conclusively that speleogenesis would not proceed without these 'exotic' mechanisms, but point out that many unanswered questions in pre-existing cave development theories cease to present problems if the alternative processes are accepted. Much of our discussion concerns '*special cases*'

of speleogenesis due to sulphuric acid dissolution. In the light of increasing evidence for more general involvement of sulphuric acid dissolution and related mechanisms, we consider that 'special cases' are actually extreme cases of speleogenesis by processes not based exclusively upon carbonic acid.

Processes appearing quantitatively insignificant in post-gestational speleogenesis may have relatively great importance before establishment of turbulent conduit flow. During inception, strong acid dissolution appears vital, though the amount of carbonate dissolved is small. Traditional dissolutional processes do not operate initially, though they commence, due to 'doubled solvency' effects (eg Ball and Jones, 1990), soon after inception. As gestation and turbulent flow development progress, the proportion of total conduit enlargement by strong acid generally decreases, but strong acid dissolution continues throughout the life of the conduit. Analyses of seepages from incipient inception horizons and discharges from deep phreatic systems, commonly confirm a dominance of sulphur-bearing ions as against carbonate and bicarbonate. Equally, as integrated drainage systems develop and hydraulic conductivity improves, relatively constant yields of sulphur-bearing ions are progressively overwhelmed by increasing production of carbonic acid reaction products. From this viewpoint the effect of 'exotic' acids is perceived as negligible - from the speleo-inception standpoint it is considerable and fundamental.

ACKNOWLEDGEMENTS

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