TEMPORAL DIAGENETIC ALTERATIONS IN ADÉLIE PENGUIN EGGSHELLS THROUGHOUT THE LATE HOLOCENE OF ANTARCTICA

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ABSTRACT

Data from scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) analysis of late Holocene Adélie penguin (*Pygoscelis adeliae)* eggshell fragments were used to investigate the role of diagenesis on paleoecological reconstructions using stable isotopes. The results of this study demonstrate that clear diagenetic alterations occur in eggshell carbonate following burial in ornithogenic, or bird formed, soils. Diagenesis progresses from blocky calcium carbonate ($CaCO_3$) rhombs in the modern eggshells to botryoidal fluorapatite crystals ($Ca_5(PO_4)_3F$), as indicated by the increased weight percentages of phosphorus and fluorine with sampling depth. Carbon weight percent was found to decrease, with statistical significance, in relation to phosphorus, indicating that carbon is preferentially removed from the eggshell through time. Diagenesis in the fossils is predictable, with early stage alterations occurring along the outer margins of the eggshells first, and slowly progressing inward towards the center. Despite these trends, the inclusion of unaltered CO_3^{2-} from the original eggshell material allows for the fossil's use in isotopic reconstructions.

ACKNOWLEDGMENTS

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DEDICATION

To J. Mark Erickson, Ph.D. Clear in thought, kind in manner, and a dedicated educator. A quiet field geologist and exceptional observer I strive to emulate.

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INTRODUCTION

Adélie penguins (*Pygoscelis adeliae)* are circum Antarctic in distribution and inhabit a number of coastal colonies during the breeding season where they rear their chicks. Inhabited colony sites are a mixture of closely spaced pebble nest mounds and rich deposits of guano (Fig. 1A). Specific colony sites may be used by the birds for millennia, and a site's continued occupation leads to the accumulation of soils characterized by degraded guano, eggshell fragments, bone (Fig 1B and 1C), molted feathers, and nesting pebbles (Emslie, 2001). After colonization of the area by penguins ceases, ancient colonies can be identified as a number of discrete pebble surface lags (Fig. 1D) with a distinctive mineralogy, a diagnostic fossil assemblage, and unique soil chemistry (Tatur, 2002).

Diagenesis is both the physical and chemical taphonomic or mineralogical changes that affect a fossil from the time of its deposition until the onset of metamorphism (Tucker, 1991). A specific diagenetic process that occurs in sediments associated with penguin colonies is called phosphatization, a process by which phosphorus is incorporated in a host carbonate (Tatur, 1987, 2002). Commonly, the phosphate mineral that is precipitated is fluorapatite, a mineral with the general composition of $Ca_5(PO_4)_3F$.

Like many minerals, though, the chemistry of fluorapatite is not fixed, and commonly PO_4^{3-} is substituted for CO_3^{2-} in the crystal lattice (Knudsen and Gunter, 2002). This diagenetic mineral is created through a number of unique surface processes specific to the colony site. Penguins consume, and hence concentrate, a number of species rich in phosphorus and fluorine. As fresh guano rapidly decomposes, chitin and bone begin decomposing, freeing phosphorus and fluorine, and allowing it to be incorporated into new minerals. Precipitation of pure fluorapatite is controlled by the reaction:

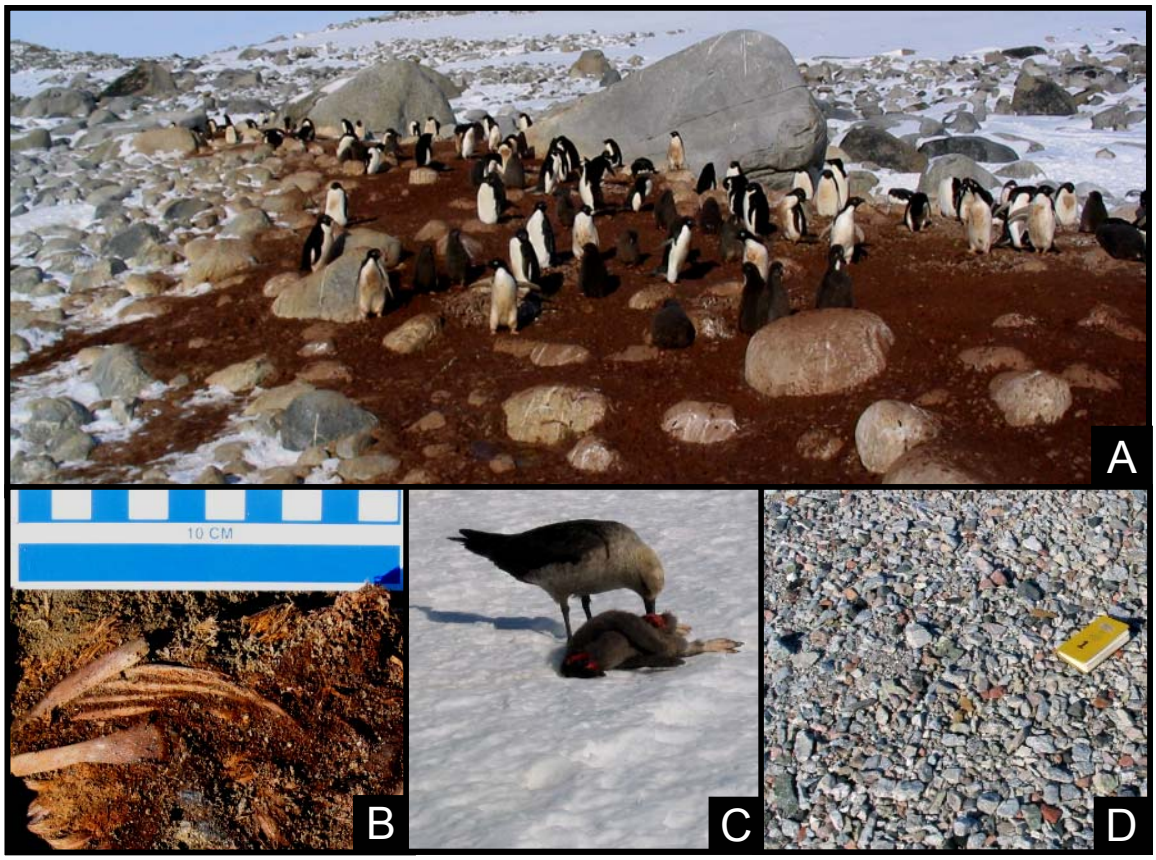

Figure 1. (A) Actively nesting penguins, with pebble nests amid actively developing ornithosols. (B) Fossilized juvenile penguin skeleton excavated from ornithosol. (C) South Polar skua, a typical predatory bird, feeding on juvenile penguin carcass. Predation is a typical cause of death among penguin chicks. (D) Well developed, wind deflated lag deposit of nesting pebbles that is typical of abandoned colony sites.

$$5Ca^{2+} + 3PO_4^{3-} + F^- \rightarrow Ca_5(PO_4)_3F$$

Despite the fact that phosphorus mineralization has been recognized in penguin colonies, little work has been done regarding how diagenesis affects the fossilized eggshells within the sediments. Specifically no studies exist that indicate how diagenesis may affect paleontological studies using isotope geochemistry.

Adélie Penguin Biology

The Adèlie penguin is the hardiest member of the genus *Pygoscelis,* and is able to tolerate heavy pack-ice conditions. Today, the birds breed from Cape Royds (77°S) in the Ross Sea, along the entire coast of the Antarctic continent, on the west coast of the Antarctic Peninsula, in the islands of the Scotia Arc, and north to the South Sandwich Islands (Ainley, 2002). Despite their tolerance of the cold, severe winter conditions force Adèlie penguins to migrate to more temperate wintering grounds near the Antarctic Polar Front (55-60°S).

In the past, Adèlie penguin dietary studies have relied on direct field observations of feeding and regurgitations (Ainley et al., 1998; Wienecke et al., 2000). More recently, however, researchers have begun to evaluate the fossilized remains of prey species preserved in penguin colonies as an indirect measure of diet (Emslie and McDaniel, 2002). Nearly 100 years of research into the diet of these birds indicate that Adèlie penguins feed primarily on euphausiids, amphipods, and fish (Ainley, 2002; Endo et al., 2002). Two krill species, *Euphausia supurba* or *E. crystallorophias,* vary depending on oceanic context; *E supurba* is the main food item in island settings, while in shelf areas a mixture of *E. supurba, E. crystallorophias*, and fish are the

main foods (Endo et al., 2002). Of interest to the present discussion, Ainley (2002) suggests that the lowest percentage of fish in Adèlie penguin diet corresponds with years of higher than average ice coverage. Krill, on the other hand are the main food source during severe winters where ice covers much of the ocean's surface (Ainley, 2002). Despite this, all prey genera are circum-Antarctic in distribution (Polito et al., 2002). For an excellent summary of dietary variations among different populations of Adélie penguins, see Ainley (2002).

The Utility of Isotopes for Solving Paleontological Problems

Recently, several workers have assessed the organic carbon, inorganic carbon, and nitrogen isotopic signatures of fossilized eggshell fragments recovered from ancient colony sediments in an attempt to reconstruct Adélie penguin diet throughout the late Holocene Epoch (Emslie and Patterson, 2004; Patterson and Emslie, 2004). Carbon and nitrogen isotopes are useful in paleoecological reconstructions because the ratio of $^{13}C/^{12}C$ and $^{15}N/^{14}N$ isotopes is related to that isotope's availability in the environment during the time of its incorporation into an organism's tissue or bone (Kelly, 2000). Of further interest, the proportion of heavier isotopes becomes systematically enriched with increasing trophic level, a condition that is related to the incorporation of the consumed tissue into the diet of another animal (Kelly, 2000).

Preliminary results by Emslie and Patterson (2004) and Patterson and Emslie (2004) identified a pronounced change in the carbon and nitrogen isotope values between 265 and 90 years ago, which they attribute to a human-induced change in Adélie penguin diet. The results suggest that the inorganic carbon values of the fossilized eggshells are generally stable through time and average between -11 and -13‰ for a period encompassing ~9,000 years. Suddenly,

beginning ~1,000 years ago, the inorganic carbon values become significantly depleted, assuming values of -20‰. Likewise, nitrogen values follow a similar trend and maintain a nearly constant level of ~13‰ throughout the late Holocene before dramatically switching to values of ~8‰ in modern samples. Finally, organic carbon values are consistent at -26‰ throughout the Holocene, before becoming slightly enriched to -24‰ in modern samples.

To Emslie and Patterson (2004) and Patterson and Emslie (2004) these results suggest that the anthropogenic removal of whales in the Antarctic foodweb left a surplus of krill in the Southern Ocean, which then became the primary prey for penguins. This hypothesis is supported by similar isotope values reported by Dunton (2001) for Antarctic Peninsula fauna. Initially, the observed isotopic signature of both the nitrogen and organic carbon appear paradoxical, but the results can be explained by Dunton (2001). In his study regarding the trophic positions of a variety of Antarctic species, Dunton (2001) found that the base source of carbon, either benthic or pelagic, would affect the consumer's isotopic ratio. In other words, the nitrogen signature reported by Emslie and Patterson (2004) and Patterson and Emslie (2004) is expressing the trophic change (of about two steps) while the organic carbon is suggesting that the source of carbon changed from a pelagic source to a more enriched benthic source. This change is consistent with their hypothesis that Adèlie penguins switched from a diet of fish to one of krill.

Statement of Problem

The focus of this project is to identify, using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX), if diagenetic alterations affect eggshell carbonate, specifically as it relates to the eggshell's use for carbonate isotopic reconstructions. It is hypothesized that: (HI)

diagenesis will affect fossilized eggshell fragments buried in guano deposits, and (H2) that diagenetic alterations will influence eggshell carbonate to the point that it may be of limited use in isotopic studies of penguin diet. Specifically, it is assumed that the original calcium carbonate composition of the eggshell will be lost and replaced by fluorapatite.

LITERATURE REVIEW

Diagenesis in avian eggshells has been studied by a number of researchers (Dauphin et al., 1998; Hayward et al., 1991; Hirsch and Packard, 1987). Dauphin et al. (1998) were concerned that eggshell fossils have been used in stratigraphic and paleoecological studies without concern for the fossils' state of preservation. Using fossilized eggshells recovered from Neogene eolianites in the Namib Sand Sea, Namibia, the work examined the microstructural and mineralogical features of the eggshells to determine if they had undergone diagenetic alteration. Dauphin et al. (1998) cautioned that the reliability of paleoecological studies is dependent on the quality of fossil preservation, and that, despite the seemingly good preservation of desert environments, diagenesis had altered the shell's original mineralogy.

Hayward et al. (1991) examined eggshell remains from extant gull species in areas affected by ash-fallout during the 1980 eruption of Mt. St. Helens. This work highlighted the rapid rate at which physical dissolution of the eggshell carbonate occurs in mildly acidic soil conditions. The study reported that, after only one year, the eggshells already began to dissolve, and that, in several year's time, the eggs had been severely eroded, leaving behind only a honeycombed mass of the original eggshell carbonate. Carbonate removal leaves numerous pore spaces, which can later be filled by diagenetic mineralization.

Though the Dauphin et al. (1998) and Hayward et al. (1991) studies illustrate that diagenesis is common in avian eggshells, no studies have addressed how avian eggshells behave on the Antarctic continent, particularly in an environment rich in phosphorus. This ecosystem is unique in being characterized by extreme desert climates and cold conditions, variables which may limit many of the physical, hydrological, and chemical processes that are necessary for the rapid decomposition or diagenetic alteration of the fossils.

Syroechkovski (1959) is credited for noting how Adélie penguin guano contributes to sedimentation in Antarctica. The soil-forming process is so rapid that it is now estimated that between 30,000 and 50,000 penguins can produce approximately 6.35 tons of dry excreta daily (Rakusa-Suszczewski, 1980, *cited in* Tatur, 2002). Owing to the process's importance to the formation of Antarctic soils, Syroechkovski (1959) proposed the term "ornithogenic soil" to describe any sedimentological or biological accumulation of material associated with avian colonies. Later, Blume et al. (1997) redefined Syroechkovski's (1959) term to "ornithosols," a classification that fits more neatly in the present nomenclature of soil scientists.

Following Syroechkovski's (1959) examination, Tedrow and Ugolini (1966), Campbell and Claridge (1966), and McCraw (1967) investigated a number of paleo-ornithosols, emphasizing age relationships and stratigraphy. In addition to these works, Orchard and Corderoy (1983), Heine and Speir (1989), and Tatur (2002) completed geochemical evaluations of both modern and ancient colony sediments.

Campbell and Claridge (1966) examined modern and abandoned colony sediments on Inexpressible Island, Ross Sea, Antarctica. Their findings indicate that, following the abandonment of the colony, organic material is broken down, with the net result being that carbon, nitrogen, and phosphorus are leached from the soil. Tedrow and Ugolini (1966) obtained

similar results and suggested that the large quantities of nitrogen and phosphate that are initially deposited as guano or other biologically produced materials will later degrade into secondary calcium phosphate. Significantly, studies by both Campbell and Claridge (1966) and McGraw (1967) found that each abandoned site has a neutral or alkaline pH, likely because of the buffering capacity of the carbonate.

Maintaining a basic pH is essential in early-stage diagenesis. Runoff or precipitation that percolates through the near-surface meteoric environment is undersaturated in its ionic content. As these fluids migrate downwards, they are able to readily dissolve various chemical constituents in the soil (Tucker 1991). The recently buried, richly organic, remains associated with ornithosols are rich in phosphorus and calcium carbonate, materials that can easily become mobile when the localized soil chemistry favors dissolution and recrystallization. With depth, migrating fluids become oversaturated in their ionic content and will begin to precipitate compounds out of solution.

Ames (1959) was the first to notice how fluorapatite replaced other minerals, particularly calcite and gypsum. In his experiments, Ames (1959) powdered calcium carbonate and exposed it to a phosphatic solution, observing that, through time, the calcium carbonate was converted to fluorapatite. His findings indicated that replacement rates are a function of pH, PO_4^{3-} content in relation to HCO_3^- concentration and calcite grain size, or surface area. Nathan and Lucas (1972, *cited in* Kohn, et al., 2002) later determined that the calcite or gypsum dissolves prior to any apatite crystallization.

Tatur (2002) summarized the current literature on the development of ornithogenic ecosystems, and puts Ames (1959) and Nathan and Lucas (1972, *cited in* Kohn, et al., 2002) into perspective as to how fluorapatite diagenesis may progress in ornithosols. Immediately

following guano deposition, between one and three weeks are needed for microbiological activity to decompose the waste. Guano decomposition is accelerated by its low albedo, as well as by the moisture content of the waste (Tatur, 2002). During this period, the excreta become a semi-liquid, homogeneous mass, composed of weathered chitin (the most prolific component of guano) and sediments (Tatur, 2002).

As the calcium phosphate in chitin decomposes, phosphatizing solutions are created, some of which precipitate as earthy masses of fluorapatite (Tatur, 2002). In an earlier work, Tatur (1987) found that concentrations of calcium and fluorine change predictably with a constant molar ratio of 0.2, one which closely reflects that of F/C in fluorapatite.Tatur (1987) quantified fluorine concentrations in krill (0.1149%), penguin excreta (0.42-0.45%), and in leached guano (0.6-1.9%), and in sediments (up to 2.3%). In most instances, Tatur (1987) noted that the fluorine was bound to calcium phosphate.

Calcium phosphate is unique in that it is both an agent and a subject of weathering processes: it can chemically degrade and dissolve some materials (notably those that contain $CaCO_3$), while precipitating secondary phosphates in their place (Tatur, 2002). Interestingly, fluorapatite is unstable in the soil and may be easily dissolved by acid leachates (Tatur, 1987).

METHODS

Field collection of eggshell and bone fragments has been carried out by Emslie and his graduate students for a variety of colonies that are circum-Antarctic in distribution. Both fossilized and modern remains have been collected. Modern eggshell samples are collected from active penguin colonies, on or nearby active nests, and represent debris from a specific breeding season. Modern eggshells analyzed for this study were collected by the author at Cape Hallett

and Inexpressible Island, Ross Sea, Antarctica (Fig. 2), and represent debris from the 2004 nesting season.

Ancient colony sites are easily distinguished from glacial sediments in coastal Antarctic locations, based on soil type and characteristic gravel lags (Fig. 1D). Once ancient colony sites are identified, excavations employed the procedures of Emslie and McDaniel (2002). The number of excavations at a particular colony is variable, and is determined by estimating the relative size and approximate age (based on findings of Baroni and Orombelli, 1994; Emslie, unpublished) of the materials.

Square meter test pits were initially prepared for excavation by removing the loose gravel lag that comprises the surface pavement. Following this removal, each excavation proceeded in 5-cm intervals, regardless of soil stratigraphy. Sediments were quantified by volume as they were excavated using buckets and were dry-sieved through a series of mesh screens that have converted phi values of 0.012ϕ, 0.11ϕ, and 0.84ϕ, respectively.

Dry-sieving removed much of the coarse, gravelly nest material while preserving the finer bone and eggshell fragments needed for radiometric and scanning electron microscope examination. Site excavation continued until the base of the ornithogenic sequence was reached, as indicated by the presence of glacially derived mineral deposits, or until permafrost prohibited further excavations. Upon completion, all pits were backfilled. Colony samples were then bagged and flown to field laboratories by helicopter. There, sediments were wet-sieved with mesh screens that have converted phi values of 0.012ϕ, 0.11ϕ, and 0.84ϕ. Wet-sieving loosened and removed any guano or sedimentological debris adhering to the fossils. All material was then air dried at 80°F and hand sorted for bone and eggshell fossils.

The recovered eggshell fragments were transported to the laboratory at the University of North Carolina Wilmington (UNCW). To determine the extent and occurrence of diagenesis within the critical time period being studied, which spans from 0-1,000 years before present (bp), seven sites, from three major regions (Fig. 2), were chosen for analysis. These sites are circum-Antarctic in distribution. Each site is physiographically unique and together the sites represent a range of diverse climatic conditions (Table 1; Fig. 2). For each sampling site, five eggshell samples were examined from each level, unless local preservation prohibited the collection of numerous fossils.

Any alterations in the fossilized eggshells could be identified by comparing fossil samples with modern eggshell chemistry and structure. Analysis was completed using a Philips XL 30S FEG scanning electron microscope (SEM), with a resolution of 2–4 nanometers (nm). Non-dispersive X-ray microanalysis of the eggshell's structure and mineralogy was completed using Phoenix EDAX software version 3.32. For analysis, eggshell fragments were broken into pieces to obtain fresh surfaces. The recently broken surface was oriented upward and glued, slightly tilted, onto an aluminum stub using colloidal graphite to permit tangential observations in the manner outlined by Grellett-Tinner et al. (2004). The mounted samples were then coated with 6 nanometers of platinum-palladium using the Cressington 208 HR Sputter Coater.

SEM analysis was conducted at 10 kilovolts, with a working distance of 7.5 mm, spot size 5, and dead time between 20–40%. Eggshells were magnified 2,000 times their actual size, and during digital acquisition a scale bar was embedded in each image. Both the weight and atomic percents of key elements were measured using EDAX software. Elements of interest included carbon, oxygen, fluorine, sodium, magnesium, aluminum, phosphorus, sulfur, and

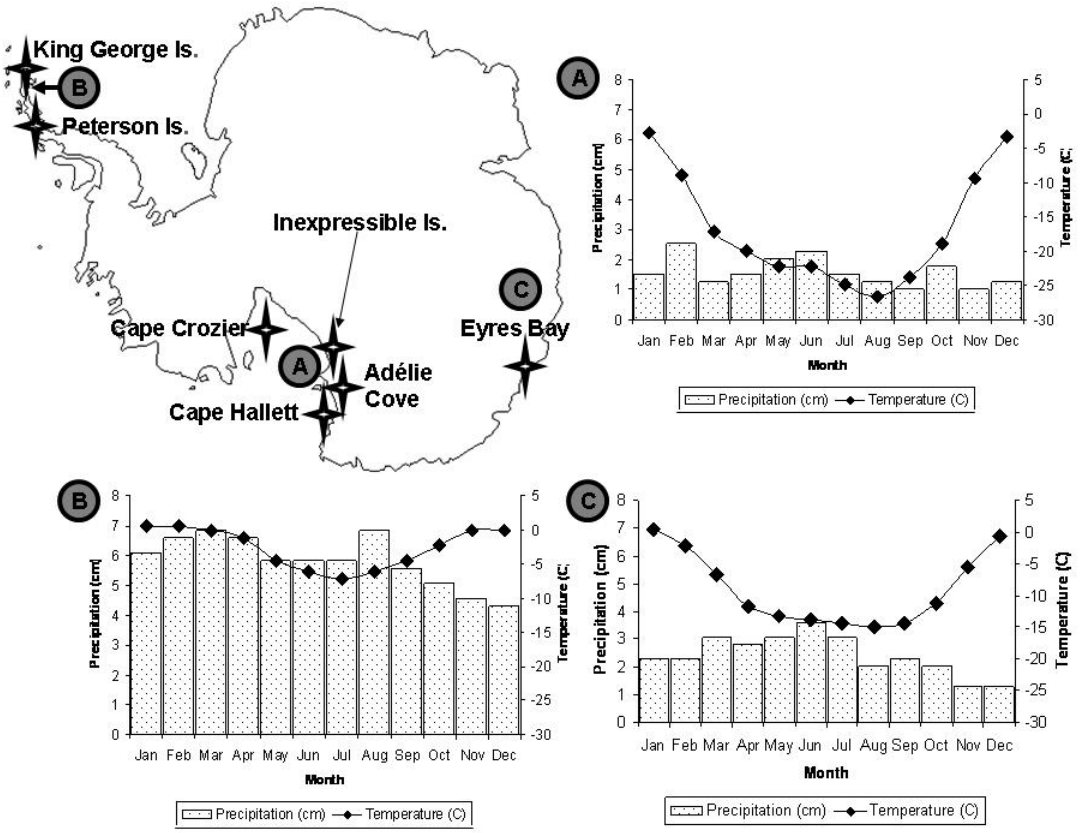

Figure 2. Location map of each sampling site in relation to regional climatic data. Stars indicate fossil localities while circled letters correspond to the climate information at (A) McMurdo Sound, Ross Island, Ross Sea (mean values for 26 year record), (B) Admirality Bay, Antarctic Peninsula (mean values for 9 year record), and (C) Casey Station, East Antarctica (mean values for 30 year record). Climatic data courtesy of www.weatherbase.com.

TABLE 1. Location and age of studied sites in Antarctica.

Site Name	Location	Latitude / Longitude	Age[1] (yrs bp)	# Levels
Cape Crozier	Ross Island, Ross Sea	77°30' S, 169°19' W	0–492	5
Ginger Island	Antarctic Peninsula	67°45' S, 68°41' W	0–720	5
Peterson Island	Eyres Bay	66°26'S, 110°30'W	0–460	5
Point Thomas	King George Island	62°09'S, 58°28'W	132–511	2
Adélie Cove	Ross Sea	74°37' S, 164°50' W	452–709	3
Cape Hallett	Ross Sea	72°19'S, 170°13'W	Modern	N/A
Inexpressible Island	Ross Sea	74°54'S 163°43'W	Modern	N/A

[1] Radiocarbon dates are from Emslie and McDaniel, 2002; Polito et al., 2002; Emslie et al., 2003; and Emslie and Woehler, 2005.

calcium. These elements were chosen based on the work of previous investigators (Hirsch and Packard, 1987), as well as preliminary work completed at UNCW. For each sample, X-ray analysis was performed in three discrete locations (Fig. 3). The first location was within the outermost region of the eggshell, encompassing the cuticle and surface crystalline layer; the second was centered in the middle of the hard, mineralized section of the egg; and the third was completed within the base of the mineralized section of the cone layer, that region directly above the membrane. The membrane was excluded from all comparisons as fossilized eggs failed to maintain this layer.

Spearman rank correlation coefficients were compiled for each element by Stephanie Fonda at the Harvard University Medical Center using SAS software version 8.02. Individual elements were tested in relationship to each of the others. This particular test was chosen owing to the fact that the Spearman rank correlations test the null hypothesis of no association between two variables against the alternative hypothesis that the variables are associated (S. Fonda, pers. comm.). Furthermore, the method is recommended when the sample size is small, and in situations when the true distribution of the variables is not known or is not close to the distributions underlying paremetric tests. The output matrixes for each fossil site may be found in Appendix A.

Each coefficient can have values between 0 and 1, with a 0-value representing no correlation and a 1-value being a perfect rank correlation between the variables. Negative coefficients indicate an inverse relationship between the two elements of interest. In other words, a negative value indicates that as one element's weight percentage increases, the other element's weight percentage decreases. For this study P values < 0.05 were considered significant.

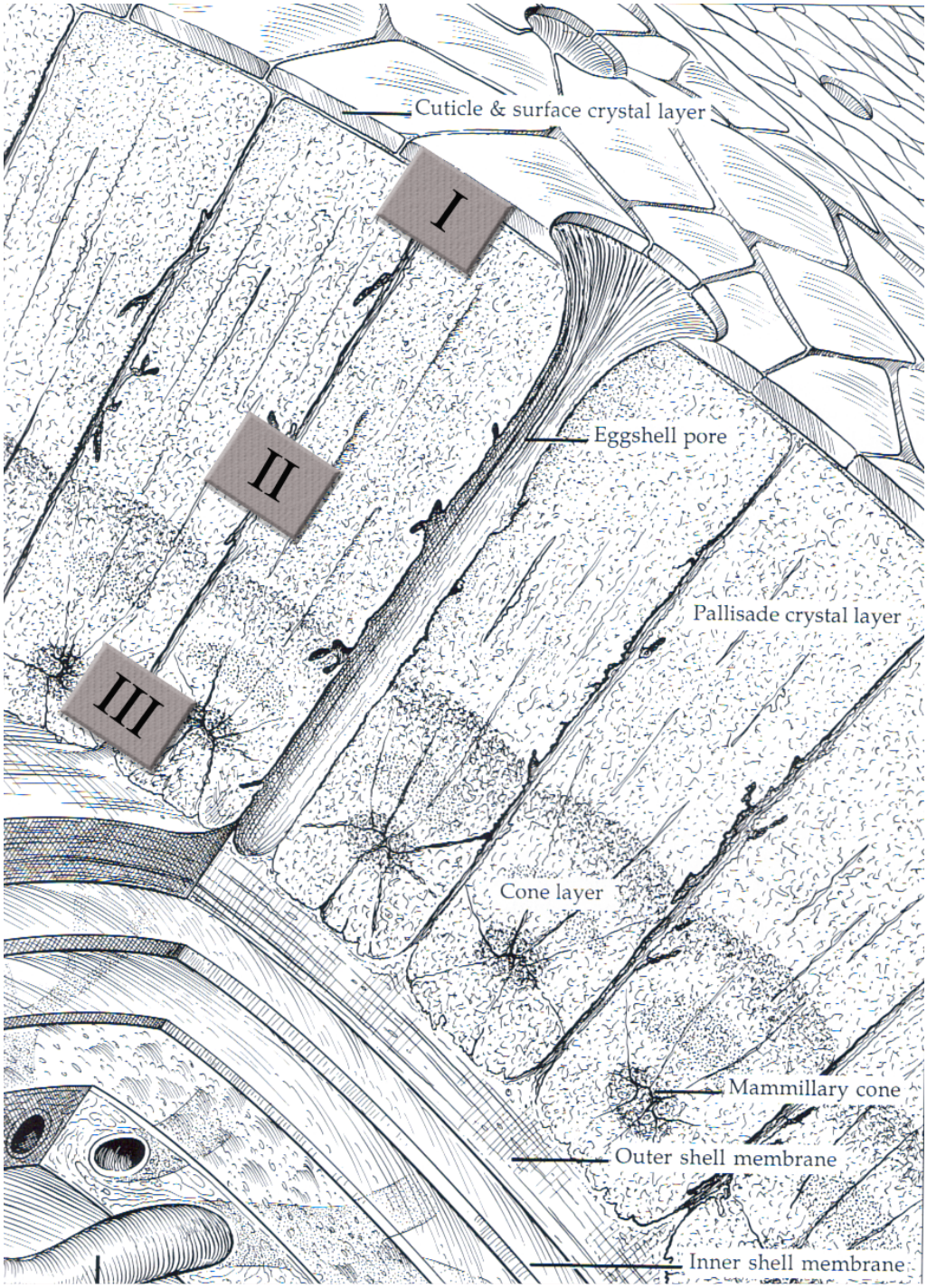

Figure 3. Cross sectional view through an avian eggshell showing its distinctive morphological features. SEM sampling locations are identified by Roman numerals I-III. Image modified from Proctor and Lynch, 1993.

Because modern penguin eggshells are composed almost exclusively of low magnesium calcium carbonate, large amounts of phosphorus and fluorine found within fossil samples are indicative of chemical changes to the original eggshell structure. While it is assumed that most of this recrystallization is in the form of fluorapatite, trace amounts of other minerals are likely.

Visual descriptions were compiled of specimens from each study site in an attempt to document any physical changes among the hand samples. Observations included: (a) whether the shells appeared chalky or brittle, (b) the overall angularity of the fragment, (c) the amount of surface pitting, dissolution, or exfoliation observed, and a (d) qualification of shell color using the Geological Society of America Rock Color Chart. This information is given in Appendix B.

RESULTS

Field Observations

Abandoned colonies are identifiable as a series of subdued nest mounds or topographically distinct gravelly hummocks. These deposits rest unconformably on glacially-derived surficial deposits or beach sands, and stand in positive relief from one-fourth meter to over one meter in height. Compositionally, the deposits in the Ross Sea region are composed of moderately well sorted, locally-derived, round-to-semi-angular mafic and ultramafic rocks.

The uppermost portion of each stratigraphic sequence consists of a wind-deflated surficial lag that grades into a bimodal conglomerate with depth. Ornithosols may be described as discontinuous, sub-parallel, gravelly lenses that are impregnated by yellowish-brown to reddish-brown, dry, guano-rich sandy loam of lower-medium to fine, sub-angular quartz, olivine,

and basalt grains. Preserved within this fine-grained, poorly indurated matrix are egg fragments, feathers, and penguin bones. Locally, platy clay horizons exist.

Commonly, site stratigraphy is not complex, with the excavations unearthing a nearly continuous series of ornithogenic sediments until glacially derived deposits are encountered. However, in the most complex example, one excavation at Cape Hallett produced a series of colony sediments interbedded with black, poorly sorted, angular, medium sand (Fig. 4). The author interprets this series to represent overwash storm deposits with subsequent colony development. In no instance can the stratigraphy at one site be correlated laterally, owing to the patchy development of the colonies through time.

Laboratory Observations

Modern Eggshell Structure and Chemistry

Modern eggshells were collected from the active portion of the Cape Hallett and Inexpressible Island colonies (Ross Sea, Antarctica) during the austral summer 2003–2004 field season. When unbroken, the eggs are rounded with one distinctively pointed pole. The eggs are white to bluish-white in color, and lack any type of visible surficial ornamentation. Under the SEM, layers I and II are composed of blocky calcite rhombs (Fig. 5A), and Layer III is a cone layer. Three distinctive, prismatic layers are prominent (Fig. 5B). Flaws between the brittle calcite rhombs in Layers I and II create a number of tiny pore spaces, all of which have nearly rounded apertures. Layers I and II are predominantly composed of calcium, carbon, and oxygen, the summation of which account for ~96% of the sample's weight.

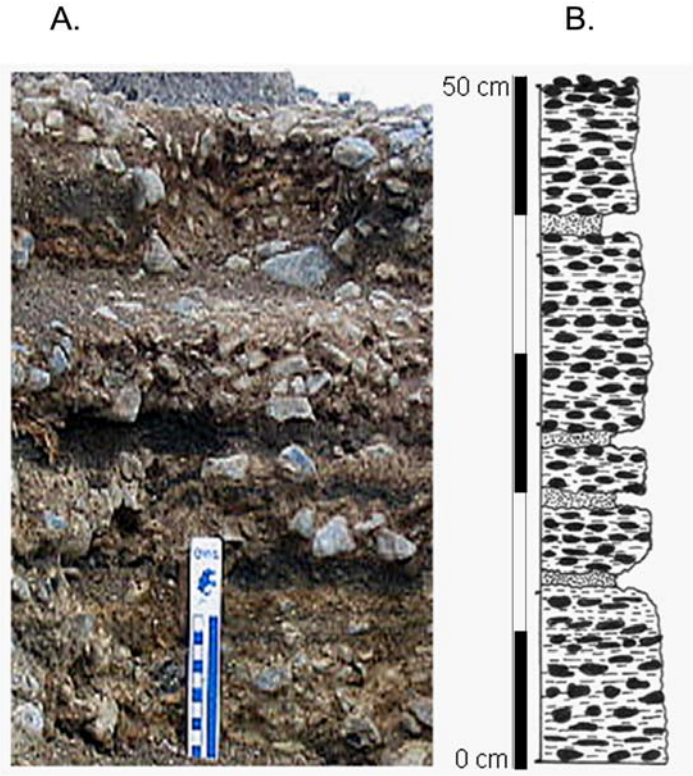

Figure 4. Ornithosol stratigraphy at Cape Hallett, Ross Sea, showing (A) Bimodal conglomerate with sharply bounded mafic beach deposits, and (B) Interpreted stratigraphic section. Scale bar in (A) is 10 cm.

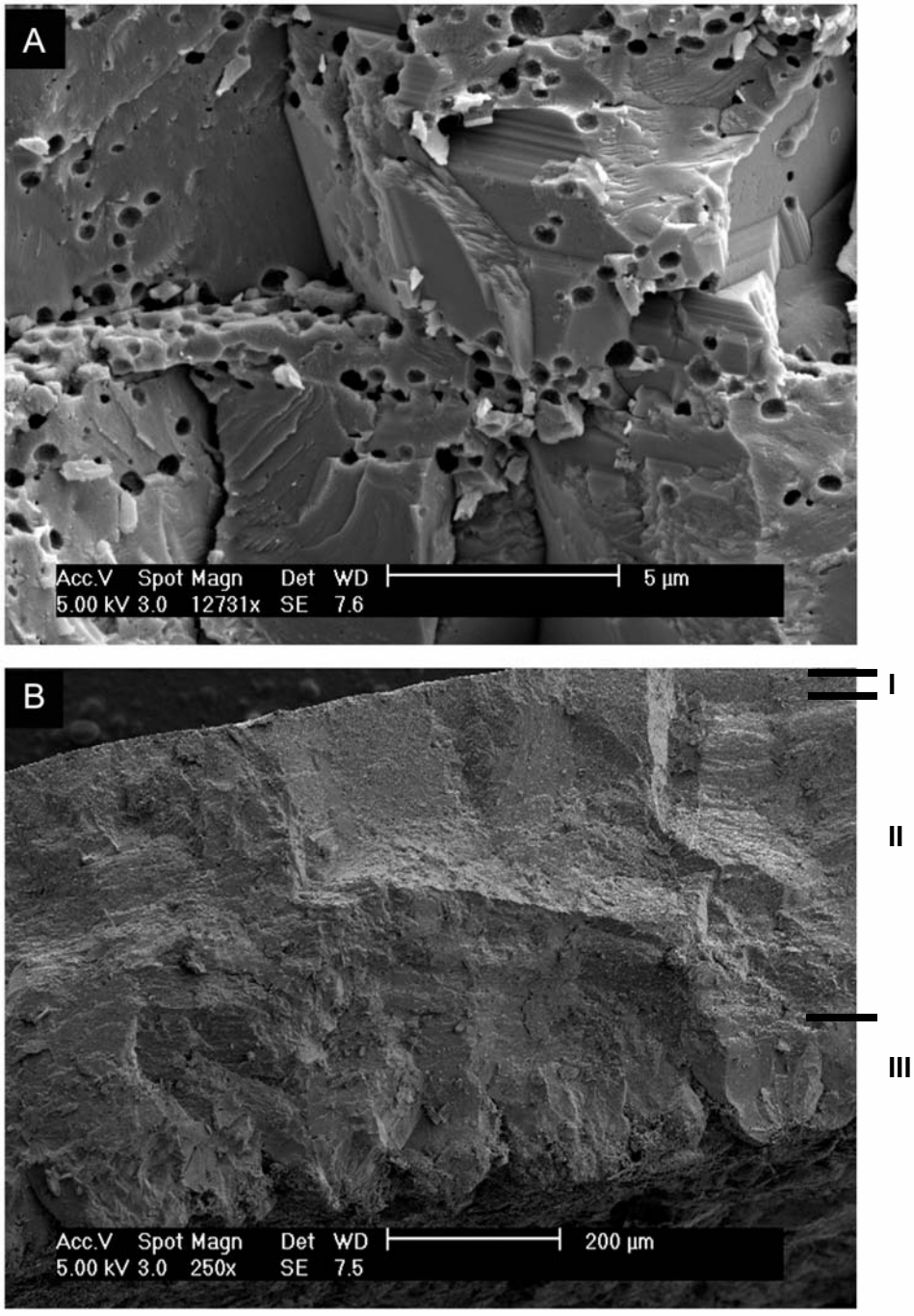

Figure 5. SEM photomicrographs of modern eggshell from Cape Hallett showing (A) Well formed calcium carbonate rhombs from Layer II. Nearly circular holes are pore spaces for the transfer of gasses, and (B) Tangential cross-section showing the three distinctive layers of modern eggshells. Roman numerals to right indicate eggshell layers.

1–1,000 bp Eggshell Structure and Chemistry

Regardless of the climatic regime in which the samples were collected, all five localities exhibited similar trends. Owing to their uniformity, only one site will be discussed in detail, but all results are reported in Appendix C. A test pit excavated on Cape Crozier, Ross Island, Ross Sea, Antarctica, has been dated by Polito et al. (2002) to be between 307 and 492 bp. All five levels will be discussed.

In hand specimens, eggshells from Level 1 are chalky, with rounded margins, and a grayish-orange-pink color (5YR 7/2). Quantitative SEM results using EDX verify that both the uppermost and lowermost sections of the eggshell fragments (layers I and III) are composed chiefly of botryoidal crystals of fluorapatite (based on EDAX chemistry), whereas the centermost sections of the eggshells are calcium carbonate. SEM images verify that the composition of layer II is identical to the palisade layer of modern specimens, and numerous, well-formed calcium carbonate rhombs exist. Additionally, there are numerous, uniformly shaped and well rounded pore spaces.

Eggshell fossils from Level 2 and Level 3 are similar to those in Level 1, with the exception that dissolution rings become prominent on many of the shell surfaces in hand samples. These features are likened to tiny craters, and are discrete locations where the calcium carbonate shell has been weakened to the point that some of the cuticle and surface crystal layer has been removed. As with fossils in Level 1, both the inner and outermost regions of the shells are composed of botryoidal fluorapatite crystals, whereas the central sections of the eggshell are well-defined rhombs of calcium carbonate.

More pronounced physical and chemical changes occur with eggshells in Levels 4 and 5. Visual inspection reveals that dissolution rings and surficial pitting become prolific in hand

specimens. Additionally, the eggshell's color becomes grayish-orange (10YR 7/4), indicating physical changes in the samples. SEM analysis of shell fragments in Level 4 suggests that shell chemistry is more homogeneous, and, while the central sections of the sample still maintain higher ratios of calcium carbonate than external regions, the differences are less pronounced than in the younger fossils. Development of these chemical changes continues in Level 5 to the point that the entire shell, regardless of sample location, has been replaced by fluorapatite. The chemical homogeneity of this oldest sample is shown in Fig. 6.

Figure 7 plots average weight percentages of fluorine, phosphorus, and carbon of the five eggshell fossils from each excavation level, as determined by EDX analysis. These data show that both the weight percentages of fluorine and phosphorus increase in the samples with sediment depth.

Statistical Analysis

The statistical results demonstrate that in all five instances there was a significant negative association between carbon and phosphorus, with typical values ranging between -0.76 and -0.83. Such results verify that, as calcium carbonate is removed from the eggshell, calcium phosphates are precipitated. This is consistent with Ames' (1959) investigation, where he determined that calcium carbonate dissolution leads to phosphate mineralization.

Data presented here indicate that there is no strong association between carbon and fluorine in the five samples, and typically values ranged between 0.16 and -0.58 (Appendix A). In most instances, P values are reflective of no correlation. The relationship between phosphorus and fluorine is the most variable, and associations were found at Cape Crozier and Ginger Island

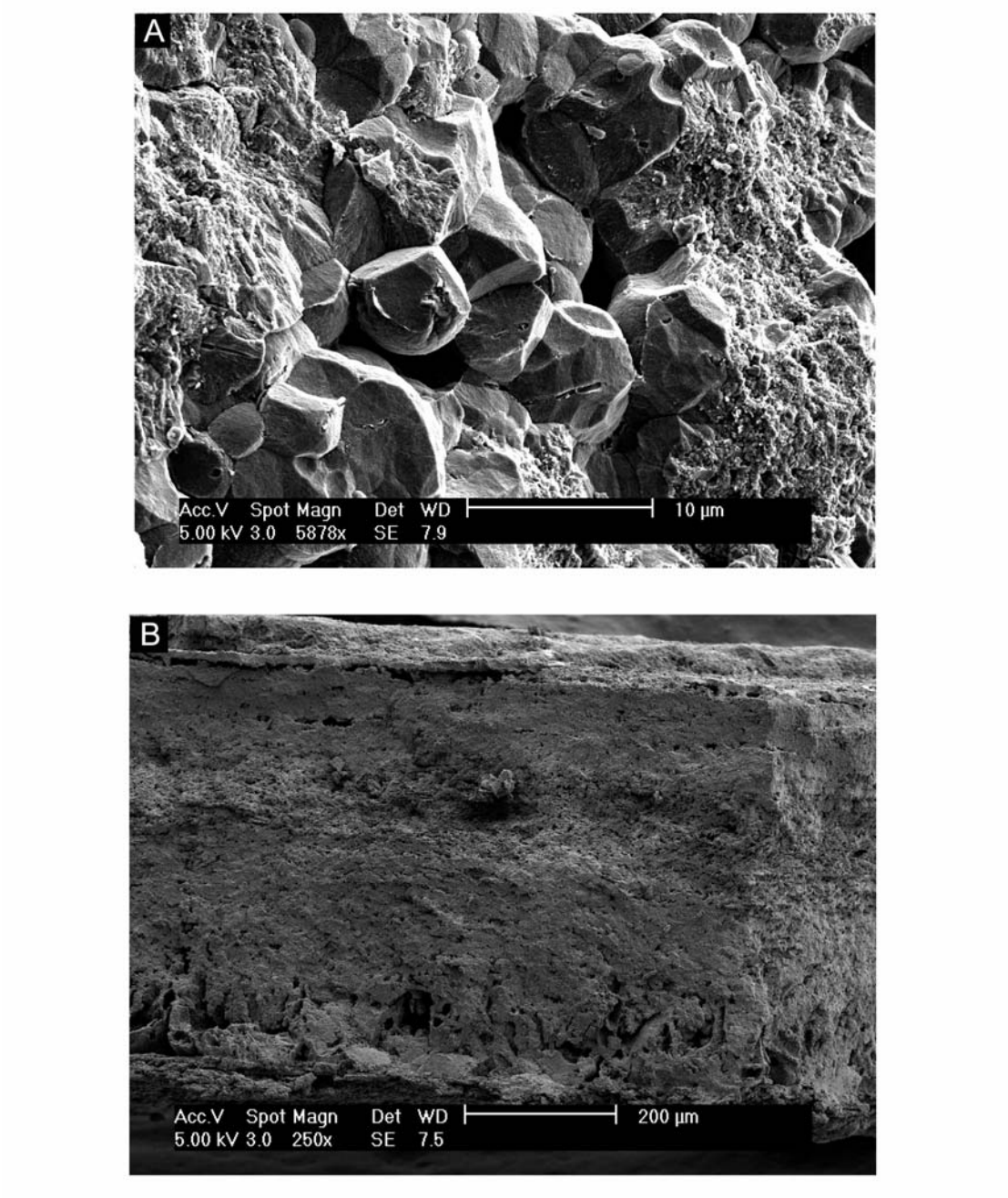

Figure 6. SEM photomicrographs of fossilized eggshell from Cape Crozier at 20 cm depth showing (A) Botryoidal fluorapatite crystals from sampling location II, and (B) Tangential cross section demonstrating the diagenetically altered appearance of older eggshell fragments. Notice that distinctive eggshell layers have been lost.

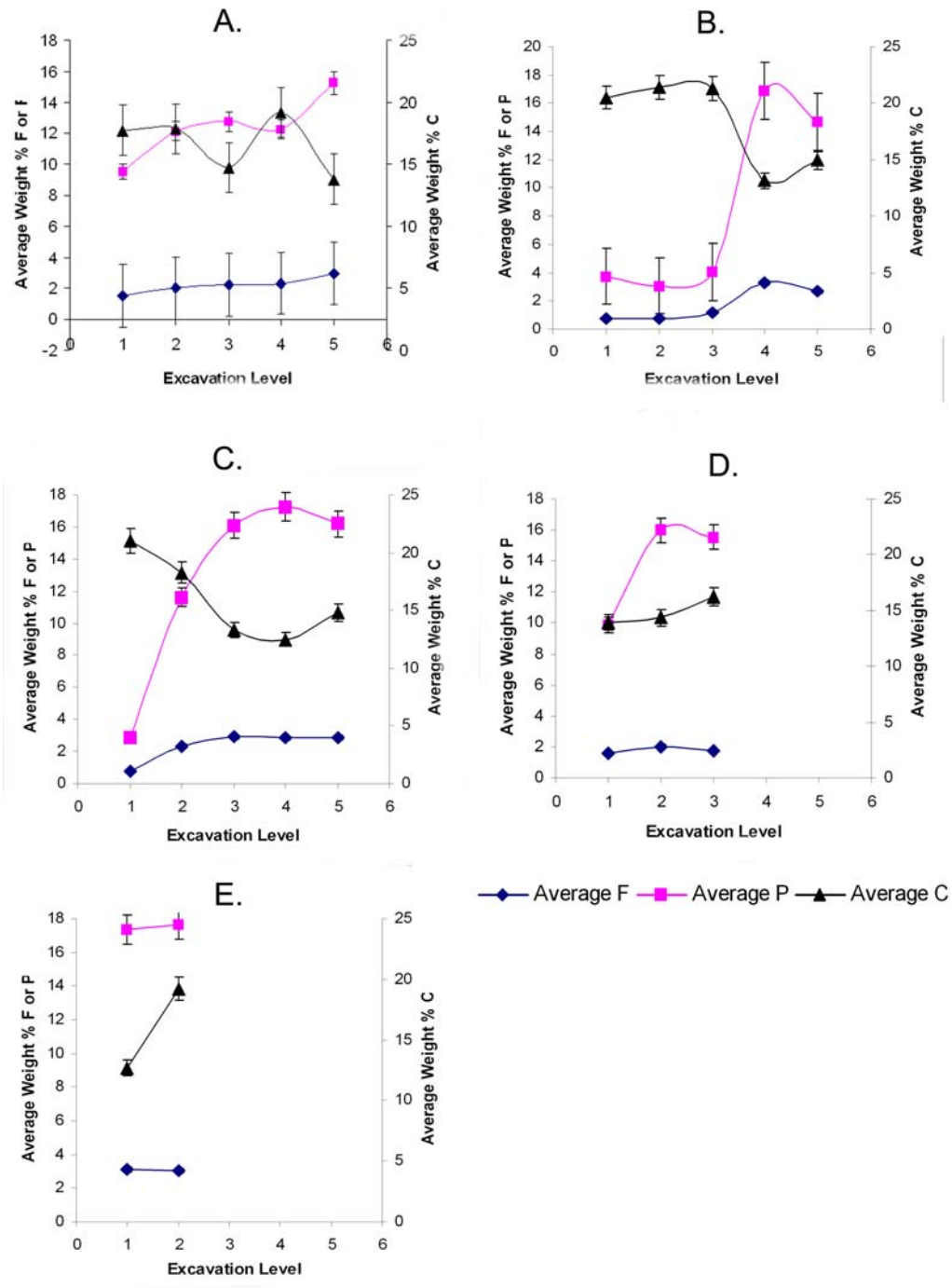

Figure 7. The relative weight percentages of fluorine, phosphorus, and carbon at (A) Cape Crozier, (B) Ginger Island, (C) Peterson Island, (D) Adélie Cove, and (E) Point Thomas. Legend is below D. 5% error bars have been included for each element.

(values of 0.69 and 0.74 respectively), while at all other sites the association was much weaker (0.45 through -0.52).

DISCUSSION

These data indicate that subtle diagenetic alterations occur following deposition of eggshells into sediments at the investigated colonies. As chitin and guano disintegrate, phosphorus and fluorine are produced, and can then migrate freely into the ornithosol. An increased percentage of phosphorus and fluorine in four of the five samples through time clearly demonstrates that the original composition of the eggshell has changed, likely because of the mineralization of fluorapatite.

The presence of fluorapatite, as shown by SEM and EDX analysis, demonstrates that water exists in the ornithosols, because it is unlikely, if not impossible, for minerals to precipitate in the absence of fluids. Simultaneously, eggshell calcium carbonate experiences dissolution. If we acknowledge that water exists in the subsurface, and that dissolution of eggshell carbonate is possible, we may conclude that dissolved inorganic carbon (DIC) from the eggshell could, potentially, mix and re-equilibrate with atmospheric sources, altering any inorganic carbon isotope ratios.

Under this premise, the inorganic carbon values reported by Emslie and Patterson (2004) and Patterson and Emslie (2004) were considered, and a mixing equation was ultimately established to determine to what extent, if any, the inorganic carbon isotopic ratio would change should there have been any contamination of atmospheric carbon during the diagenetic process. Work proceeded as outlined by Eby (2004). Having an already established isotope value for one

of our end members (i.e. the carbon values in the modern eggshells), it was necessary to determine the isotopic value for any carbonate that precipitated under normal atmospheric conditions as a result of diagenesis. For these purposes, it is assumed that carbonate is precipitating at 1ºC, a value selected after examining the climatic data reported in Fig. 2. It is also assumed that precipitation occurs in equilibrium with atmospheric CO_2 ($\delta^{13}C$ = -7‰) using the equation:

$$1{,}000\ ln\ \alpha = F_{Calcite} / T^2$$

Where $F_{Calcite}$ = Fractionation factor for calcite = $-3.63 + 1.194 \times 10^6$
T = temperature in °K

$1{,}000\ ln\ \alpha = -3.63 + 1.194 \times 10^6 / (274.15)^2$

$1{,}000\ ln\ \alpha = 12.2564$
$ln\ \alpha = 0.01225$
$e^{ln\ \alpha} = e^{0.01225}$
$\alpha = 1.0123$

$\delta^{13}C = \alpha\ (-7‰ + 1{,}000) - 1{,}000 =$
$\delta^{13}C = 1.0123\ (-7‰ + 1{,}000) - 1{,}000 =$

$\delta^{13}C = 5.24‰$

This $\delta^{13}C$ value could then be used as an end member in a mixing equation where the:

$$\delta \text{ value of the mixture} = fA\ \delta A + fB\ \delta B$$

where *fA* is equal to the fraction of end member *A* in the mixture, *δA* equals the $\delta^{13}C$ value of end member *A* (-20‰), *fB* is equal to the fraction of end member *B* in the mixture, and *δB* equals the $\delta^{13}C$ value of end member *B* (5.24‰). Computations using Excel solver suggest that the fraction of the original carbonate (i.e. *A*) is 70%, while the remaining 30% reflects the values of carbonate precipitated with atmospheric carbon (i.e. *B*). This equation may now be written:

δ value of the mixture = fA δA + fB δB

$= 0.7(-20‰) + 0.3(5.24)$
$= -14 + 1.57$
$=$ mixture $\delta^{13}C$ value of -12.43‰

This value falls between the $\delta^{13}C$ values for inorganic carbon (-12 and -13) reported by Emslie and Patterson (2004) and Patterson and Emslie (2004). This demonstrates that the inorganic calcium carbonate's dramatic change in $\delta^{13}C$ may be reflective of atmospheric mixing following deposition rather than any dietary change, where a positive enrichment in the isotopes is reflective of a new mixture of the original and atmospheric sources of carbon.

Despite diagenetic alterations in the inorganic carbon, however, the nitrogen and organic carbon ratios may be unchanged, owing to the fact that nitrogen would not participate in carbonate dissolution. Furthermore, organic carbon may be preserved in the ornithosols owing to the fact that the buffering effect of the eggshell carbonate might be significant enough to neutralize any acids (Davis, 1999)

SEM and EDX analysis reveals that diagenetic changes occur rapidly in the eggshells, as indicated by the homogeneous fluorapatite chemistry of the samples with depth. Some variation occurs between samples from different sites, and is inferred to be the result of differences in soil moisture levels between the sites. In excavation layers one and two, the eggshells are heterogeneous, and fluorapatite is found exclusively on the outermost and innermost portions of the eggshells at sampling locations I and III (Fig. 8A). This trend suggests that dissolution of the eggshell carbonate and impregnation of calcium phosphate follows a predictable pattern that may be correlated with age. In the deepest sediments, eggshell structure is homogeneous (Fig. 8B), with phosphorus and fluorine comprising much of the sample. Physically, the samples appear to be entirely composed of botryoidal fluorapatite crystals under the SEM.

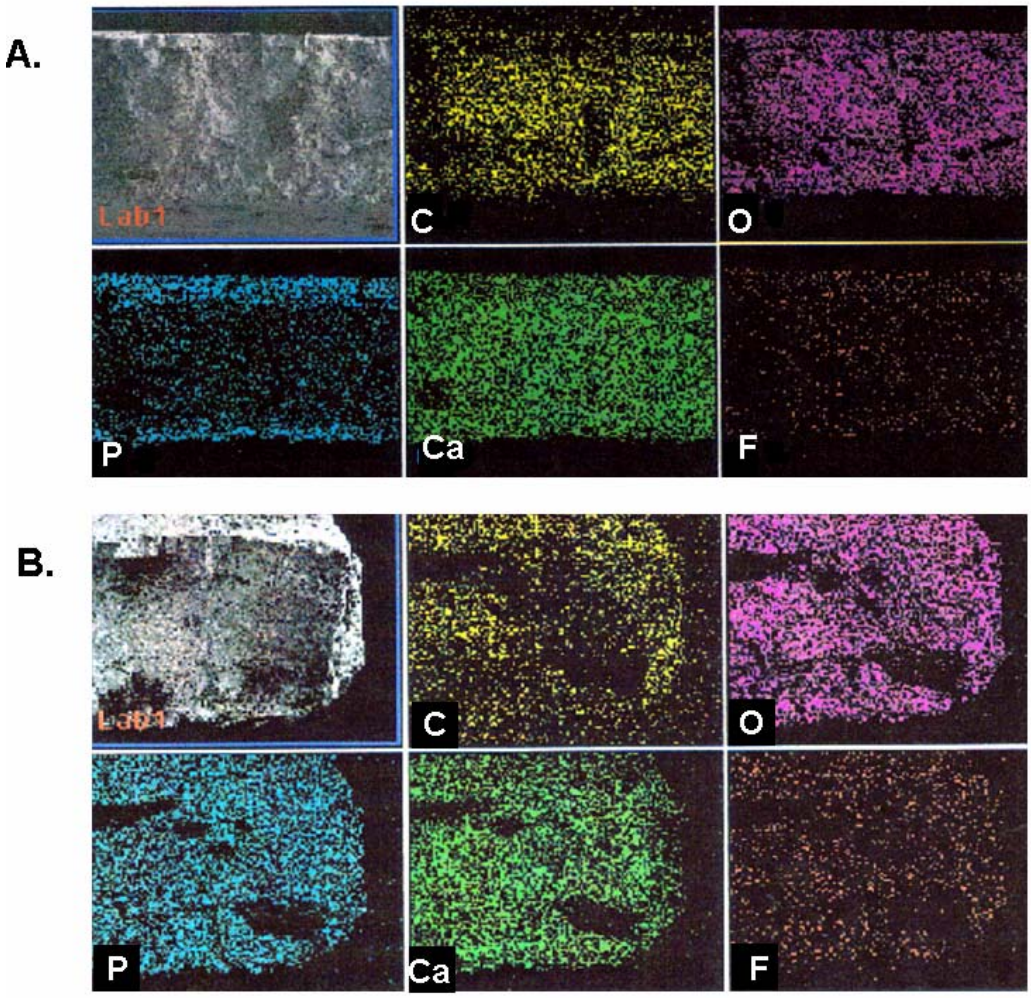

Figure 8. EDX maps showing the distribution of elements of interest in: (A) Eggshell fossil from Cape Crozier at 10 cm depth. Notice that fluorine and phosphorus concentrations are preferentially found along the outer margins of the eggshell. (B) Eggshell fossil from Cape Crozier at 25 cm depth showing the homogenous distribution of phosphorus and fluorine.

CONCLUSIONS

SEM microanalyses of fossilized eggshells preserved in ornithosols indicate that diagenetic alterations follow a predictable pattern that is a function of the fossil's age. Data suggest that complete chemical recrystallization and diagenetic alteration of the fossilized eggshells occurs rapidly, and is complete at the basal layers at each study site.

Alterations in the eggshell's mineralogy do not appear to influence the organic and nitrogen isotopic signatures of the fossils. Despite this, mixing with atmospheric carbon has been documented in the inorganic carbonate, where values of a calculated mixture (-12.43‰) correspond with values reported by Emslie and Patterson (2004) and Patterson and Emslie (2004). Due to this, it seems likely that the signal recorded by Emslie and Patterson (2004) and Patterson and Emslie (2004) may represent diagenetic alterations, and may be of limited use in paleoecological studies relating to penguin diet. Despite this, the use of isotope technology in paleoecological reconstructions, using organic carbon and nitrogen isotopes, may still be possible, and lends support to the hypothesis advanced by Emslie and Patterson (2004) and Patterson and Emslie (2004).

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APPENDIX A

Spearman rank correlation coefficients and p-values of C, P, and F in the fossilized penguin eggshell samples.

Cape Crozier (n = 75)

	C	P	F
C	1		
P	-0.76 (<.0001)	1	
F	-0.57 (<.0001)	0.69 (<.0001)	1

Ginger Island (n = 75)

	C	P	F
C	1		
P	-0.76 (<.0001)	1	
F	-0.48 (<.0001)	0.74 (<.0001)	1

Peterson Island (n = 75)

	C	P	F
C	1		
P	-0.83 (<.0001)	1	
F	-0.23 (.047)	0.45 (<.0001)	1

Adélie Cove (n = 43)

	C	P	F
C	1		
P	-0.81 (<.0001)	1	
F	-0.32 (.038)	0.46 (.002)	1

Point Thomas (n = 24)

	C	P	F
C	1		
P	-0.79 (<.0001)	1	
F	0.16 (.443)	-0.52 (.009)	1

APPENDIX B
Physical characteristics of penguin eggshells in hand samples

Location	Level	Shell Description
Cape Crozier	1	Chalky, minor amounts of surface pitting, rounded edges with crisp margins. Grayish-orange-pink (5YR 7/2).
	2	Chalky, some amounts of surface pitting, rounded edges with crisp margins. Some membrane still preserved. In some samples, exfoliation has begun to weaken the parallel layers of the shell producing small gaps. Grayish-orange-pink (5YR 7.2).
	3	Chalky, with moderately strong surface pitting, rounded edges and crisp margins. Exfoliation prominent. Grayish-orange-pink (5YR 7.2).
	4	Chalky, semi-angular shells with rounded edges. Visibly pitted surfaces. Exfoliation dominant. Grayish-orange (10YR 7/4).
	5	Chalky, semi-angular shells with round edges and pitted surfaces. Exfoliation dominant. Grayish-orange (10YR 7/4).
Ginger Island	1	Brittle, angular shells, blocky margins. Some visible pitting. Grayish-orange-pink, (10R 8/2).
	2	Brittle, angular shells, blocky margins. Some visible pitting. Grayish-orange-pink, (10R 8/2).
	3	Less brittle, somewhat chalky, angular shells with soft margins (some rounding). Grayish-orange-pink, (10R 8/2).
	4	Chalky, fragile, angular, pitted shells with muted, rounded edges. Exfoliation common. Pale red, (10YR 5/4).
	5	Chalky, fragile, very pitted, angular shell fragments with rounded margins. Some exfoliation. Moderate-yellowish-brown, (10YR 5/4).
Peterson Island	1	Chalky, semi-angular shells with rounded margins. Some pitting. Bluish-white, (5B 9/1).
	2	Chalky, semi-angular shells with rounded margins. Some pitting and exfoliation. Bluish-white, (5B 9/1).
	3	Chalky, semi-angular shells with rounded margins. Pitting and exfoliation common. Grayish-orange (10YR 7/4).
	4	Chalky, semi-angular shells with rounded margins. Pitting common and some exfoliation. Pale-yellowish-brown (10YR 6/2).
	5	Chalky, semi-angular shells with rounded margins. Some surface pitting. Pale-yellowish-brown. (10YR 6/2).

Location	Level	Shell Description
Adélie Cove	1	Chalky, semi-angular shell fragments with rounded margins. Surface pitting and some exfoliation common. Moderate-yellowish-brown (10YR 5/4).
	2	Chalky, semi-angular shell fragments with rounded margins. Surface pitting and exfoliation common. Moderate-yellowish-brown (10YR 5/4).
	3	Chalky, semi-angular shell fragments with rounded margins. Surface pitting and exfoliation common. Moderate-yellowish-brown (10YR 5/4).
Point Thomas	1	Semi-angular shell fragments with rounded margins. Surface pitting and some exfoliation. Pale-yellowish-brown (10YR 6/2).
	2	Semi-angular shell fragments with rounded margins. Surface pitting and some exfoliation. Pale-yellowish-brown (10YR 6/2).

APPENDIX C

Calculated elemental weight percentages from EDX

Sample ID	Shell Site	C	O	F	Na	Mg	Al	P	S	Ca	Weight %
C1-1 (1)	I	10.58	26.76	1.81	2.12	0.56	0.62	17.72	0.83	39.01	100.01
C1-1 (1)	II	20.09	35.24	0.34	0.26	0.06	0.10	2.94	0.31	40.65	99.99
C1-1 (1)	III	18.65	28.19	1.97	1.66	1.18	0.88	12.33	1.08	34.06	100.00
C1-1 (2)	I	19.05	36.33	2.22	1.48	0.38	0.17	8.06	0.23	32.08	100.00
C1-1 (2)	II	18.83	34.72	0.36	0.23	0.15	0.12	3.02	0.30	42.26	99.99
C1-1 (2)	III	14.91	28.33	1.89	1.39	0.35	0.00	17.15	0.73	35.26	100.01
C1-1 (3)	I	17.14	34.02	1.63	1.16	0.21	0.00	9.58	0.61	35.64	99.99
C1-1 (3)	II	22.54	41.44	0.56	0.19	0.07	0.05	2.12	0.14	32.87	99.98
C1-1 (3)	III	14.49	31.82	2.51	1.86	0.70	0.09	16.34	0.70	31.50	100.01
C1-1 (4)	I	14.53	30.29	2.99	2.12	0.95	0.86	16.02	0.84	31.39	99.99
C1-1 (4)	II	22.29	41.43	0.46	0.18	0.07	0.05	2.28	0.21	33.03	100.00
C1-1 (4)	III	19.20	35.72	1.42	0.91	0.40	0.16	5.24	0.34	36.61	100.00
C1-1 (5)	I	13.19	28.09	1.85	1.42	0.20	0.00	13.95	0.51	40.80	100.01
C1-1 (5)	II	23.65	42.40	0.65	0.29	0.12	0.05	2.43	0.24	30.16	99.99
C1-1 (5)	III	17.13	34.88	2.37	1.58	0.54	0.21	13.75	0.67	28.87	100.00
C1-2 (1)	I	16.49	31.40	1.50	1.14	0.17	0.00	12.47	0.55	36.28	100.00
C1-2 (1)	II	21.16	38.18	0.37	0.09	0.03	0.03	2.70	0.31	37.14	100.01
C1-2 (1)	III	15.69	33.83	2.31	1.87	3.76	0.74	16.15	0.69	24.96	100.00
C1-2 (2)	I	15.78	30.61	2.86	1.44	0.27	0.07	16.17	0.32	32.49	100.01
C1-2 (2)	II	35.19	21.01	1.43	0.98	0.46	0.46	10.01	0.57	29.88	99.99
C1-2 (2)	III	25.61	30.24	1.98	1.37	0.72	0.70	8.81	0.60	29.97	100.00
C1-2 (3)	I	14.16	32.74	3.78	2.55	1.01	0.91	17.27	0.62	26.96	100.00
C1-2 (3)	II	16.92	32.11	1.47	0.84	0.23	0.08	8.70	0.34	39.31	100.00
C1-2 (3)	III	16.85	31.59	1.86	1.07	0.39	0.07	9.63	0.15	38.38	99.99
C1-2 (4)	I	17.30	31.17	3.50	2.53	0.88	0.87	16.24	0.67	26.84	100.00
C1-2 (4)	II	20.35	34.87	1.32	1.01	0.73	0.73	3.65	0.60	36.74	100.00
C1-2 (4)	III	12.64	31.72	2.11	1.56	0.16	0.00	15.87	0.34	35.58	99.98
C1-2 (5)	I	13.06	29.17	1.64	1.37	0.49	0.57	12.85	0.47	40.38	100.00
C1-2 (5)	II	15.36	34.31	2.33	1.41	0.17	0.00	12.67	0.39	33.37	100.01
C1-2 (5)	III	11.54	24.91	1.97	1.30	0.21	0.00	18.59	0.00	41.49	100.01
C1-3 (1)	I	13.37	32.83	2.57	1.57	0.20	0.00	13.79	0.48	35.21	100.02
C1-3 (1)	II	16.20	32.17	2.08	1.59	0.76	0.76	10.82	0.58	35.05	100.01
C1-3 (1)	III	14.60	28.59	2.59	1.34	0.51	0.00	17.76	0.20	34.41	100.00
C1-3 (2)	I	13.66	34.31	3.63	2.35	0.81	0.79	15.07	0.54	28.86	100.02
C1-3 (2)	II	19.99	36.12	1.22	0.94	0.73	0.68	3.09	0.36	36.87	100.00

Sample ID	Shell Site	C	O	F	Na	Mg	Al	P	S	Ca	Weight %
C1-3 (2)	III	9.97	29.15	2.98	1.86	0.69	0.70	16.40	0.45	37.79	99.99
C1-3 (3)	I	10.68	30.51	3.29	2.24	0.80	0.83	16.93	0.59	34.13	100.00
C1-3 (3)	II	22.14	40.71	0.44	0.20	0.03	0.00	2.76	0.22	33.50	100.00
C1-3 (3)	III	8.76	27.68	2.38	1.18	0.10	0.00	16.67	0.22	43.01	100.00
C1-3 (4)	I	19.10	31.58	3.10	2.22	0.39	0.19	16.30	0.17	26.96	100.01
C1-3 (4)	II	20.22	37.40	1.21	0.78	0.36	0.23	3.91	0.26	35.64	100.01
C1-3 (4)	III	8.61	26.83	2.05	1.77	0.16	0.00	20.44	0.52	39.63	100.01
C1-3 (5)	I	12.17	32.33	2.99	1.89	0.28	0.09	15.72	0.32	34.21	100.00
C1-3 (5)	II	16.13	31.46	0.55	0.21	0.06	0.00	3.91	0.19	47.48	99.99
C1-3 (5)	III	15.72	27.99	2.31	1.38	0.67	0.36	17.90	0.80	32.87	100.00
C1-4 (1)	I	14.58	34.25	3.35	2.16	0.80	0.78	13.33	0.60	30.15	100.00
C1-4 (1)	II	22.03	41.08	1.87	1.01	0.45	0.17	4.37	0.13	28.90	100.01
C1-4 (1)	III	21.95	31.80	3.07	2.16	1.59	0.85	14.04	1.09	23.47	100.02
C1-4 (2)	I	14.29	32.68	3.33	2.11	0.39	0.07	15.94	0.25	30.94	100.00
C1-4 (2)	II	20.78	31.99	2.79	1.98	0.78	0.84	10.57	0.51	29.77	100.01
C1-4 (2)	III	13.28	26.93	2.99	2.35	1.01	0.98	18.57	0.77	33.13	100.01
C1-4 (3)	I	20.41	26.18	2.26	1.83	0.22	0.06	16.63	0.00	32.41	100.00
C1-4 (3)	II	18.71	34.01	1.15	0.80	0.36	0.23	5.12	0.18	39.44	100.00
C1-4 (3)	III	16.86	25.64	2.11	0.98	0.24	0.00	16.56	0.46	37.14	99.99
C1-4 (4)	I	9.67	30.59	2.09	1.53	0.31	0.28	18.14	0.44	36.95	100.00
C1-4 (4)	II	20.25	39.73	1.15	0.45	0.00	0.00	5.86	0.16	32.40	100.00
C1-4 (4)	III	14.12	30.67	2.45	1.15	0.87	0.00	17.01	0.08	33.66	100.01
C1-4 (5)	I	17.23	36.17	2.96	1.89	0.80	0.78	10.54	0.49	29.14	100.00
C1-4 (5)	II	20.17	39.85	2.25	1.17	0.40	0.17	6.26	0.15	29.58	100.00
C1-4 (5)	III	43.56	25.37	1.26	0.82	2.13	0.19	11.31	1.70	13.66	100.00
C1-5 (1)	I	12.08	30.21	3.45	2.45	1.05	1.10	17.70	1.11	30.84	99.99
C1-5 (1)	II	10.66	27.37	3.04	2.30	0.97	1.07	18.28	1.09	35.21	99.99
C1-5 (1)	III	15.04	31.29	3.37	2.12	1.54	0.79	16.62	0.71	28.52	100.00
C1-5 (2)	I	10.73	31.88	3.40	2.36	0.81	0.77	16.27	0.65	33.13	100.00
C1-5 (2)	II	13.10	33.35	2.85	1.92	0.69	0.72	12.50	0.40	34.47	100.00
C1-5 (2)	III	12.93	30.93	2.62	1.93	0.74	0.75	14.04	0.58	35.48	100.00
C1-5 (3)	I	28.11	25.41	2.32	1.37	0.25	0.07	13.91	0.28	28.28	100.00
C1-5 (3)	II	9.57	30.20	3.09	2.01	0.71	0.66	17.20	0.54	36.02	100.00
C1-5 (3)	III	11.59	29.59	3.15	1.96	0.89	0.79	17.23	0.52	34.28	100.00
C1-5 (4)	I	11.68	33.21	3.64	2.35	0.80	0.81	16.15	0.56	30.80	100.00
C1-5 (4)	II	18.00	36.63	1.62	0.90	0.23	0.00	7.11	0.00	35.51	100.00
C1-5 (4)	III	12.25	34.52	2.81	1.59	1.09	0.25	17.22	0.46	29.82	100.01
C1-5 (5)	I	11.27	31.79	3.50	2.39	0.87	0.85	17.55	0.71	31.06	99.99

Sample ID	Shell Site	C	O	F	Na	Mg	Al	P	S	Ca	Weight %
C1-5 (5)	II	16.89	35.10	1.92	1.35	0.60	0.65	9.94	0.43	33.12	100.00
C1-5 (5)	III	13.12	31.57	3.82	2.66	1.13	1.13	16.91	1.19	28.47	100.00
Glsur (1)	I	23.60	42.48	0.54	0.21	0.06	0.07	2.23	0.18	30.63	100.00
Glsur (1)	II	22.91	40.24	1.21	0.84	0.47	0.28	2.18	0.12	31.75	100.00
Glsur (1)	III	22.49	38.70	0.62	0.25	0.32	0.00	2.68	0.21	34.72	99.99
Glsur (2)	I	16.99	31.70	0.65	0.38	0.28	0.19	3.02	0.27	46.51	99.99
Glsur (2)	II	21.26	38.08	0.12	0.31	0.17	0.22	2.37	0.28	37.18	99.99
Glsur (2)	III	22.75	28.68	0.58	0.42	0.35	0.12	4.15	0.00	42.95	100.00
Glsur (3)	I	22.28	37.94	1.10	0.78	0.56	0.28	2.25	0.19	34.61	99.99
Glsur (3)	II	21.42	37.25	0.50	0.20	0.04	0.13	2.57	0.15	37.73	99.99
Glsur (3)	III	23.97	40.13	0.50	0.19	0.07	0.10	2.73	0.19	32.11	99.99
Glsur (4)	I	15.57	28.86	0.51	0.41	0.18	0.09	4.19	0.25	49.93	99.99
Glsur (4)	II	18.54	33.64	0.40	0.21	0.09	0.11	3.02	0.27	43.72	100.00
Glsur (4)	III	18.49	33.55	0.73	0.67	0.64	0.22	3.34	0.16	42.18	99.98
Glsur (5)	I	21.95	33.70	1.46	1.18	0.84	0.82	4.48	0.45	35.11	99.99
Glsur (5)	II	21.34	34.49	1.37	0.99	0.77	0.75	3.16	0.43	36.69	99.99
Glsur (5)	III	13.81	22.80	1.43	1.25	0.96	0.65	13.94	0.44	44.72	100.00
Gl-2 (1)	I	20.74	33.75	0.40	0.23	0.09	0.14	3.65	0.23	40.76	99.99
Gl-2 (1)	II	21.10	35.15	0.99	0.62	0.41	0.25	2.79	0.13	38.58	100.02
Gl-2 (1)	III	18.88	33.43	0.31	0.19	0.30	0.00	3.64	0.00	43.25	100.00
Gl-2 (2)	I	23.51	42.06	0.54	0.26	0.07	0.00	2.68	0.10	30.77	99.99
Gl-2 (2)	II	23.70	41.72	1.23	0.73	0.41	0.23	2.02	0.19	29.77	100.00
Gl-2 (2)	III	21.38	37.32	1.02	0.75	0.67	0.18	2.43	0.24	36.00	99.99
Gl-2 (3)	I	21.33	39.24	0.40	0.24	0.12	0.12	2.76	0.23	35.56	100.00
Gl-2 (3)	II	23.02	42.65	0.58	0.25	0.13	0.08	2.14	0.13	31.02	100.00
Gl-2 (3)	III	20.93	35.25	0.96	0.84	0.69	0.22	3.00	0.05	38.06	100.00
Gl-2 (4)	I	23.58	36.51	1.07	0.92	0.32	0.17	3.10	0.06	34.27	100.00
Gl-2 (4)	II	22.20	38.11	0.41	0.26	0.18	0.14	2.45	0.21	36.04	100.00
Gl-2 (4)	III	20.82	36.76	0.66	0.49	0.62	0.07	4.59	0.05	35.95	100.01
Gl-2 (5)	I	19.52	34.95	0.92	0.71	0.42	0.18	3.26	0.27	39.76	99.99
Gl-2 (5)	II	23.10	39.90	1.24	0.84	0.48	0.29	2.37	0.06	31.72	100.00
Gl-2 (5)	III	17.84	32.00	0.66	0.32	0.55	0.00	4.99	0.31	43.35	100.02
G1-3 (1)	I	20.41	36.52	0.39	0.18	0.00	0.05	2.80	0.23	39.42	100.00
G1-3 (1)	II	22.84	38.99	1.40	0.73	0.43	0.27	2.27	0.00	33.08	100.01
G1-3 (1)	III	17.35	33.46	0.90	0.29	0.25	0.05	3.97	0.06	43.67	100.00
Gl-3 (2)	I	22.14	39.30	1.02	0.68	0.36	0.14	2.09	0.19	34.07	99.99
Gl-3 (2)	II	24.44	41.03	0.63	0.28	0.06	0.00	2.68	0.29	30.59	100.00
Gl-3 (2)	III	32.93	34.50	1.29	1.83	0.43	0.53	2.80	0.15	25.54	100.00

Sample ID	Shell Site	C	O	F	Na	Mg	Al	P	S	Ca	Weight %
GI-3 (3)	I	25.80	37.91	2.07	1.27	0.85	0.77	5.11	0.51	25.71	100.00
GI-3 (3)	II	23.66	40.60	1.29	0.73	0.42	0.21	2.43	0.17	30.48	99.99
GI-3 (3)	III	27.90	38.33	1.95	0.94	0.56	0.18	5.15	0.00	24.98	99.99
GI-3 (4)	I	13.77	31.60	1.94	1.04	0.53	0.23	11.14	0.31	39.44	100.00
GI-3 (4)	II	12.51	26.86	0.39	0.27	0.11	0.16	2.62	0.10	56.99	100.01
GI-3 (4)	III	16.10	32.39	0.52	0.36	0.27	0.22	3.72	0.36	46.05	99.99
GI-3 (5)	I	22.31	34.91	1.98	1.19	0.76	0.64	6.56	0.45	31.21	100.01
GI-3 (5)	II	20.22	37.38	0.44	0.29	0.18	0.07	1.88	0.00	39.53	99.99
GI-3 (5)	III	17.29	32.11	1.06	0.38	0.32	0.15	5.74	0.26	42.70	100.01
GI-4 (1)	I	11.04	32.71	3.45	2.14	1.51	0.80	18.51	0.65	29.19	100.00
GI-4 (1)	II	10.21	35.38	2.88	1.26	0.15	0.00	16.79	0.37	32.96	100.00
GI-4 (1)	III	9.16	30.40	2.41	1.37	0.72	0.33	18.53	0.56	36.53	100.01
GI-4 (2)	I	11.46	33.42	4.07	2.22	1.05	0.79	16.54	0.62	29.83	100.00
GI-4 (2)	II	10.40	32.84	4.06	1.86	0.97	0.80	16.81	0.60	31.66	100.00
GI-4 (2)	III	10.03	31.98	3.21	1.65	0.44	0.00	18.09	0.43	34.18	100.01
GI-4 (3)	I	17.32	33.65	4.06	1.75	0.68	0.11	15.34	0.37	26.71	99.99
GI-4 (3)	II	21.36	34.06	3.44	1.36	0.79	0.52	15.54	0.63	22.30	100.00
GI-4 (3)	III	15.32	28.48	2.62	1.20	0.40	0.00	17.91	0.14	33.93	100.00
GI-4 (4)	I	15.06	36.57	4.05	1.84	1.15	0.08	15.20	0.12	25.94	100.01
GI-4 (4)	II	10.75	35.34	3.19	1.42	0.29	0.19	15.92	0.21	32.68	99.99
GI-4 (4)	III	16.64	33.28	3.39	1.72	0.60	0.00	15.43	0.39	28.55	100.00
GI-4 (5)	I	13.60	32.80	2.60	1.35	0.49	0.18	17.20	0.65	31.12	99.99
GI-4 (5)	II	10.08	32.07	2.75	1.20	0.36	0.20	17.59	0.41	35.33	99.99
GI-4 (5)	III	14.61	29.48	3.15	2.14	1.16	0.86	17.97	0.82	29.79	99.98
GI-5 (1)	I	12.96	30.50	2.54	1.16	0.64	0.09	18.95	0.29	32.85	99.98
GI-5 (1)	II	12.41	34.79	4.48	2.07	1.16	0.84	16.71	0.66	26.88	100.00
GI-5 (1)	III	24.85	32.24	3.95	1.82	1.26	0.92	13.55	0.84	20.57	100.00
GI-5 (2)	I	12.61	27.26	2.73	1.71	0.76	0.72	17.99	0.91	35.32	100.01
GI-5 (2)	II	16.01	29.64	2.45	0.93	0.09	0.00	16.69	0.53	33.65	99.99
GI-5 (2)	III	11.40	25.03	2.49	1.44	0.76	0.61	18.96	0.72	38.59	100.00
GI-5 (3)	I	12.52	33.01	3.48	1.59	0.77	0.07	17.29	0.36	30.90	99.99
GI-5 (3)	II	10.51	33.93	3.72	1.60	0.62	0.07	17.53	0.37	31.65	100.00
GI-5 (3)	III	17.06	33.27	2.84	1.09	0.50	0.00	16.23	0.44	28.57	100.00
GI-5 (4)	I	16.57	35.76	2.84	1.51	0.83	0.71	11.20	1.38	29.19	99.99
GI-5 (4)	II	20.02	38.82	0.40	0.20	0.17	0.15	3.08	0.35	36.80	99.99
GI-5 (4)	III	16.51	34.26	2.01	0.82	0.45	0.00	11.17	0.43	34.36	100.01
GI-5 (5)	I	11.71	30.82	2.62	1.37	0.67	0.22	19.03	0.39	33.17	100.00
GI-5 (5)	II	18.67	36.36	0.67	0.20	0.08	0.00	4.51	0.37	39.13	99.99

Sample ID	Shell Site	C	O	F	Na	Mg	Al	P	S	Ca	Weight %
GI-5 (5)	III	10.09	31.01	2.62	1.26	0.56	0.21	17.63	0.37	36.25	100.00
PI1-1 (1)	I	20.45	37.48	0.95	0.64	0.35	0.20	2.58	0.09	37.26	100.00
PI1-1 (1)	II	23.43	37.94	0.95	0.70	0.33	0.21	2.26	0.13	34.05	100.00
PI1-1 (1)	III	22.51	36.23	1.26	0.96	0.71	0.68	2.50	0.41	34.73	99.99
PI1-1 (2)	I	20.83	35.43	0.80	0.69	0.29	0.13	2.45	0.13	39.24	99.99
PI1-1 (2)	II	18.98	34.00	0.73	0.41	0.24	0.18	2.46	0.32	42.66	99.98
PI1-1 (2)	III	20.93	36.61	0.97	0.61	0.37	0.23	2.01	0.22	38.04	99.99
PI1-1 (3)	I	22.62	27.50	0.26	0.11	0.05	0.07	3.82	0.34	45.23	100.00
PI1-1 (3)	II	26.77	40.02	0.61	0.19	0.07	0.00	3.03	0.11	29.19	99.99
PI1-1 (3)	III	22.41	38.36	0.71	0.20	0.25	0.08	3.64	0.10	34.24	99.99
PI1-1 (4)	I	18.28	34.71	0.35	0.19	0.05	0.04	3.05	0.25	43.09	100.01
PI1-1 (4)	II	20.90	38.25	0.47	0.23	0.06	0.12	2.63	0.08	37.26	100.00
PI1-1 (4)	III	19.84	35.36	0.53	0.22	0.09	0.04	3.09	0.18	40.63	99.98
PI1-1 (5)	I	19.34	36.25	0.87	0.59	0.36	0.20	2.67	0.00	39.73	100.01
PI1-1 (5)	II	20.24	34.02	1.06	0.93	0.73	0.76	2.97	0.49	38.79	99.99
PI1-1 (5)	III	18.33	32.09	0.91	0.95	0.65	0.64	3.18	0.40	42.86	100.01
PI1-2 (1)	I	13.19	33.42	3.60	1.60	1.06	0.17	16.87	0.67	29.42	100.00
PI1-2 (1)	II	15.73	41.49	1.11	0.57	4.01	0.23	10.90	0.39	25.58	100.01
PI1-2 (1)	III	12.57	33.58	3.67	1.51	1.49	0.09	17.26	0.62	29.23	100.02
PI1-2 (2)	I	30.55	29.36	3.39	2.65	2.17	2.01	12.51	1.21	16.16	100.01
PI1-2 (2)	II	19.12	32.94	4.15	2.29	1.96	2.14	14.69	0.86	21.84	99.99
PI1-2 (2)	III	21.06	28.05	3.80	2.75	2.01	2.11	15.55	1.40	23.29	100.02
PI1-2 (3)	I	19.71	34.37	0.58	0.18	0.14	0.10	2.90	0.17	41.84	99.99
PI1-2 (3)	II	20.41	33.91	1.53	0.84	0.55	0.34	3.00	0.22	39.20	100.00
PI1-2 (3)	III	21.23	32.31	1.81	1.34	1.04	0.94	3.54	0.41	37.38	100.00
PI1-2 (4)	I	14.16	43.22	1.89	0.86	3.71	0.08	12.86	0.58	22.65	100.01
PI1-2 (4)	II	17.74	37.05	0.91	0.48	0.60	0.10	3.16	0.22	39.73	99.99
PI1-2 (4)	III	29.06	26.12	1.83	1.94	1.54	0.44	13.93	1.01	24.14	100.01
PI1-2 (5)	I	10.28	27.96	2.16	1.11	0.64	0.39	19.12	1.00	37.35	100.01
PI1-2 (5)	II	18.84	32.08	1.68	0.44	0.64	0.09	9.92	0.47	35.84	100.00
PI1-2 (5)	III	10.67	28.54	3.06	1.66	1.48	1.14	18.07	1.01	34.37	100.00
PI1-3 (1)	I	24.53	28.88	2.30	1.28	0.60	0.33	14.83	0.89	26.36	100.00
PI1-3 (1)	II	9.19	26.26	2.15	0.66	0.38	0.00	18.31	0.82	42.22	99.99
PI1-3 (1)	III	21.88	33.09	3.90	2.05	0.98	0.87	13.06	0.57	23.60	100.00
PI1-3 (2)	I	12.97	30.67	3.23	1.28	0.80	0.14	16.35	0.24	34.31	99.99
PI1-3 (2)	II	14.63	33.88	3.90	1.69	1.27	0.84	14.28	0.85	28.66	100.00
PI1-3 (2)	III	14.36	31.96	3.55	1.28	0.91	0.16	16.49	0.38	30.91	100.00
PI1-3 (3)	I	11.19	34.70	3.31	1.06	0.40	0.00	16.79	0.40	32.14	99.99

Sample ID	Shell Site	C	O	F	Na	Mg	Al	P	S	Ca	Weight %
PI1-3 (3)	II	10.01	33.09	3.39	1.26	0.82	0.00	17.73	0.50	33.20	100.00
PI1-3 (3)	III	15.66	31.55	3.71	1.56	1.12	0.74	14.96	0.65	30.05	100.00
PI1-3 (4)	I	9.71	30.46	2.35	1.32	0.68	0.25	17.38	0.59	37.27	100.01
PI1-3 (4)	II	16.31	33.86	2.72	1.47	0.77	0.70	11.15	1.01	32.01	100.00
PI1-3 (4)	III	16.96	32.18	2.59	1.04	0.53	0.00	14.97	0.76	30.97	100.00
PI1-3 (5)	I	6.79	22.09	1.85	0.73	0.57	0.35	18.66	0.63	48.33	100.00
PI1-3 (5)	II	7.27	25.65	2.12	0.82	0.60	0.00	18.20	0.09	45.24	99.99
PI1-3 (5)	III	8.46	23.92	2.46	1.19	0.84	0.57	18.25	0.60	43.71	100.00
PI1-4 (1)	I	13.89	34.30	4.16	1.77	1.37	0.80	15.48	0.81	27.42	100.00
PI1-4 (1)	II	13.43	34.66	4.35	1.79	1.59	0.86	15.97	0.67	26.69	100.01
PI1-4 (1)	III	25.60	29.41	3.34	1.48	1.35	1.15	13.93	0.89	22.84	99.99
PI1-4 (2)	I	11.20	27.32	3.32	1.66	1.27	0.84	18.61	0.98	34.79	99.99
PI1-4 (2)	II	9.64	26.53	3.02	1.56	1.19	0.76	19.16	0.77	37.36	99.99
PI1-4 (2)	III	10.87	29.10	3.46	1.71	1.12	0.78	17.84	0.72	34.40	100.00
PI1-4 (3)	I	10.97	23.67	1.97	1.09	0.96	0.43	20.66	0.74	39.51	100.00
PI1-4 (3)	II	9.56	24.92	2.71	1.24	0.86	0.60	18.06	0.55	41.50	100.00
PI1-4 (3)	III	15.29	25.57	2.73	1.48	1.27	0.64	17.66	0.97	34.39	100.00
PI1-4 (4)	I	9.03	24.51	1.91	1.00	0.46	0.00	20.26	0.07	42.76	100.00
PI1-4 (4)	II	7.14	20.54	1.70	1.14	0.83	0.48	18.97	0.79	48.40	99.99
PI1-4 (4)	III	20.83	32.03	2.01	1.22	1.01	0.72	7.75	0.69	33.72	99.98
PI1-4 (5)	I	9.45	25.16	2.49	1.37	0.83	0.66	18.39	0.61	41.05	100.01
PI1-4 (5)	II	10.26	32.42	2.58	0.93	0.48	0.00	18.61	0.30	34.41	99.99
PI1-4 (5)	III	10.15	26.31	2.67	1.30	0.86	0.69	17.62	0.62	39.77	99.99
PI1-5 (1)	I	10.75	33.98	3.01	1.09	0.46	0.00	16.20	0.37	34.15	100.01
PI1-5 (1)	II	10.14	32.13	2.78	1.26	0.64	0.29	17.83	0.66	34.27	100.00
PI1-5 (1)	III	9.98	31.37	2.99	1.37	0.53	0.00	17.30	0.37	36.08	99.99
PI1-5 (2)	I	12.20	33.45	4.24	1.58	1.26	0.76	16.13	0.66	29.72	100.00
PI1-5 (2)	II	10.60	31.45	3.57	1.36	1.36	0.73	17.82	0.63	32.47	99.99
PI1-5 (2)	III	14.61	29.85	2.45	0.67	0.73	0.21	17.20	0.94	33.34	100.00
PI1-5 (3)	I	15.66	32.94	2.38	1.15	1.53	0.37	15.73	0.46	29.78	100.00
PI1-5 (3)	II	9.87	34.73	0.77	0.35	0.71	0.00	17.50	0.14	35.94	100.01
PI1-5 (3)	III	14.13	33.46	2.35	0.75	2.22	0.00	17.01	0.37	29.72	100.01
PI1-5 (4)	I	28.30	30.71	3.48	1.75	1.63	1.02	12.62	0.84	19.65	100.00
PI1-5 (4)	II	24.76	29.20	3.21	1.64	1.68	1.06	14.38	0.83	23.24	100.00
PI1-5 (4)	III	27.42	29.70	2.68	0.99	0.92	0.45	13.91	0.73	23.20	100.00
PI1-5 (5)	I	8.78	31.16	2.58	1.00	0.17	0.00	17.76	0.33	38.22	100.00
PI1-5 (5)	II	9.90	33.43	3.02	0.87	0.27	0.00	16.41	0.13	35.97	100.00
PI1-5 (5)	III	15.72	34.77	3.39	1.30	0.71	0.36	15.38	0.64	27.72	99.99

Sample ID	Shell Site	C	O	F	Na	Mg	Al	P	S	Ca	Weight %
AC3-1 (1)	I	17.81	32.18	2.81	2.81	1.33	0.73	14.25	1.17	26.91	100.00
AC3-1 (1)	II	18.45	36.45	1.01	0.73	0.36	0.15	3.68	0.28	38.89	100.00
AC3-1 (1)	III	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
AC3-1 (2)	I	17.86	35.31	2.52	2.64	1.56	0.78	13.25	1.53	24.55	100.00
AC3-1 (2)	II	11.06	34.24	1.66	2.33	0.80	0.13	16.37	1.16	32.25	100.00
AC3-1 (2)	III	12.44	33.37	2.56	2.58	0.70	0.00	16.29	0.97	31.09	100.00
AC3-1 (3)	I	11.84	35.46	2.27	2.30	1.10	0.20	17.49	0.96	28.38	100.00
AC3-1 (3)	II	18.57	34.80	0.99	0.99	0.45	0.09	6.55	0.39	37.16	99.99
AC3-1 (3)	III	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
AC3-1(4)	I	25.00	34.83	1.20	1.20	1.09	0.75	3.20	0.56	32.18	100.01
AC3-1(4)	II	19.72	36.64	0.89	0.72	0.35	0.19	2.17	0.08	39.23	99.99
AC3-1(4)	III	21.45	37.83	1.20	1.09	0.74	0.67	2.32	0.42	34.28	100.00
AC3-1 (5)	I	13.50	30.30	1.79	2.04	0.80	0.00	17.72	1.33	32.51	99.99
AC3-1 (5)	II	9.10	29.24	1.78	2.43	1.14	0.64	18.47	1.39	35.82	100.01
AC3-1 (5)	III	12.37	31.86	2.90	2.80	1.29	0.80	16.56	1.15	30.27	100.00
AC3-2 (1)	I	11.72	31.32	1.80	1.88	0.66	0.00	18.27	0.64	33.71	100.00
AC3-2 (1)	II	12.24	32.59	2.91	3.16	1.57	1.08	17.51	1.60	27.34	100.00
AC3-2 (1)	III	17.26	34.21	2.06	2.36	0.53	0.00	16.40	0.36	26.82	100.00
AC3-2 (2)	I	17.87	34.78	2.35	2.10	1.01	0.11	15.81	0.89	25.38	100.30
AC3-2 (2)	II	13.57	29.32	0.91	0.90	0.20	0.00	10.02	0.34	44.75	100.01
AC3-2 (2)	III	28.98	28.82	2.05	2.28	1.64	0.74	11.37	1.14	22.98	100.00
AC3-2 (3)	I	10.59	31.06	2.27	1.90	0.70	0.00	18.37	1.04	34.07	100.00
AC3-2 (3)	II	10.19	30.17	2.07	1.92	0.51	0.00	18.03	1.26	35.84	99.99
AC3-2 (3)	III	14.37	30.60	1.74	2.08	0.54	0.22	17.03	1.34	32.08	100.00
AC3-2 (4)	I	16.97	34.33	0.89	0.96	0.25	0.16	7.70	0.48	38.27	100.01
AC3-2 (4)	II	9.51	28.81	2.45	2.47	1.21	0.65	18.14	0.99	35.75	99.98
AC3-2 (4)	III	14.40	28.49	1.85	1.70	1.35	0.28	17.74	0.87	33.34	100.02
AC3-2 (5)	I	9.65	32.86	1.80	2.03	0.93	0.14	19.07	0.72	32.81	100.01
AC3-2 (5)	II	12.25	31.51	2.79	2.71	1.32	0.84	18.13	1.28	19.18	90.01
AC3-2 (5)	III	15.98	32.26	2.52	2.25	0.66	0.05	16.22	0.40	29.67	100.01
AC3-3 (1)	I	15.55	33.82	3.10	2.40	1.46	0.78	16.52	0.87	25.50	100.00
AC3-3 (1)	II	18.83	34.46	1.53	1.26	0.79	0.70	7.19	0.77	34.48	100.01
AC3-3 (1)	III	15.01	30.48	2.60	2.27	1.47	0.73	17.73	0.87	28.84	100.00
AC3-3 (2)	I	9.40	22.69	1.76	1.94	1.02	0.59	20.81	1.01	40.78	100.00
AC3-3 (2)	II	17.63	35.45	1.33	1.00	0.30	0.12	6.50	0.15	37.52	100.00
AC3-3 (2)	III	21.13	24.48	1.38	1.27	0.73	0.16	15.76	0.76	34.34	100.01
AC3-3 (3)	I	13.19	32.85	1.95	1.71	0.49	0.00	17.47	0.87	31.47	100.00
AC3-3 (3)	II	13.92	27.82	1.94	1.96	1.26	0.70	17.98	1.12	33.29	99.99

Sample ID	Shell Site	C	O	F	Na	Mg	Al	P	S	Ca	Weight %
AC3-3 (3)	III	11.70	30.16	2.05	1.75	0.63	0.00	18.21	0.44	35.06	100.00
AC3-3 (4)	I	16.58	29.70	2.25	2.00	1.35	0.78	15.55	0.92	30.87	100.00
AC3-3 (4)	II	11.27	28.05	1.00	0.92	0.51	0.00	14.26	0.51	43.49	100.01
AC3-3 (4)	III	10.78	28.92	1.44	1.36	0.87	0.00	18.89	0.46	37.28	100.00
AC3-3 (5)	I	22.69	29.25	1.58	1.71	0.83	0.26	15.46	0.61	27.61	100.00
AC3-3 (5)	II	25.43	22.85	1.66	2.08	0.92	0.79	15.36	0.90	30.02	100.01
AC3-3 (5)	III	21.24	20.54	0.63	0.75	0.00	0.00	15.53	0.20	41.12	100.01
PT1-1 (1)	I	20.06	18.63	1.12	0.38	0.24	1.71	16.92	0.94	39.99	99.99
PT1-1 (1)	II	12.57	37.07	4.38	1.38	0.79	2.38	15.80	0.87	24.75	99.99
PT1-1 (1)	III	12.38	37.00	4.50	1.35	0.88	2.48	15.86	0.93	24.62	100.00
PT1-1 (2)	I	10.24	30.92	3.13	1.05	0.64	3.18	18.54	1.30	31.00	100.00
PT1-1 (2)	II	9.82	32.35	3.16	1.11	0.82	2.44	18.29	1.16	30.85	100.00
PT1-1 (2)	III	10.66	34.28	3.01	0.53	0.20	3.03	17.98	0.81	29.51	100.01
PT1-1 (3)	I	16.28	33.59	2.93	1.16	0.21	3.03	16.41	0.94	25.45	100.00
PT1-1 (3)	II	9.65	29.86	2.72	0.99	0.67	2.21	18.91	1.20	33.80	100.01
PT1-1 (3)	III	12.42	35.52	2.99	0.62	0.22	3.16	17.72	1.04	26.30	99.99
PT1-2 (1)	I	10.04	29.09	2.81	1.03	0.64	3.23	20.12	1.16	31.88	100.00
PT1-2 (1)	II	9.43	29.37	2.25	0.39	0.22	2.57	18.98	0.82	35.99	100.02
PT1-2 (1)	III	9.75	29.71	2.31	0.70	0.64	3.25	18.14	0.80	34.70	100.00
PT1-2 (2)	I	13.96	24.77	2.15	0.82	0.55	2.36	18.50	0.78	36.11	100.00
PT1-2 (2)	II	10.01	35.85	3.94	1.06	0.69	1.73	16.83	0.77	29.13	100.01
PT1-2 (2)	III	10.12	33.73	3.28	0.96	0.62	1.90	17.74	0.92	30.73	100.00
PT1-2 (3)	I	8.07	29.62	2.56	0.97	0.65	2.24	19.57	0.79	35.52	99.99
PT1-2 (3)	II	8.10	31.36	2.82	1.07	0.83	2.00	18.62	1.02	34.18	100.00
PT1-2 (3)	III	10.39	35.44	2.88	0.62	0.07	2.10	17.84	0.58	30.09	100.01
PT1-2 (4)	I	17.09	39.30	4.51	1.23	1.00	4.08	13.99	1.03	17.75	99.98
PT1-2 (4)	II	17.51	34.84	2.29	0.55	0.84	5.14	15.37	0.99	22.45	99.98
PT1-2 (4)	III	16.41	38.16	4.31	1.46	1.07	4.10	14.36	0.87	19.26	100.00
PT1-2 (5)	I	13.22	31.91	3.29	0.94	0.76	3.33	17.36	1.18	28.01	100.00
PT1-2 (5)	II	8.63	31.54	3.05	1.01	0.76	1.81	18.91	0.86	33.42	99.99
PT1-2 (5)	III	10.13	33.08	2.98	0.76	0.25	2.54	18.42	0.65	31.19	100.00
M1	I	23.90	41.12	0.19	0.20	0.04	0.00	3.25	0.07	31.22	99.99
M1	II	22.64	39.16	0.15	0.16	0.15	0.00	2.99	0.26	34.50	100.01
M1	III	22.83	29.85	0.19	0.29	0.26	0.10	3.95	0.17	42.37	100.01
M2	I	23.16	34.93	0.16	0.37	0.35	0.08	4.40	0.35	36.20	100.00
M2	II	20.07	36.18	0.11	0.16	0.09	0.07	2.86	0.15	40.30	99.99
M2	III	23.49	34.92	0.15	0.49	0.47	0.15	3.17	0.00	37.15	99.99
M3	I	24.15	41.67	1.27	0.65	0.42	0.17	2.04	0.15	29.48	100.00

Sample ID	Shell Site	C	O	F	Na	Mg	Al	P	S	Ca	Weight %
M3	II	23.22	40.84	1.13	0.67	0.39	0.19	1.85	0.12	31.59	100.00
M3	III	26.18	38.61	0.06	0.20	0.34	0.05	1.90	0.26	32.39	99.99
M4	I	24.14	38.66	0.11	0.17	0.07	0.00	2.80	0.25	33.81	100.01
M4	II	18.90	35.06	0.13	0.24	0.17	0.04	2.62	0.25	42.58	99.99
M4	III	21.24	38.14	0.12	0.32	0.73	0.11	1.74	0.30	37.29	99.99
M5	I	22.48	29.14	0.64	0.42	0.27	0.18	3.24	0.17	43.47	100.01
M5	II	17.18	30.10	0.00	0.00	0.00	0.00	2.30	0.00	50.42	100.00
M5	III	19.67	32.22	0.34	0.17	0.38	0.18	3.66	0.38	43.00	100.00