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Calcium Phosphate Coatings on the Yalour Islands, Antarctica: Formation and Geomorphic Implications

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Abstract

The formation of calcium phosphate rock coating and its influence in geomorphic processes were investigated on the Yalour Islands (Antarctica). amples of coating on the metamorphosed andesitic rock are composed of a ~25 μm-thick, white, shiny, relatively hard layer of hydroxylapatite (Hp) with traces of calcite and quartz. Scanning electron micrographs, X-ray diffractograms, Fourier Transform Infrared (FTIR) spectra, and in situ analysis of the chemical composition of the coatings suggest that the calcium phosphate coating is formed mainly through the decomposition of penguin excrement from nearby penguin rookeries and subsequent precipitation of Hp in micropits on the surface of the rock from solutions containing high amounts of calcium and phosphorus. These coatings undergo abiotic and biotic weathering processes that lead to the accumulation of secondary Hp as "flakes" and infillings in microcracks. The coatings give the dark, metamorphosed andesitic rock a shiny, light-colored surface. The coatings can decrease the permeability and increase the albedo of the rock, thereby limiting moisture infiltration (into the rock) and changing the rock's temperature. Based on theoretical estimates, a change of albedo from 0.2 to 0.3 significantly decreases the radiative heating of the rock during the summer months. These changes to rock properties will influence geomorphic processes such as freeze-thaw, thus affecting rock weathering and hence the evolution of the local landscape.

Introduction

In Antarctica, calcium phosphate minerals are known to accumulate in ornithogenic soils derived from guano of krill-eating penguins (Tatur, 1989; Tatur and Myrcha 1989; Tatur and Kreck, 1990). Apatite, $Ca_5(PO_4)_3(F,Cl,OH)$, is the dominant phosphate mineral identified in these soils as well as in the guano layer. Tatur and Kreck (1990) estimated that apatite content in a leached guano layer ranges from 30 to 60%. Keys and Williams (1981) also reported the crystallization of calcium phosphate on penguin or skua rookeries established on andesitic outcrops. Another calcium phosphate mineral identified in Antarctic soils is brushite, $CaHPO_4 \cdot 2H_2O$ (Tatur and Kreck, 1990). In phosphatized rock zones underlying ornithogenic soils, Tatur and Kreck (1990) identified a number of aluminum phosphate minerals such as leucophosphite, $[K_{0.31}(NH_4)_{1.69}]_{2.0}(Fe_{2.66–3.74}Al_{0.26–1.34})_4(PO_4)_4(F_{0.31}OH_{0.69})_2 \cdot 4H_2O$; minyulite, $KAl_2(F_{0.82}OH_{0.18})(PO_4)_2 \cdot 4H_2O$; taranakite, $[K_{1.4–1.9}(NH_4)_{1.1–1.6}]_3(Fe_{0–0.6}Al_{4.4–5.0})_5(PO_4)_8 \cdot 4H_2O$ and other X-ray amorphous aluminum phosphate phases.

Another important occurrence of phosphate minerals is in surface coatings of rocks. Tatur and Kreck (1990) reported the presence of aluminum phosphate minerals in a white crust on the surface of stones exposed to guano solution in maritime Antarctica. They also observed apatite in association with struvite, $Mg(NH_4)PO_4 \cdot 6H_2O$, as a hard banded crust on the surface of rocks and stones. Surface coatings ("patina", "rock varnish", or "desert varnish") are generally associated with arid regions, although, as Summerfield (1991, p. 136) noted, coatings have also been found in more humid environments. Oberlander (1994) and Dorn (1994) discussed in great depth the origin of such varnish and its use as an environmental indicator for dating or as evidence for climatic change. However, little has been discussed regarding the impact of rock varnish on subsequent geomorphic processes (e.g., weathering); Merrill (1898) is an early exception. Although, Tatur and his coworkers (Tatur, 1989; Tatur and Myrcha 1989; Tatur and Kreck, 1990) have conducted extensive investigation of the mineralogy of surface coatings of phosphate minerals in maritime Antarctica, they did not address the influence of coatings in geomorphic processes and landscape evolution. In studies conducted in Antarctica, Markov et al. (1970), Glasby, et al. (1981), Conca (1984), Conca (1985), Conca and Malin (1986), Conca and Astor (1987), and Winkler (1987) have identified coatings and their possible role in the development of several landforms, notably tafoni. In addition to influencing moisture flow within the rock below coatings, the increase in rock surface hardness may also help protect the rock from abrasion (Allen, 1978; Conca, 1984): desert varnish decreases "the friability of the exterior surface" (Conca, 1985, p. 68). Desert varnish studies from the Antarctic (e.g., Glasby et al., 1981; Johnston et al., 1984; Johnston and Cardile, 1984; Hayashi and Miura, 1989; Ishimaru and Yoshikawa, 1995) indicate that the varnish has a thickness of 0.3 to 1.0 mm with an abrupt junction between the varnish and the host rock; is generally dark brown; and comprises a "poorly-ordered hydrated ferric oxide polymer" (Hayashi and Miura, 1989, p. 78) of evaporative origin, derived from chemical weathering of the substrate rock. In cold environments, these coatings may take thousands of years to form (Weed and Norton, 1991).

Although the coating described in this study has a different composition and origin than the classic desert varnishes described for the Antarctic, the geomorphic implications are thought to be similar. The objective of this paper is to elucidate the origin of the calcium phosphate coating found on the metamorphosed andesite on the Yalour Islands, Antarctica. Specifically, we characterize the mineralogical and chemical composition of the calcium phosphate coating. We also suggest that rock coating can influence the character of reflected solar radiation and emitted long-wave radiation (Fortescue,1980, cited in Dorn, 1998). Moreover, understanding the properties of calcium phosphate minerals in Antarctica has profound implications for the

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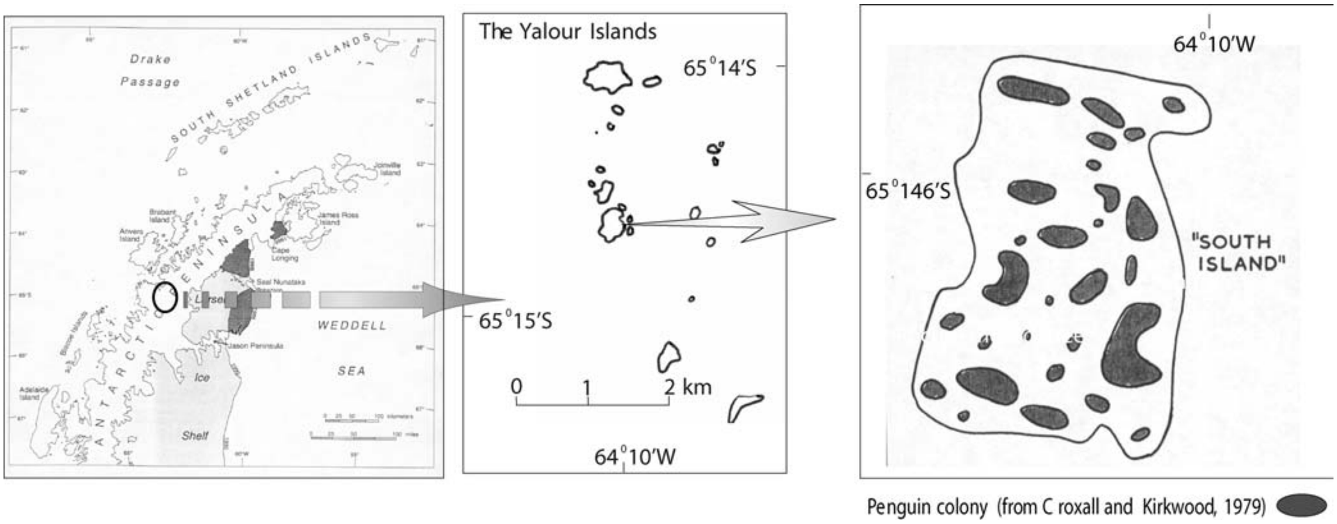


FIGURE 1. Location of the study area.

establishment of vegetation because P is one of the six major elements (the others are N, Ca, Mg, S, and K) needed for plant growth.

Study Area

Rock samples were collected from the Yalour Islands (65°14′S, 64°10′W), a small group of islands and rocks ~2.0 km^2 in an area just west of the Antarctic Peninsula (Fig. 1) on the east side of the Penola Strait (Hattersley-Smith, 1991). The general landscape of the study area is shown in Fig. 2. The sampling was "opportunistic" insofar as it resulted from a landing on these islands for quite different purposes. However, it was immediately apparent to one of the authors (K. H.) that he had never seen coatings like these anywhere else in Antarctica, and so samples were collected. Extensive searching through Antarctic bibliographies, databases and libraries elicited almost no scientific information pertaining to these islands. Charcot (1911) referred to landings on the Jallour Islands (alternate spelling) but made no references to geology or the presence of life; it was noted, though, that the islands were in open water much of the time when other nearby water was still ice covered (Charcot, 1911, pp. 61 and 66). Croxall and Kirkwood (1979) provided three references pertaining to penguin counts, with the value of 10,400 nests (Smith, 1958) being considered a minimum overall estimate. It is noticeable that the colonies of penguins mirror the distribution of well-developed roches moutonnées that occur on the islands. The geological studies of Curtis (1966, Fig. 8) identified the Yalour Islands (as "Jalour Islands") but provided no petrographic information. From geological studies in the surrounding areas (e.g., Elliot, 1964; Curtis, 1966), coupled with the present mineral analysis of the bedrock, it appeared that the Yalour Islands are comprised of metamorphosed andesite.

Gremmen et al. (1994) described the epilithic macrolichen vegetation of this area and showed that in areas with high concentrations of phosphate, communities of *Mastodia-Rinodina* are common; they also noted that these communities are characteristic of sites strongly influenced by animals, such as penguin colonies. Specifically, Gremmen et al. (1994, p. 466) identified *Mastodia-Rinodina* complexes over 100 m inland on the Yalour Islands in the areas influenced by penguins. Patches of the Antarctic grass (*Deschampsia antarctica*) were seen by one of the authors (K. H.) and were also noted by Gremmen et al. (1994). Climatic data from the nearby Argentine Islands (Van Rooy, 1957) indicated a mean annual air temperature of –5.7°C; mean summer (Dec., Jan., Feb.) air temperatures are –0.3°C but with a standard deviation of 2.33. Summer relative humidity values are high, 84–87%, and mean relative sunshine is also fairly high (Van Rooy, 1957). Given that rock temperatures are a product of radiation input rather than air temperatures (Hall, 1997; Hall and André, 2001), the relatively high incidences of radiation indicate that summer rock temperatures will be positive, with values as high as +30°C to be expected.

Methods

SAMPLE COLLECTION

Three types of samples were separated from the rock fragments collected from the Yalour Islands for detailed investigation of their mineralogical and chemical composition. These samples are (1) metamorphosed andesite (the predominant rock type in the study area), (2) the white coating, or veneer of white materials, on the surface of metamorphosed andesite, and (3) flakes or patches of translucent whitish materials adhering to rock cavities with abundant root growth. To minimize contamination from the metamorphosed andesite, samples of white coating used in X-ray diffraction and infrared analyses were separated by a 1.0-mm-diameter microdrill operated at about 10,000 rpm under a dissecting microscope. Samples of flakes were taken by peeling them from the cavities of the rocks under the dissecting microscope, using fine forceps and tweezers.

The mineral composition of the metamorphosed andesite and the white coating was determined using a Rigaku X-ray diffraction system. Samples of flakes were not analyzed using X-ray diffraction primarily because of very small quantities. X-ray diffraction analysis was conducted on a sample that was randomly mounted on a silicon sample holder using acetone. The powder mount was scanned from 3 to 90 °2Θ at ambient condition using Cu K radiation generated at 50 kV and 150 mA. Collection of the diffractogram was done in a step-scan mode of 0.05 °2Θ and at a collection time of 2 s per step. Estimates of the relative amounts of plagioclase feldspars were based on the separation between –132 and 131 and between 111 and 1–11 X-ray reflections as suggested in Huang (1986).

ELECTRON MICROSCOPY AND CHEMICAL ANALYSIS

The submicroscopic surface morphology of rock, coating, and flake samples was examined using a Philips XL30 Scanning Electron

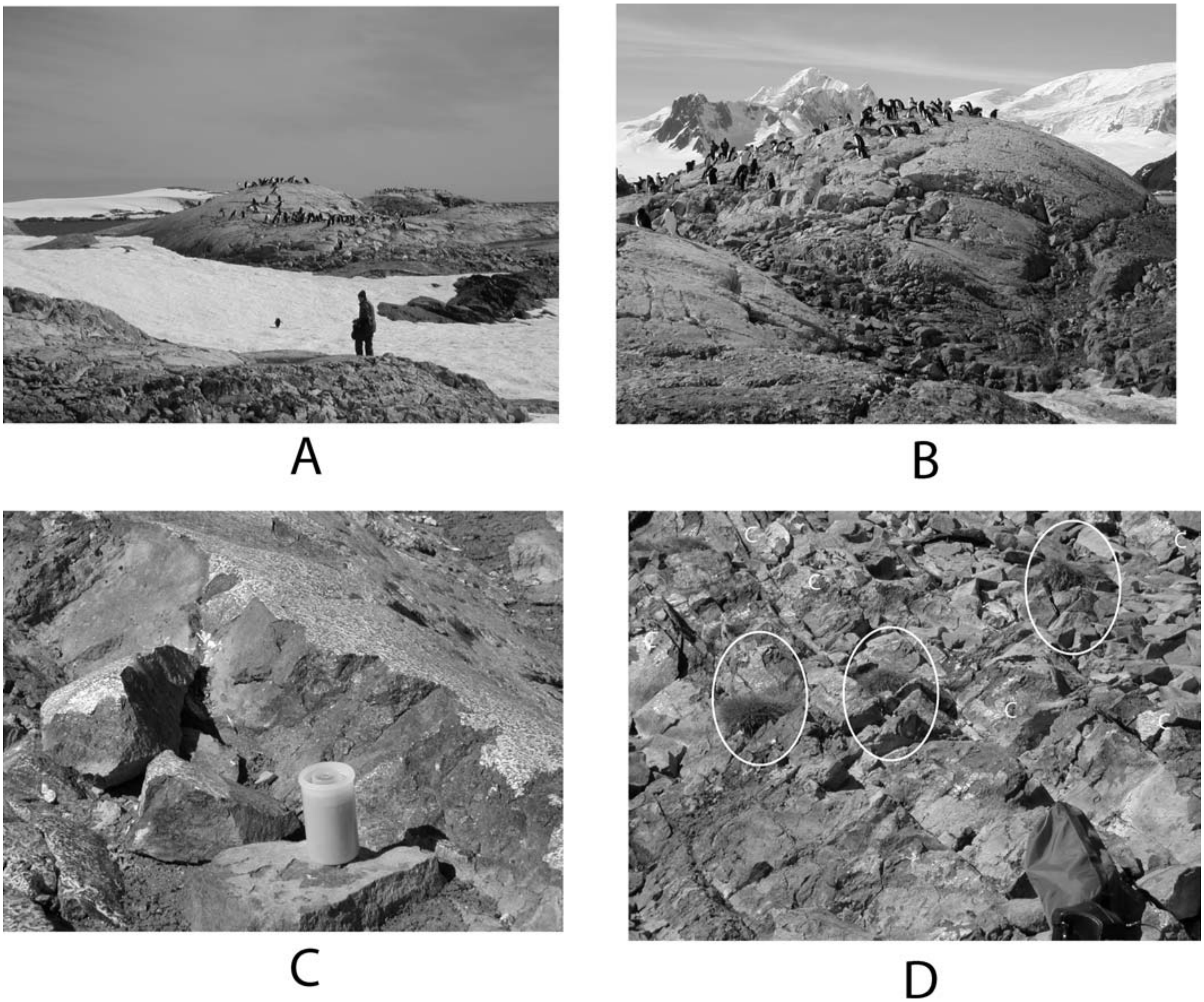


FIGURE 2. (A) General view across South Island showing penguins on roches moutonnées, snow cover, and proximity to the sea. (B) View of the roches moutonnées, with penguins, and the smoothed, coated surface. Note the ice cover on the Antarctic Peninsula just behind the island. (C) Detail of the surface coating (film canister for scale). (D) View across an inter-roches moutonnées area showing patches of the grass Deschampsia antarctica *(in circles) and remnants of coatings on the weathered rocks (shown by the letter "C").*

Microscope equipped with EDAX energy dispersive system (SEM-EDS). Samples of the white coating, andesitic fragments, and flakes were mounted onto an aluminum stub using double-sided tape, then sputter-coated with gold (Au) for 60 s prior to analysis. Once Au-coated, the morphology of the samples was examined under SEM while the semiquantitative chemical composition was determined using standardless EDS technique. The chemical composition was conducted on ten subareas (5–10 μm^2) in each sample. The mean corrected (Z—atomic number, A—absorption, and F—fluorescence factors) elemental composition was determined in an energy dispersive spectrum collected for 200 s from 0 to 20 keV. Due to the near overlap of the Au and phosphorus (P) energy peaks in the SEM-EDS system, analysis of the chemical composition of the white coating was conducted on samples without the Au coating. The spatial distribution of Ca, P, Si, Al, and C in coating, flake, and metamorphosed andesite samples was determined using the X-ray mapping capability of SEM-EDS at a setting of 1024×800 matrix with a collection time of 20 ms.

FOURIER TRANSFORM INFRARED ANALYSIS

Infrared analysis of rock, coating, and flake samples was conducted using Perkin Elmer 200 Fourier Transform Infrared Spectrometer (FTIR). A pellet composed of approximately 1:100 ratio of sample to KBr was prepared by pressing the mixture using a manual press. The KBr pellet was subjected to the IR beam for ~1 min and the interferogram was recorded from 400 to 2000 cm^{-1} wavenumbers. Identification of the molecular group corresponding to major regions of IR absorption bands was based on Kodama (1985).

Results

METAMORPHOSED ANDESITE

Metamorphosed andesitic rocks appear to predominate on the Yalour Islands (Figs. 1 and 2), although, as noted above, no detailed petrographic studies have been undertaken. The mineral composition of the metamorphosed andesite consists of plagioclase feldspars albite

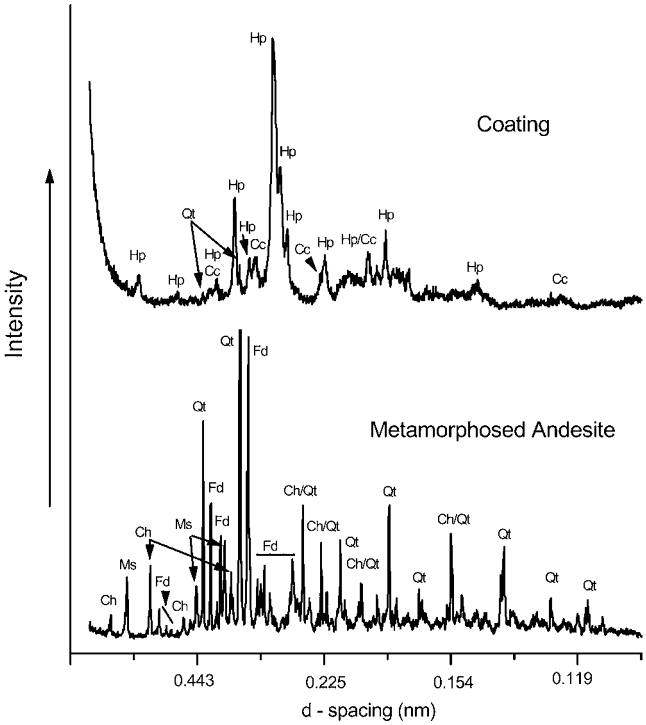


FIGURE 3. X-ray diffractograms of coating and metamorphosed andesite samples. Hp = hydroxylapatite, Qt = quartz, Cc = calcite, Ch = chlorite, Ms = muscovite, Fd = feldspars.

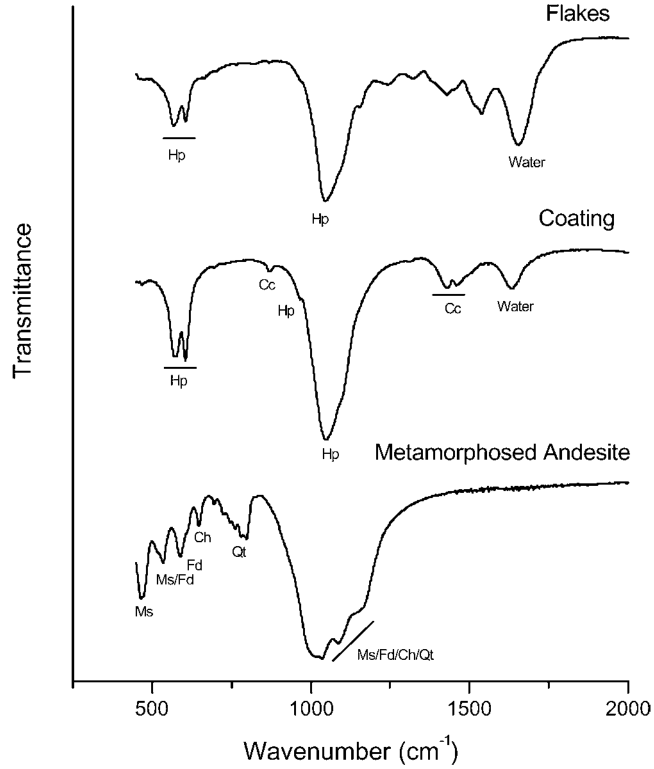


FIGURE 4. Fourier Transform Infrared spectra of flakes, coating, and metamorphosed andesite samples. Hp = hydroxylapatite, Qt = quartz, Cc = calcite, Ch = chlorite, Ms = muscovite, Fd = feldspars.

(Ab), $(Na,K)Al_3SiO_8$, anorthite (An), $CaAl_2SiO_8$, quartz (Qt), SiO_2, muscovite (Ms), $KAl_2(Si_3Al)O_{10}(OH,F)_2$, and chlorite (Ch), $(Mg,Al,Fe)_6(Si,Al)_4O_{10}(OH)_8$ (Figs. 3 and 4; Table 1). Based on the separation of −132 and 131 between 0.267 and 0.285 nm reflections and 111 and 1–11 between 0.375 and 0.385 nm X-ray reflections (Huang, 1986), the calculated ratio of An/(An + Ab) is ~0.20. The higher proportion of Ab to An is also shown by the higher amount of Na compared to Ca (Table 1). The contents of Mg and Fe and X-ray reflections at 0.707, 1.41, 0.354 and 0.252 (Fig. 3) indicate that the chlorite is probably a clinochlore. The presence of X-ray reflections at 1.0 nm and the corresponding d_{002} reflections at 0.5 nm (Fig. 3) show that muscovite is the species of mica present in the metamorphosed andesitic rock. The presence of ~3% P indicates the presence of phosphate-containing minerals in the metamorphosed andesite. Electron micrographs show some dissolution micropits on the surface of uncoated metamorphosed andesite (Fig. 5a, b).

THE WHITE COATING

The roches moutonnées that are covered with white coatings are inhabited by penguins and located close to the sea (Figs. 2a, 2b). Figure 2c shows a detail of the white coating on the surface of the metamorphosed andesite. Patches of *Deschampsia antarctica* are found within weathered bedrock between the roches moutonnées (Fig. 2d). This white (10YR 8/1 d) coating is of varying thickness but is normally ~25 μm thick, is shiny and relatively hard (hardness ~5 on the Moh's scale because it can be scratched by a knife blade), and fills most of the small indentations on the surface of metamorphosed andesite. In some parts of the coating, cracks filled with whitish materials are quite recognizable as well as layers of varying thickness (10 to 50 μm). Remnants of biological activity are also indicated by the presence of fungal hyphae and spores (Fig. 5c, d).

The mineral composition of the white coating on the surface of the metamorphosed andesite is dominated by hydroxylapatite (Hp), $Ca_5(PO_4)_3OH$, with traces of calcite (Cc), $CaCO_3$, and quartz (Qt), (SiO_2) (Figs. 3 and 4; Table 1). Some of the X-ray reflections for Cc are masked by the strong reflections for Hp and designated as Hp/Cc reflections (Fig. 3). The relatively higher intensities of the X-ray reflections for Hp compared to Cc indicate a higher amount of Hp than Cc. Scanning electron micrographs show a smooth and homogeneous morphology that may indicate that Hp and Cc are intimately mixed in the white coating (Fig. 5b). This is also shown by the uniform spatial distribution of Ca, P, and C in the white coating (Fig. 6).

FLAKES

The chemical composition of the flakes is quite similar to that of the coating and is dominated by Ca, P, C, and O (Table 1). The mineral composition is also similar to the coating and consists of Hp, Cc, and traces of Qt (Figs. 4 and 6). Calcite as a discrete entity is shown by adsorption at 870, 1430–1439 cm^{-1} wavenumber (Fig. 4), and the distinct distribution of carbon in the sample (Fig. 6). These flakes contain abundant evidence of biological activity such as plant roots (Fig. 5g), spores, and mycelia (Fig. 5d, f, h).

Discussion

FORMATION OF CALCIUM PHOSPHATE COATING

The formation of calcium phosphate minerals on the Yalour Islands could be attributed mainly to biological activity associated with penguin rookeries. For instance, krill, the main food source for penguins, contains high amounts of Ca and P (Everson, 1987) which are necessary for the formation of hydroxylapatite. The formation of rock phosphate as insular guano was attributed directly or indirectly to bird droppings (Cook, 1983). The abrupt boundary between the metamorphosed andesite and the calcium phosphate coating (Fig. 5b) coupled with the limited weathering (as shown by micropitting) suggests that the crystallization of Hp on the rock surface is primarily the product of external sources and that little or no Hp formation results from rock weathering. The amount of P in metamorphosed andesitic rocks (~3%) is higher than the average crustal content of P (~0.1%) and indicates that the Hp might have penetrated and crystallized in microfractures of the metamorphosed andesitic rock. However, it should be noted that the elemental composition was determined by SEM-EDS with a ±10% uncertainty. The accumulation of calcium phosphate from penguin rookeries has been reported earlier from other parts of the continent, particularly from the maritime Antarctic areas (Tatur, 1989; Tatur and Keck, 1990). The precipitation of Hp on metamorphosed andesite from the breakdown of penguin droppings must have resulted from the favorable environmental conditions, such as sufficient rainfall coupled with evaporation by sun or wind or freezing and thawing, to superconcentrate the contents of Ca and P in guano solutions (Tatur and Keck, 1990), and exceed the solubility product of Hp to crystallize Hp.

The presence of coatings on the roches mouttonnées provides some indirect information pertaining to the age of the coatings. As there are no striations in the coatings themselves, the coatings must postdate glaciation. Because the coating is the product of ornithological attributes (guano), it requires colonization of the area by the penguins. Thus, the development of this coating can only have occurred after penguins came ashore once the ice had gone. The problem is that there are no data on the dates of ice loss for these islands. Nevertheless, recognizing the close proximity of glaciers to the islands, the time period must be on the order of only a few thousand years at the most. The layering within the coating suggests gradual accumulation over time, but the rate of accumulation is all but impossible to calculate because there are no data on the parameters needed, e.g., precipitation, input of seawater, guano production and dispersion, rock temperatures, and evaporation rates. Thus, the best that can be said is that the coating is postglacial and that the formation period was not long (a few thousand years at most); the relative thinness of the coating (<25μm) and the probable time span for its development in the Antarctic (many thousands of years: Weed and Norton, 1991) appear to support this suggestion.

The numerous micropits observed on the rock surface under SEM may have been a weathering source for Cc and Qt found in the white coating. The amount of Ca^{2+} released from the breakdown of anorthite (Ca-feldspars) and the CO_3^{2-} in the environment might have exceeded the solubility product of Cc to crystallize into Cc. Ca^{2+} from the decomposition of guano can also result in the formation of Cc. The Si released from the weathering of feldspars might have resulted in the formation of Qt observed in the coating. However, the absence of detectable crystalline phases of Al in the coating or flakes might indicate that the Al release from the weathering of feldspars might be lost through leaching or might have accumulated in amorphous forms that are not detectable by the methods employed.

DEVELOPMENTAL SEQUENCE

From the information presented in this paper, the stages in the formation of an Hp coating involve the decomposition of penguin droppings and the subsequent precipitation of Hp on metamorphosed andesite. Adequate amounts of water and the presence of organisms combined with optimal temperatures are needed to decompose the penguin guano. As with any other organic matter, the breakdown of penguin excrement leads to the formation of H_2CO_3 resulting from the reaction of water and CO_2 that was liberated from organic matter decomposition (Stevenson, 1994). Carbonic acids might have initiated the formation of the micropits observed on the surface of the metamorphosed andesite (Fig. 5a). These micropits may also have formed by subaerial weathering prior to their being coated, but their formation may still have been a result of organic acids in the penguin guano. Whatever the cause, once pitted, the rock surface will be conducive to the precipitation of Hp because the micropits retain the guano solution containing Ca and P until the solution reaches supersaturation with respect to Hp and hence initiates the crystallization of Hp coating on the surface of the metamorphosed andesite (Fig. 5b). The presence of one of the essential growth elements (i.e., P) on Hp may trigger the growth of organisms such as fungus on the Hp coating, as shown by the presence of hyphae (Fig. 5c) and spores (Fig. 5d) within the coating. Epilithic macrolichen also grow in phosphate-rich environments (Gremmen et al., 1994). The production of organic acids from these organisms can initiate subsequent breakdown of precipitated Hp and the formation of pseudomorphosed hyphae and spores (Fig. 5c, d, f, h).

TABLE 1

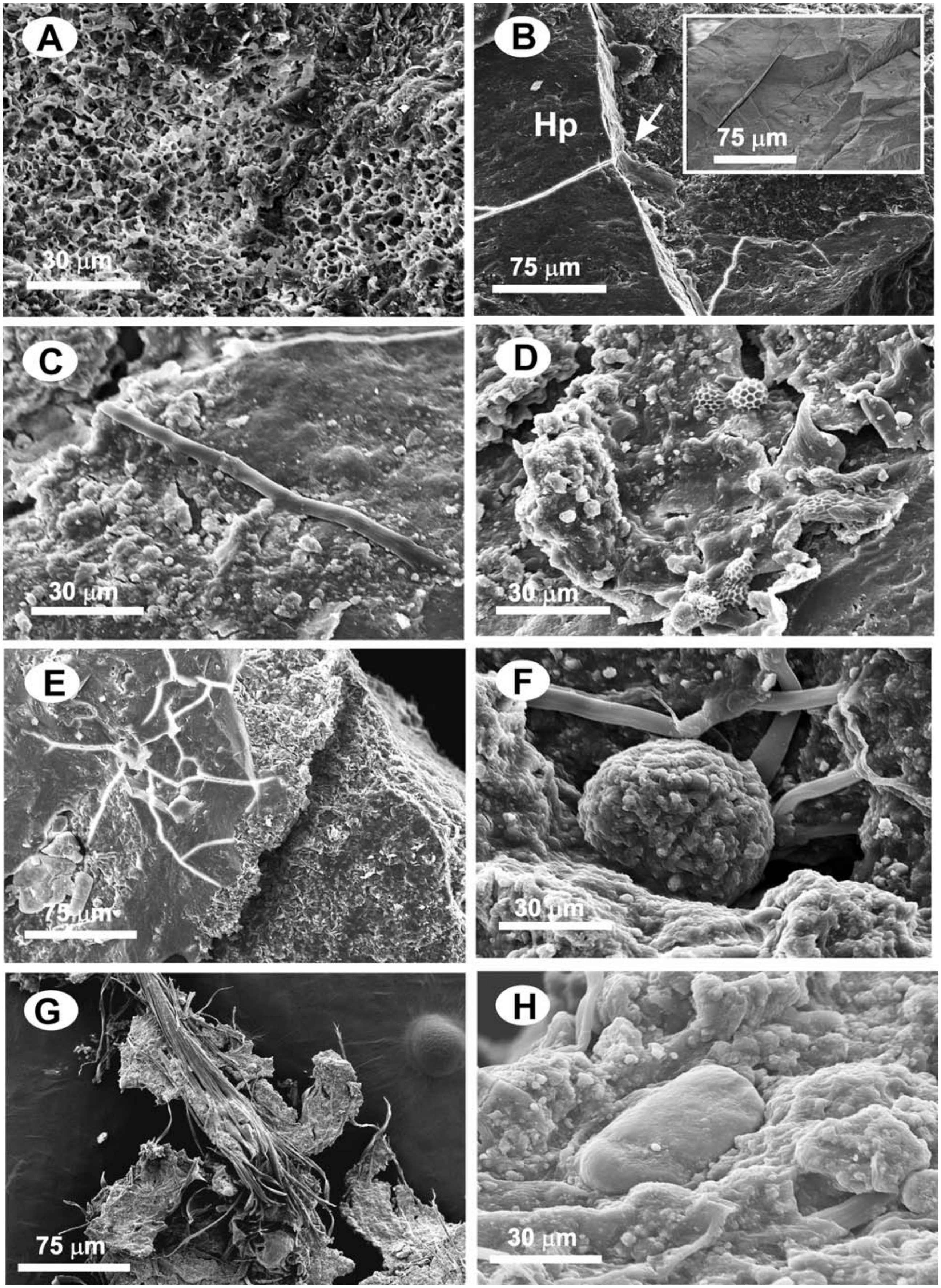
Mean (and standard deviation) of elemental composition (weight %) of coating, flakes and metamorphosed andesite as determined semi-quantitatively using an energy dispersive system. Each value is a mean from 10 measurements.

	Crust	Flakes	Metamorphosed andesite
Carbon	10.0 (2.34)	17.5 (3.60)	8.2 (1.32)
Oxygen	52.6 (8.4)	29.3 (7.43)	45.6 (3.46)
Sodium	2.2 (0.39)	0.64 (0.46)	3.2 (2.0)
Magnesium	1.3 (0.37)	0.74 (0.26)	1.1 (0.30)
Aluminum	0.92 (0.70)	0.60 (0.34)	12.7 (1.01)
Silicon	1.6 (0.73)	2.3 (1.48)	19.6 (1.29)
Phosphorus	13.6 (2.75)	18.8 (1.97)	3.4 (1.32)
Potassium	0.32 (0.18)	0.46 (0.17)	2.4 (0.83)
Calcium	17.0 (6.52)	28.7 (4.31)	0.86 (0.25)
Titanium	0.08 (0.02)	0.33 (0.17)	0.12 (0.05)
Iron	0.42 (0.19)	0.73 (0.34)	2.8 (1.11)

Other weathering processes acting on the Hp coating could be purely abiotic (e.g., thermal stress/shock: Hall and André 2001), as indicated by the cracks in the coatings that are filled up with (secondary) Hp (Fig. 5e); indeed, Aleksandrov and Siminov (1981) noted an association of thermally derived small cracks and desert varnish at the Molodezhnyi Oasis, Antarctica. The product of the weathering processes (biotic and abiotic) acting on Hp coating results in the formation of Hp flakes as well as secondary accumulation of Hp on other parts of the rock surface. Like an Hp coating, Hp flakes are conducive to the growth of organisms, as shown by the vigorous root growth (Fig. 5g). From our results, there seems to be a continuous breakdown and formation of Hp on the Yalour Islands that started with the breakdown of penguin droppings on both former and present-day rookeries and cycled through the accumulation of secondary Hp in cracks and pseudomorphosed hyphae and spores.

IMPLICATIONS FOR GEOMORPHIC PROCESSES

Where it occurs, the presence of the phosphatic coating on the surface of metamorphosed andesite has several geomorphic implications. First, its impervious nature means that the hydraulic conductivity is extremely, if not totally, inhibited. Within this environment the ramifications are that: (a) any potential for chemical weathering is absent; (b) freeze-thaw is inhibited, as are (c) wetting and drying and (d) salt weathering. The formation of this coating thus significantly impacts future weathering, essentially inhibiting any rock weathering processes while, and where, the coating is in place. Second, the coating, while it survives, will help protect the rock from wind or


A
30 μm
B
Hp
75 μm
75 μm
C
30 μm
D
30 μm
E
75 μm
F
30 μm
G
75 μm
H
30 μm

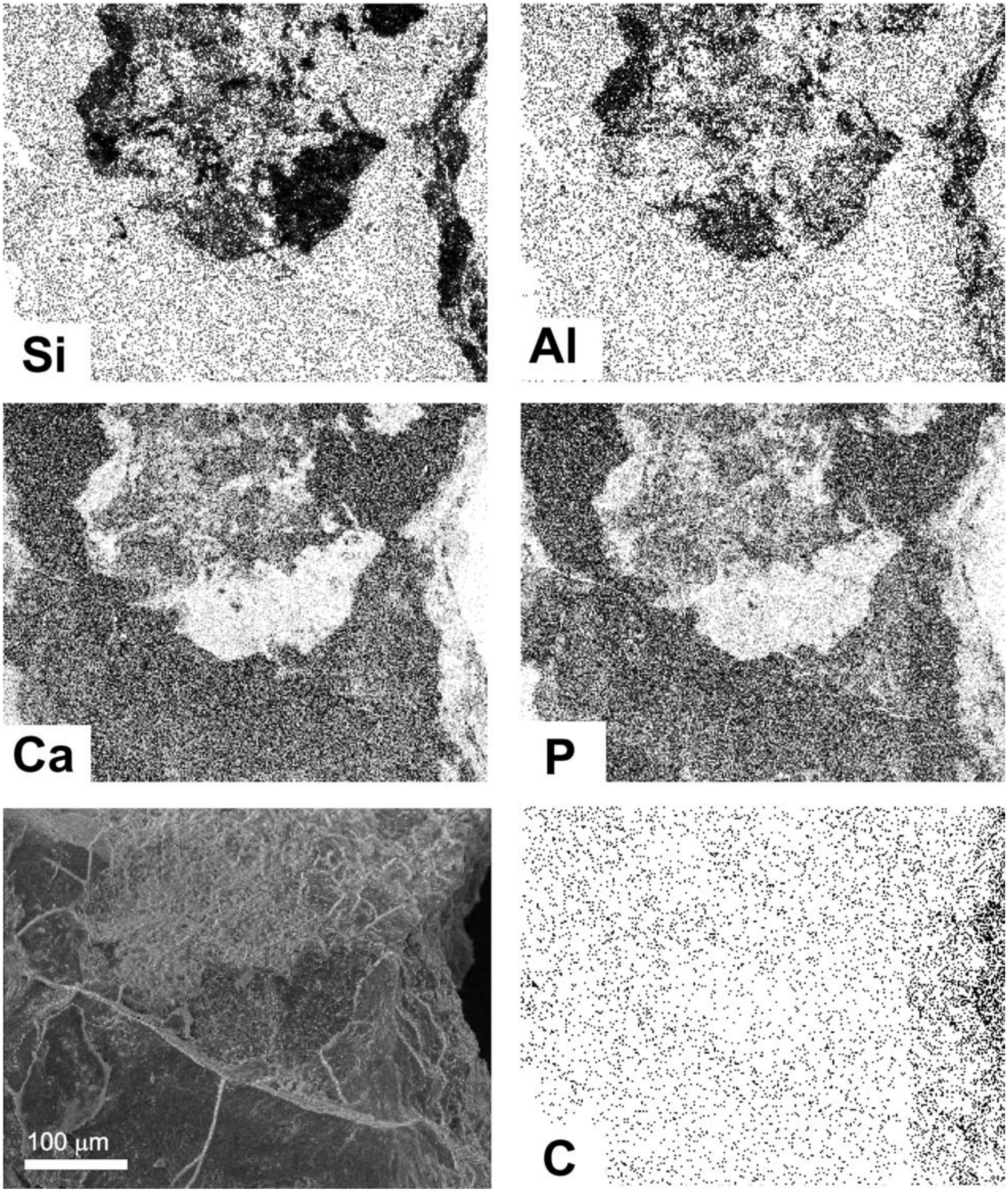


FIGURE 6. Distribution of silicon (Si), aluminum (Al), calcium (Ca), phosphorus (P), and carbon (C) in calcium phosphate coating on andesitic rock of the Yalour Islands (Antarctica).

←

FIGURE 5. Scanning electron micrographs of calcium phosphate coating on andesitic rocks from the Yalour Islands (Antarctica). (A) Micropits on the surface of metamorphosed andesite, (B) sharp boundary between calcium phosphate coating and metamorphosed andesite and layering (inset), (C) and (D) pseudomorphosed fungal hyphae and fungal spores, respectively, (E) cracks on rock coating filled with calcium phosphate, (F) rounded calcium phosphate in flake samples, (G) abundant root growth on flakes, (H) another rounded accumulation of calcium phosphate in flake samples.

TABLE 2

Mean net all-wave radiation balance (W m^{-2}) for the andisitic rock using METEONORM® for bare rock (albedo: 0.2) and rock with coating (albedo: 0.3)

Month	Albedo = 0.2	Albedo = 0.3
January	143	118
February	76	60
March	16	9
April	−11	−13
May	−22	−22
June	−23	−23
July	−21	−21
August	−16	−17
September	1	−5
October	68	52
November	143	117
December	178	149
Year Mean	**44**	**34**

water-driven abrasion. Third, indirectly, the impervious nature of the coating will serve to increase surface-water runoff in the areas where it occurs. This increase may have ramifications for water-regulated redistribution of penguin guano from the rock surfaces, which in turn may influence biological activity.

In addition to the direct impact on weathering processes outlined above, the coating also influences the thermal condition of the rock as a result of changes in albedo (e.g., Warke and Smith, 1998). Waragai (1998), from a study in the Karakoram Mountains, shows, in part, the derivation of a rock varnish as a product of evaporative processes owing to high rock temperatures resulting from radiative input. The very dark metamorphosed andesite is transformed to a shiny, light-colored, high-albedo-surface rock material by the hydroxylapatite coating. The increase in albedo might lower the temperature of the metamorphosed andesite and inhibit thermal expansion of minerals (Mercer, 1963; Dorn, 1998). Indeed, calculations of radiative exchange (using the METEONORM® software) from a change in albedo from 0.2 to 0.3 for a horizontal surface at the Yalour Islands clearly demonstrate that even such a small increase can have a significant impact on radiation budget (Table 2). As rock temperature will be greatly influenced by net all-wave radiation balance, the small increase in albedo may have significant thermal responses. While not affecting the net loss for the winter months (May to August), the change in albedo decreases the radiative heating significantly for the summer months (December = 16% less radiation absorption, January = 17.5%, February = 21%, and March = 44%). Further, the timing of radiative warming is offset at the end of winter as September experiences a net loss and October has 23.5% less absorption for the higher albedo surface. Thus, as Miotke (1982) has noted, the increase in albedo has the potential to exert a significant influence on the thermal regime of the rock; Mercer (1963) observed that while a dark diabase could reach a surface temperature of +20°C, a light-colored rock may only get just above 0°C. However, the decrease in temperatures will not help with processes such as freeze-thaw because the generally impervious nature of the coating prohibits water from being available for any freezing. Conversely, the decrease in extent of thermal variability that the rock experiences from the increased albedo may inhibit weathering by thermal stresses and hence, in comparison to the darker, uncoated local rock, help preserve the coated outcrops.

Paradise (1993) (cited in Dorn, 1998) reported that where rock coatings formed in fractures, these may increase localized water penetration that facilitates frost weathering, thereby leading to rock breakdown and loss of the coating; conversely, Conca (1985) noted that the development of the coating could decrease surface friability. Although no cavernous weathering (taffoni) was present on the Yalour Islands, Conca and Astor (1987) showed how the water flux within a rock is influenced by the distribution of surface coatings to, in their studies, explain the origin of taffoni. From the perspective of the arguments presented here, the key part of the argument by Conca and Astor (1987, p. 152) is that the coating decreases the permeability of the upper surface of the rock. That decrease in permeability then affects surface runoff. Thus, it seems clear that surface coatings can play a role in subsequent geomorphic processes. It was hard to derive an accurate estimate of the extent of the coating on the Yalour Islands, but it was noticeable that the sides and lower parts of the roches moutonnées were all coated; it appeared that coatings were absent mainly in lower (inter-roches moutonnées) areas, which were much more broken and showed development of plants.

Summary and Conclusions

These observations provide new information regarding the properties and formation of calcium phosphate coatings in Antarctica and for the Yalour Islands in particular. The chemistry, mineralogy, and sequential development of the calcium phosphate coating from decomposition of penguin droppings to the precipitation of hydroxylapatite on the surface of metamorphosed andesite are detailed. The data also show that the metamorphosed andesite undergoes weathering and that the breakdown of Ca-feldspars might have contributed Ca ions necessary for the formation of hydroxylapatite, calcite, and possibly quartz. While the chemistry and origin of the coating seem clear, it cannot yet be explained exactly why this phenomenon took place only, from visual appraisal, on the Yalour Islands and nowhere else in this region. This question needs further investigation, both spatial (to determine the extent of coatings in this region) and site specific (i.e., why did it occur here?) to better understand the causative mechanisms. Although the investigation in to the origin of hydroxylapatite coatings seems well developed, implications for geomorphic processes need further study. Basically, the influence of calcium phosphate coatings on geomorphic processes are due to lower temperature resulting from the transformation of dark surface of the rock to high albedo light surface and the decrease in the penetration of water into the rock because of the impervious nature of the coating. It is suggested, particularly as there are significant biological influences (e.g., lichens and fungi) in the weathering of coatings and rock, that rock coatings in the Antarctic need further study.

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