

Phosphate minerals formed by reaction of bird guano with basalt at Cooks Head Rock and Green Island, Otago, New Zealand

C. A. Landis¹ and D. Craw^{1*}

Abstract The seldom-described potassium-bearing phosphate minerals taranakite and leucophosphate occurs as veins, crusts, and alteration pools in jointed basalt of a sea stack and in basaltic breccia of Green Island off the Otago coast. All occurrences are microcrystalline aggregates. Electron microprobe analyses of taranakite reveal compositions very similar to the ideal formula. In contrast, leucophosphate analyses are lower in potassium and richer in titanium and aluminium than previously studied occurrences. Both localities host seabird populations and it is inferred that bird guano supplied both the phosphorus and potassium essential to these minerals. Aluminium, iron, and titanium, on the other hand, are probably derived from the basalt host rock.

Keywords phosphate minerals; taranakite; leucophosphate; soils; guano; Cooks Head Rock; Green Island; Otago

INTRODUCTION

Phosphate deposits abound in the islands of the south-west Pacific where seabirds deposit guano on roosting sites. Large deposits arise where climatic and geological conditions permit accumulation, but in most localities much of the phosphatic guano is washed into the sea by rain or waves. Remnants of guano in these latter sites can be preserved in fractures and depressions in bedrock. There, in the presence of water, the guano can be corrosive and react with the rock to form phosphatic minerals as replacement zones and as crusts at the surface. These alteration zones are termed “Redonda” phosphorites after a well-studied deposit from the Caribbean (Morgan 1915; Hutchinson 1950).

Most phosphatic reaction zones form in tropical or subtropical islands where there is a distinct dry season and limestone substrate (Hutchinson 1950; Stoddart & Scoffin 1983; Dix 1988). In these localities, the principal phosphate minerals are carbonate fluorapatite or Al/Fe³⁺ phosphates (Hutchinson 1950). Phosphate alteration zones are rarer in consistently moist climates, but the potassium phosphate taranakite may form under these conditions. The type locality of taranakite is the Sugarloaf Islands, 1 km offshore from New Plymouth in central western North Island (Fig. 1; Hector & Skey 1866), an area of perennially damp climate with annual precipitation of 1525 mm (McLintock 1966). At this locality, the taranakite occurs in thin veins where it has formed by reaction with the hornblende andesite substrate (Morgan 1928).

¹Department of Geology, University of Otago, P.O. Box 56, Dunedin, New Zealand.

*Author for correspondence: Email: dave.craw@stonebow.otago.ac.nz

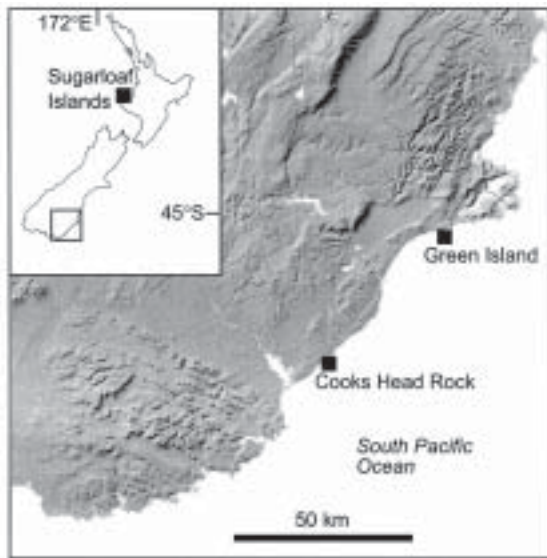


Fig. 1 Digital elevation model of the south-eastern South Island of New Zealand (from www.geographx.co.nz), showing the localities mentioned in this study. Sugarloaf Islands (Taranaki) is the original locality for taranakite.

Potassium phosphate minerals are not common in nature, and their parageneses are poorly understood. Because minerals such as taranakite can form under perennially damp conditions, they are also known from limestone cave sediments (Sakae & Sudo 1975; White 1981). It is possible that they may also be present in soils in which phosphate is an important constituent either artificially or naturally (Bannister & Hutchinson 1947; Haseman et al. 1950; Reed 1965; Kampf 1977). Here we present geological and mineralogical data on occurrences of island potassium phosphate minerals from Cooks Head Rock and Green Island off the east Otago coast. These localities are frequently damp but overall are drier than offshore Taranaki.

Localities

Cooks Head Rock (Fig. 1, 2) is a distinctive 24-m-high promontory in the intertidal zone at the north end of Chrystalls Beach. The rock is alkaline basalt of Miocene age, an outlier of the Dunedin Volcanic Complex (Coombs et al. 1986). It is highly jointed, but is more resistant to erosion than the adjacent weakly metamorphosed Mesozoic metasediments. Phosphatic veins filling fractures were sampled from the upper slopes of the promontory, more than 20 m above sea level (Fig. 2). This phosphatic material is uncommon on Cooks Head Rock, and occurs only in and adjacent to cavities and fractures. Cooks Head Rock is a popular resting place for small numbers of gulls.

Green Island is a small (400 m across) island rising 42 m above sea level approximately 2 km offshore from Dunedin (Fig. 1). The island is an erosional remnant of basaltic pyroclastics from the Miocene Dunedin volcano (Coombs et al. 1986). Phosphatic material occurs mainly as thin coatings on exposed spheroidally weathered tuff and in fractures and cavities within tuff. Most of this phosphatic material is associated with guano from the numerous seabirds which roost and nest on the island. The little blue penguin (*Eudyptula minor*) is particularly common on Green Island and is probably the main contributor to guano associated with the phosphate minerals described here (P. Schweigman pers. comm. 2002). Local phosphatic alteration of tuff has also occurred, with associated phosphatic crusts and veins within the upper 3 cm of the substrate.

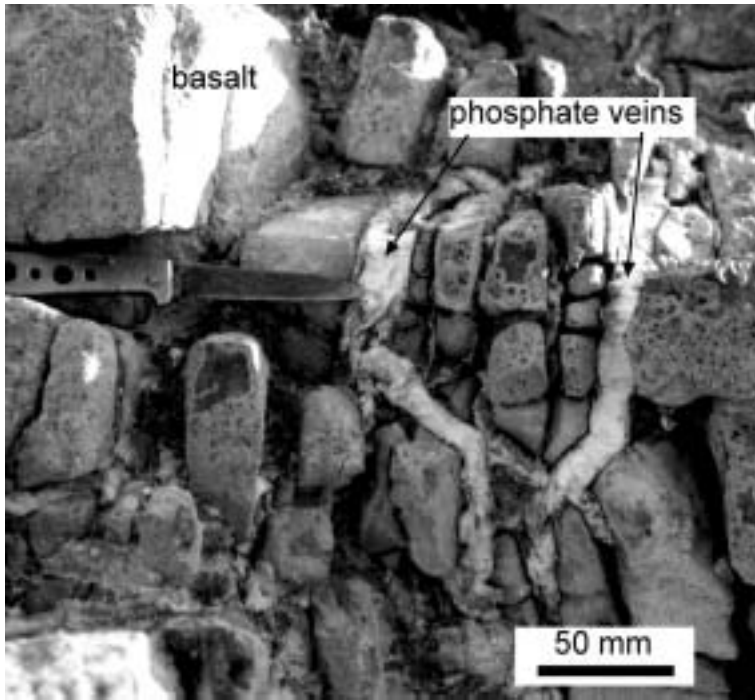


Fig. 2 Veins of taranakite and leucophosphite (white, near knife point) in joints in Cooks Head Rock, a basaltic outlier of the Dunedin Volcano.

Annual precipitation along the Otago coast ranges from 760 to 815 mm (McLintock 1966) and both Cooks Head Rock and Green Island are within the zone receiving sea spray during rough weather.

SAMPLE DESCRIPTION

Cooks Head Rock

Material obtained from Cooks Head Rock consists of phosphatic crust up to 2 cm thick coating phosphate-altered basalt in joints and fractures. Fresh basalt consists of 0.05–0.1 mm equigranular subhedral plagioclase, titaniferous augite, Ti-magnetite, and olivine. Primary minerals are usually unaltered except for minor brown clay coatings on fractures and rims in olivine. A 1–3 cm paler zone of altered basalt occurs adjacent to joints and fractures. Primary minerals and textures are recognisable through much of this altered zone, but olivine is almost wholly altered to brown clays. Irregular pools of cryptocrystalline phosphatic alteration material are distributed throughout these altered zones, locally connected to form a matrix which contains relict primary grains with altered margins (Fig. 3). A distinct 1–10 mm rim to the altered zone consists mainly of cryptocrystalline alteration material with scattered relict primary plagioclase laths. Magnetite, augite, and olivine are absent from this rim.

The phosphatic crust consists principally of microcrystalline taranakite (identification of principal X-ray diffraction peaks and microprobe analysis; Table 1; Fig. 4). Dark spheres (0.01–0.1 mm) of another phosphate mineral, cryptocrystalline leucophosphite, have developed

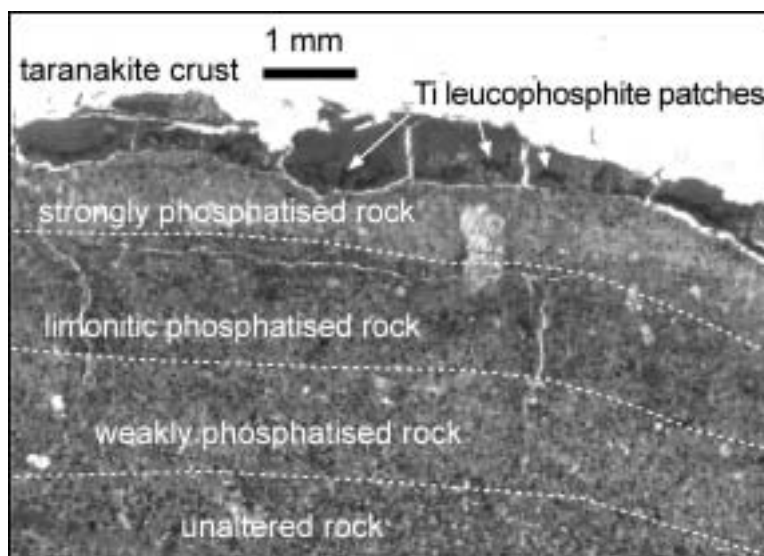
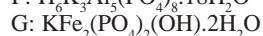
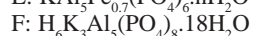
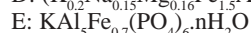
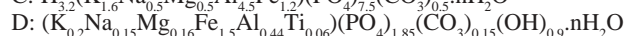
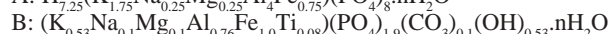
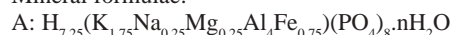


Fig. 3 Thin section image from fresh basalt, through phosphatised basalt to taranakite crust. Sample is from Cooks Head Rock.

Table 1 Microprobe analyses of phosphate minerals, east Otago, compared with taranakite from the original locality. Fe₂O₃ = total Fe as Fe₂O₃. A, taranakite, Cooks Head Rock; B, leucophosphate, Cooks Head Rock; C, taranakite, Green Island; D, leucophosphate, Green Island; E, taranakite, Sugarloaf Islands (Hector & Skey 1866); F, ideal taranakite (Sakae & Sudo 1975); G, ideal leucophosphate.

	A	B	C	D	E	F	G
SiO ₂	0.4	0.0	0.0	0.0			
TiO ₂	0.2	1.7	0.0	1.2			
Al ₂ O ₃	14.2	10.3	17.5	6.4	21.43	18.99	
Fe ₂ O ₃	3.6	21.1	6.9	31.6	4.45		40.6
MnO	0.0	0.0	0.0	0.0			
MgO	0.7	1.4	1.4	1.7			
CaO	0.0	0.0	0.0	0.0	0.55		
Na ₂ O	0.5	0.8	1.1	1.2	trace		
K ₂ O	5.8	6.6	5.6	2.5	4.20	10.53	12.0
P ₂ O ₅	39.4	36.1	40.3	34.5	35.05	42.30	36.0
Cl	0.2	0.0	0.0	0.0	0.46		
H ₂ O					33.06	28.18	11.4

Mineral formulae:



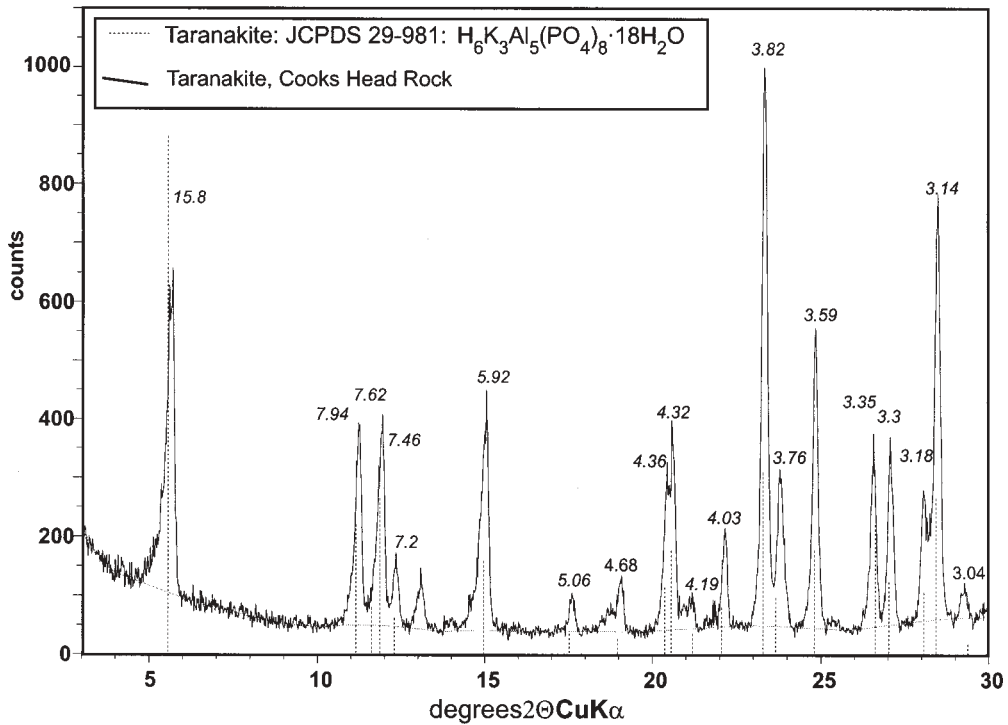


Fig. 4 X-ray diffractogram of taranakite sample from Cooks Head compared with standard.

Table 2 XRF analyses of Cooks Head Rock: phosphatic crust, altered basalt, and fresh basalt. Fe_2O_3 = total Fe as Fe_2O_3 ; LOI, loss on ignition.

	Phosphatic crust alteration zone	Basalt: outer rim of zone	Basalt: inner altered	Basalt: fresh
SiO_2	0.94	23.35	35.04	43.49
TiO_2	0.77	1.99	2.18	3.02
Al_2O_3	19.29	15.46	13.08	14.63
Fe_2O_3	12.47	9.78	8.28	12.90
MnO	0.00	0.00	0.00	0.18
MgO	0.13	0.08	0.13	8.51
CaO	0.01	0.09	0.12	10.21
Na_2O	0.00	0.00	0.58	4.81
K_2O	11.27	7.88	7.06	1.76
P_2O_5	55.59	42.30	33.82	0.45
LOI				0.86
Total	100.47	100.93	100.29	100.82

within the taranakite, locally coalescing into amorphous dark masses (Table 1; Fig. 3). The leucophosphate is too widely dispersed to separate for X-ray diffraction study, but microprobe analyses are definitive.

Boundaries are sharp between the phosphatic rim and altered basalt zone, and between altered and fresh rock (Fig. 3). X-ray fluorescence analyses (Table 2) of phosphatic crust, rim, altered zone, and fresh rock show a 10-fold increase in phosphate content from fresh rock to altered rim. This phosphatic material is concentrated in millimetre-scale alteration pools which tend to become more common towards the margin. However, the distribution of these pools is highly irregular, and a microprobe traverse from fresh rock to taranakite crust which avoided these alteration pools shows that the distribution of phosphate in altered basalt is approximately uniform throughout. Identification of principal X-ray diffraction peaks confirms that taranakite is present within the alteration pools; the presence of other phosphate minerals has not been confirmed.

Green Island

Basaltic tuffs which make up most of this island consist of fragments of a variety of volcanic rock types, dominated by basalt. Basement schist fragments up to 10 cm across also occur. Basaltic clasts are typically fine grained or aphanitic, with flow-aligned feldspar phenocrysts (up to 3 mm). Vesicles are filled with zeolite. Phosphate-altered tuff occurs in the upper few centimetres of some outcrops, with thin phosphatic crusts and veins up to 5 mm wide. Clasts have been partially altered during weathering to clays, but relict feldspars are generally preserved in a matrix of cryptocrystalline clays. These clays are commonly accompanied by phosphatic material in the outer 2–3 cm of the tuffs. Phosphatisation and weathering have occurred together, and phosphatic mineral aggregates are pervaded by limonite. The phosphate mineral is predominantly leucophosphite with minor taranakite. Both minerals are confirmed by X-ray diffraction and microprobe analyses.

MINERAL COMPOSITIONS

Major element composition of taranakite from Cooks Head Rock (Table 1) is similar to ideal stoichiometric taranakite (Bannister & Hutchinson 1947; Sakae & Sudo 1975). Approximately 3.5% Fe₂O₃ is substituted for Al₂O₃, and K₂O₃ is low due to H⁺ and NH₂⁺ substitution (Table 3; Sakae & Sudo 1975). Minor F and Cl (Table 3) presumably replace phosphate ion. The water content calculated from H (Table 3), allowing for ammonium, is only about 29%, but the material analysed contained a small amount of inseparable, and less hydrous, leucophosphite. The water content of low-K taranakite may be as high as 33% (Hector & Skey 1866; Table 1).

Table 3 Volatile element analyses, east Otago phosphatic crusts. C, H, O, and N were analysed by Carlo Erber Analytical Analyser; Cl was determined by oxygen-filled flask method; F was determined with a selective ion electrode. The samples from Cooks Head Rock consist mainly of taranakite with lesser leucophosphite; in the Green Island sample, leucophosphite is predominant over taranakite.

	Cooks Head	Cooks Head	Green Island
C	0.50	0.59	1.14
H	3.20	3.39	2.29
N	0.72	0.63	1.01
Cl		0.2	
F		0.5	
Calculated volatile constituents			
CO ₂	1.8	2.2	4.2
(NH ₄) ₂ O	1.5	1.3	2.0
H ₂ O	27.0	29.1	18.0

Leucophosphite from Cooks Head Rock contains appreciable Al and Ti compared with that predicted from the mineral formula (Table 1; Bannister & Hutchinson 1947). The K content is low, partly due to substitution by hydroxyl associated with Ti substitution for Fe. The volatile content (H_2O , NH_4 , and CO_2) is not determinable directly because of the fine grain size. An estimate of 21–22% volatiles calculated by difference from microprobe analyses (Table 1) is higher than the amount expected from the mineral formula. However, it is reasonable in comparison to leucophosphite analyses obtained from Green Island (see below; Table 3). The small carbon content of bulk material is calculated as carbonate for the leucophosphite which is deficient in P compared with the ideal formula (Table 1).

Phosphatic material from Green Island contains both leucophosphite and taranakite. Leucophosphite dominates in the outer crust on the rock, which was analysed for volatiles (Table 3). Minor taranakite is detectable in X-ray diffractograms but is optically indistinguishable from leucophosphite. Inside the crust, very fine grained leucophosphite and taranakite are intimately mixed, and are discernible only by microprobe. High Fe_2O_3 in taranakite microprobe analyses (Table 1, analysis C) may be partly due to the presence of interstitial very fine grained limonite. Leucophosphite is similar to that from Cooks Head Rock, including the high TiO_2 content. The higher iron content at Green Island may be partly due to the presence of dispersed limonite, as in the taranakite. Volatile contents calculated from microanalysis (Table 3) suggest lower water content than Cooks Head Rock material, which is consistent with the dominance of leucophosphite over taranakite at Green Island. Calculated CO_2 and NH_4 contents for bulk Green Island material are higher than for Cooks Head Rock (Table 3).

DISCUSSION

The most notable feature of these phosphate localities is the presence of the two rare phosphate minerals taranakite and leucophosphite to the exclusion of other phosphate minerals normally found associated with altered guano on limestone islands (e.g., apatite, whitlockite; Rodgers 1989) as well as on granitic (Gregory & Rodgers 1989) and andesitic (McConnell 1943) islands. Further, these phosphate minerals are both K-rich, whereas the host rock is K-poor, so substrate composition is unlikely to be the cause of their precipitation. Similarly, Hutchinson (1950) reported leucophosphite formation on serpentine with negligible K content. The most likely explanation for the occurrence of these potassic phosphate minerals lies in their lower solubility (than many phosphate minerals) which allows preservation in a damp climate. Haseman et al. (1950, 1951) suggested that K-Al-Fe phosphates such as taranakite and leucophosphite may form in damp soils; see also discussion in Reed (1965). Although taranakite and leucophosphite have not yet been documented from soils, the east Otago occurrences provide further evidence that phosphate could be fixed in soils in these minerals.

The mechanism of concentration of K in these minerals is uncertain. Some solution and replacement of basalt by phosphates has occurred, but there is no evidence for extensive removal of basalt to concentrate the potassium. The geometry of the alteration zones (Fig. 3) suggests that replacement has been on a volume-for-volume basis, whereas derivation of the K from the basalt requires removal of at least 6 times as much basalt as is replaced by phosphate (Table 2). More likely, the K (like the phosphate) is of biological origin, being derived from the original guano. Analyses of seabird guano range from 0.2 to 2% dry weight K_2O (Hutchinson 1950; Fugler 1985; Cullen 1988). Most island phosphate deposits contain little or no K, presumably because of rapid leaching (Aston 1909; Hutchinson 1950). However, if the K is fixed in insoluble minerals, it can be preserved. All the east Otago phosphate minerals are deficient in K compared with ideal formulae (Table 1). These minerals may act as local K absorbers, with progressive replacement of H by K in the

structure as guano is continually leached and the resultant solutions percolate through the substrate. Alternatively, K (and Na) may have been derived from ocean salt spray. Chemical analyses (Table 2) suggest that silica may also be present as an alteration product, but petrographic study has not revealed opal, quartz, or any other siliceous phase.

Study of phosphate minerals within Italian cave sediments (Fiore & Laviano 1991) interprets taranakite layers to have formed by reaction of clay minerals with guano-derived phosphatic solutions. A similar origin for some Otago taranakite occurrences is also possible. This would involve initial weathering of the basaltic substrate to form clays followed by reaction with guano-derived phosphatic fluids to form taranakite and leucophosphite. This could explain occurrences within weathered basalt. However, open joints and cavities in the basalt were filled by direct precipitation.

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