

Acid sulphate alteration in a magmatic hydrothermal environment, Barton Peninsula, King George Island, Antarctica

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Abstract

Volcanic-hosted advanced argillic alteration on Barton Peninsula comprises an assemblage of chalcedonic silica, alunite family minerals, pyrophyllite, pyrite, native sulphur, zunyite and rutile, characteristic of an acid sulphate-type epithermal system. The minerals minamiite, $(\text{Na}_{0.36}\text{Ca}_{0.27}\text{K}_{0.1}\square_{0.27})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$, and zunyite, $\text{Al}_3\text{Si}_5\text{O}_{20}(\text{OH},\text{F})_{18}\text{Cl}$, are reported at this locality, and in Antarctica, for the first time. The WNW-striking, 1 km-long zone of alteration is hosted by early Tertiary andesitic rocks and contained in a 1.5 km-wide depression, rimmed by an arcuate ridge, probably representing a volcanic crater or small caldera structure.

Stability relations of minerals in the advanced argillic alteration zone indicate alteration took place under acidic conditions in the near-surface environment. Mineralogical and textural evidence also suggest alteration occurred in a magmatic hydrothermal system, possibly with a magmatic steam component, rather than in a superepithermal or steam-heated environment.

KEYWORDS: volcanic-hosted argillic alteration, acid sulphate-type epithermal system, Antarctica.

Introduction

VOLCANIC- and plutonic-related hydrothermal processes are an integral part of subduction and arc magmatism. As the site of subduction of proto-Pacific and Pacific oceanic lithosphere beneath the Antarctic plate for most of the Mesozoic and Cenozoic (Thomson *et al.*, 1983; Storey and Garrett, 1985), the Antarctic Peninsula offers excellent opportunities for the study of hydrothermal processes in a relatively simple subduction setting. Analogous areas, such as the South American Andes, host numerous, well-documented, hydrothermally altered and mineralised volcano-plutonic rocks (e.g. Sillitoe, 1991) so it is important to evaluate to what extent these processes have affected similar rocks within the Antarctic Peninsula.

Barton Peninsula, in the Mesozoic–Cenozoic arc-setting of King George Island, South Shetland

Islands, comprises a sequence of early Tertiary lavas and volcanoclastic rocks, intruded by a small granodiorite to quartz-diorite stock. This area was chosen for study on the basis of previous reports of 'quartz–pyrite lodes' and hydrothermal alteration (Ferguson, 1921; Barton, 1965; Littlefair, 1978*a,b*; Cox *et al.*, 1980; Davies, 1982). Detailed field work by the author confirmed the presence of extensive areas of hydrothermal alteration in the volcanic sequence on Barton Peninsula. In particular, advanced argillic alteration NE of the pluton proved to be far more intense than previous reports suggested. Geological and mineralogical evidence presented in this study indicate that the alteration is a volcanic-hosted epithermal system of acid sulphate type and the first documented on the Antarctic continent.

Recognition that some acid sulphate systems represent the upper expression of underlying magmatic hydrothermal systems centred on shallow intrusive stocks (Sillitoe, 1973; Sillitoe and Bonham, 1984; Bove *et al.*, 1990), coupled with their links to

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mineralization processes, has stimulated world-wide research interest in this alteration type. Acid sulphate alteration results from extreme base-leaching by very low-pH fluids (Hemley and Jones, 1964; Meyer and Hemley, 1967; Hemley *et al.*, 1969; Knight, 1977). These acid fluids can be produced by different mechanisms in supergene, steam-heated and magmatic hydrothermal environments (Rye *et al.*, 1992); hence, discrimination of the environment of formation of a particular acid sulphate system requires careful consideration of its geological, mineralogical, geochemical and isotopic characteristics.

This paper describes the geological and mineralogical attributes of the alteration on Barton Peninsula, with special emphasis on alunite mineral chemistry, and suggests a possible geological setting and genetic model for the acid sulphate system.

General geology

Barton Peninsula (centred on latitude 62°14'S, longitude 58°44'W) is on the SW side of King George Island, the largest of the South Shetland Islands. The South Shetland Islands are a 550 km-long, NE-trending archipelago, separated from the northern tip of the Antarctic Peninsula by Bransfield Strait (Fig. 1). The islands are part of the Antarctic Peninsula magmatic arc, formed as a result of essentially continuous easterly subduction of proto-Pacific and Pacific oceanic lithosphere beneath the Antarctic plate during the Mesozoic and Cenozoic (Thomson *et al.*, 1983; Storey and Garrett, 1985).

Calc-alkaline magmatic arc rocks forming King George Island are mainly Upper Cretaceous to Lower Miocene subaerial volcanic and volcanoclastic rocks, commonly containing terrestrial plant fossils, and intruded by hypabyssal dykes, plugs and small plutons (Birkenmajer *et al.*, 1991). Fossiliferous marine and glaciomarine sedimentary rocks are more abundant in Oligocene–Lower Miocene units (Birkenmajer *et al.*, 1991). Quaternary alkaline volcanic rocks crop out along the SE side of the island.

The volcanic succession on Barton Peninsula is divided into two units separated by an angular unconformity (Davies, 1982). The lower volcanic unit crops out mainly in the S and W coastal section (Fig. 1) and comprises a mixture of green and purple lapilli tuffs and tuff breccias, with some thin layers of fine-grained ash tuff and minor intercalated andesite flows. A mudstone-siltstone unit on the SW side of the peninsula contains plant fossils of early Tertiary age (Del Valle *et al.*, 1984; Tokarski *et al.*, 1987).

The upper volcanic unit crops out over large parts of the peninsula, including all areas of high elevation (Fig. 1). The unit is dominated by a sequence of

subhorizontal lava flows with subordinate, intercalated lapilli tuffs. Rocks are mainly dark green, fine-grained, commonly plagioclase- and pyroxene-phyric, porphyritic, andesite volcanic flows. Individual lava flows are up to 80 m thick and form prominent topographic steps, especially on hill tops.

A small intrusive stock is exposed on the NW flank of Noel Hill (Fig. 1). It is approximately 1 km long in a NW–SE direction, 0.8 km across at its widest point, and is exposed from sea level to an altitude of approximately 250 m. Most of the stock consists of homogeneous, pinkish-grey, medium- to coarse-grained, equigranular granodiorite. However, in places the percentage of mafic minerals increases and the rock is grey, medium-grained, equigranular quartz-diorite. The pluton is mostly fresh and unaltered, although it is cut by pinkish-white, streaky, felsic segregations, aplite veins and minor mm-scale quartz veins at a few localities. Contacts with the volcanic country rocks are exposed on the SW and SE sides of the pluton and are intrusive. In the immediate vicinity of the pluton, mafic volcanic flows are dark grey, fine-grained, hornfelsed, silicified and propylitically altered, with disseminated and mm-scale veinlets and stringers of sulphide minerals.

Geochronological control — summary of previous and new data

A Tertiary age for volcanic rocks on Barton Peninsula was first suggested on the basis of petrographic similarity to rocks of known age elsewhere on King George Island (Davies, 1982). In addition, Tertiary flora have been unequivocally identified from the fossil plant locality on the SW side of the peninsula (Del Valle *et al.*, 1984; Tokarski *et al.*, 1987).

In this study, andesitic lavas from the upper volcanic unit on Barton Peninsula were dated at 40.0 ± 1.3 to 45.3 ± 1.4 Ma using conventional K–Ar whole rock methods (Table 1), confirming an early Tertiary age for the volcanism.

The Noel Hill pluton has yielded radiometric ages between 42 and 55 Ma for the central granodiorite phase and 60 to 63 Ma for the marginal quartz-diorite phase (Grikurov *et al.*, 1970; Watts, 1982; Birkenmajer *et al.*, 1983; Smellie *et al.*, 1984; Park, 1989). On the basis of petrographic and geochemical similarities, Davies (1982) suggested that, although the pluton intrudes the volcanic rocks, they are broadly coeval and comagmatic; a conclusion supported by Smellie *et al.* (1984).

It is thus concluded that volcanic and plutonic rocks on Barton Peninsula are of early Tertiary age and discrepancies in the radiometric ages of the Noel

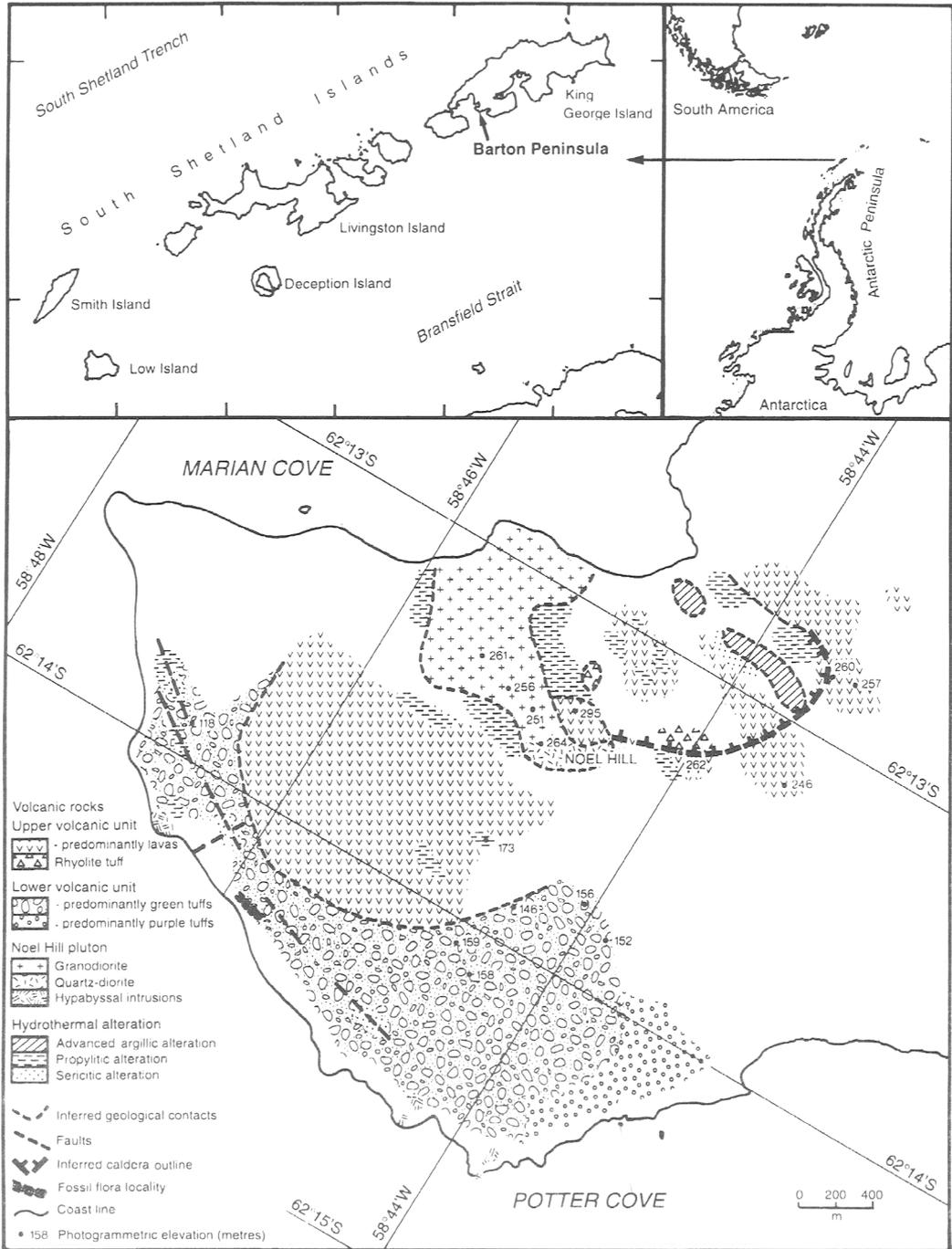


FIG. 1. Location and geology of Barton Peninsula, King George Island, Antarctica.

TABLE 1. New whole rock K-Ar data for Barton Peninsula volcanic rocks

Sample number	Rock type	%K	Atm. ⁴⁰ Ar (nl)	Atm. ⁴⁰ Ar (%)	Vol. rad. ⁴⁰ Ar (nl/g)	Age (Ma)
P.2111.1	Andesite	0.936	1.55	32.72 ± 1.03%	1.5946 ± 1.12%	43.3 ± 1.3
P.2111.2	Andesite	0.929	2.12	43.31 ± 1.01%	1.4599 ± 1.27%	40.0 ± 1.3
P.2111.2	Andesite	0.929	1.37	30.61 ± 1.01%	1.5098 ± 1.09%	41.3 ± 1.2
P.2101.1	Andesite	1.288	3.54	43.15 ± 1.01%	2.2961 ± 1.26%	45.3 ± 1.4
P.2101.2	Andesite	1.197	2.83	41.69 ± 1.00%	1.9529 ± 1.23%	41.5 ± 1.3

All analyses were carried out at the NERC Isotope Geosciences Laboratory, Keyworth, Nottingham. Ar isotopes were determined on a MM1200 mass spectrometer and K analyses performed using flame photometry with a lithium internal standard

Hill pluton can be accounted for by the affects of hydrothermal alteration.

Hydrothermal assemblages — previous studies

During the first geological mapping on Barton Peninsula, Ferguson (1921) noted the presence of large 'quartz-pyrite lodes' which he ascribed to metasomatic replacement accompanying intrusion of the nearby diorite. Barton (1965) mapped several quartz-pyrite lodes and breccias in 'shatter zones' close to the pluton and also concluded they were the result of intrusion-related metasomatism. Littlefair (1978*a*) described quartz, alunite, natroalunite, kaolinite, native sulphur, pyrite and pyrophyllite as the most prominent constituents of the assemblage, along with minor gypsum, barite and diaspore. He suggested this advanced argillic alteration could be the result of low-temperature, volcanic-related, epithermal-solfataric processes (Littlefair, 1978*a,b*). In contrast, Cox (1981) concluded the fluids responsible had a magmatic origin and resulted from devolatilization of the adjacent intrusive body during crystallisation. Most recently, Park (1991) concluded that the advanced argillic alteration was the result of high-level, volcanic-related hydrothermal processes of acid sulphate type.

Hydrothermal assemblages — field relations and mineralogy

Three main areas of alteration are delineated on Barton Peninsula. Their distribution, field relations and alteration mineralogy are described in detail below.

Sericitic alteration, W Barton Peninsula. Sericitic alteration occurs in a NW-striking fault zone cutting the lower volcanic sequence on the W side of the peninsula (Fig. 1). The fault zone has a strike length of 1.5 km and contains patches of intense sericitic

alteration in a broad outer envelope of iron oxide-staining and propylitic alteration. Within the alteration zone some primary volcanic textures are preserved and original rocks were mainly tuffs typical of the lower volcanic unit.

The sericitic alteration assemblage is dominated by chalcedonic silica and fine-grained muscovite (sericite), with lesser quantities of pyrite, epidote, chlorite, carbonate and rutile. Traces of pyrrhotite, chalcopryrite, bornite and hematite occur associated with the pyrite. In some specimens relict clasts are replaced almost entirely by chalcedonic silica, whereas sericite dominates in the tuff matrix.

In places small, mm-wide, usually monomineralic, quartz veins transect the altered rocks. These are commonly drusy in nature suggesting open-space filling.

Propylitic alteration adjacent to the Noel Hill stock. Volcanic rocks surrounding the Noel Hill intrusive stock have undergone contact metamorphism and propylitic alteration (Fig. 1). Precursor rocks were mainly porphyritic andesite flows and altered plagioclase and pyroxene phenocrysts are still evident.

Immediately adjacent to the Noel Hill stock, the volcanic country rocks are hornfelsed, and corundum, indicative of metamorphism of Al-rich rocks, locally constitutes as much as 30% of the rock. Cordierite is also present and magnetite and green hercynite occur as discrete phases. Beyond the immediate environs of the pluton, hornfelsed rocks are propylitically altered and, on the NE side of the pluton, the propylitic alteration grades into a zone of advanced argillic alteration described below.

The propylitically altered rocks are silicified, iron oxide-stained and contain up to 15% sulphide minerals in mm-scale veinlets and disseminations. The alteration assemblage is dominated by a fine-grained, granular groundmass of anhedral quartz and feldspar and feldspar phenocrysts are commonly

altered to sericite, epidote and carbonate. Epidote, chlorite and biotite occur in aggregates preferentially associated with opaque minerals and, in some cases, pseudomorph primary pyroxene phenocrysts. Minor phases include patches of muscovite, sparse blue tourmaline, disseminations of small, brown rutile crystals and minor quantities of apatite.

Opaque minerals occur as disseminations and veinlets. Disseminated opaque minerals are mainly pyrrhotite, pyrite and magnetite. Magnetite contains spinel (hercynite) exsolution lamellae along (111) planes and has associated minor ilmenite. Veins comprise pyrite, pyrrhotite, magnetite and minor chalcopryrite with associated epidote and chlorite, and some have halos of fine-grained sericite.

Advanced argillic alteration, NE Barton Peninsula. Rocks in the largest area of hydrothermal alteration, NE of Noel Hill (Fig. 1), are more intensely altered than previous reports suggested (Littlefair, 1978b; Park, 1991). The alteration is hosted by upper volcanic unit rocks and is a linear, WNW-striking, structurally controlled zone of advanced argillic alteration, approximately 1 km long and 200 m wide, surrounded by a halo of less intense propylitic alteration. The whole area of alteration is contained within a 1.5 km-wide depression, rimmed by an arcuate ridge on the western and southern sides, and cut off on the northern side by Marian Cove (Fig. 1). It is possible that this physiographic feature represents the faulted boundary of a small, volcanic crater or caldera structure.

Advanced argillic alteration is spectacular in the field, and complete textural and mineralogical destruction of precursor lithologies has occurred. Resultant rocks are bleached a pale yellow-pink-light grey colour and have a characteristic porous and vuggy texture (Fig. 2A).

Chalcedonic silica is the dominant component, commonly showing light and dark concentric banding suggestive of replacement fronts (Fig. 2B). Petrographically, most of the silica occurs as fine-grained, anhedral aggregates, many with spherulitic textures indicative of chalcedony. Areas of coarser-grained quartz occur in the rock matrix and lining vugs and vein walls. This coarse-grained quartz contains distinctive, concentric, fluid inclusion-rich zones, within which the inclusions have crystallographically controlled preferred orientations. Perpendicular to the quartz *c*-axis, fluid inclusion-rich zones have euhedral, hexagonal morphologies (Fig. 2C). However, external morphologies of individual quartz crystals are usually anhedral, unless they project into open space, and the fluid inclusion-rich zones can be correlated across grain boundaries (Fig. 2D,E). In addition, areas of 'plumose' quartz also occur in which small, blade-

shaped domains of uniform extinction represent individual quartz crystallites (Fig. 2F). Much of the other quartz has undulose extinction and some crystals contain alunite inclusions.

Alunite family minerals are abundant, both interspersed throughout the rock matrix, and also as cross-cutting, late-stage, monomineralic veins and breccia matrices, cementing monomict, light grey, chalcedonic silica clasts (Fig. 3A,C).

In places fibrous pyrophyllite is abundant, along with scattered crystals of zunyite ($\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH},\text{F})_{18}\text{Cl}$). The presence of zunyite, confirmed by electron probe microanalysis (Table 2), is reported for the first time at this locality, and in Antarctica. In thin section, zunyite occurs as small, euhedral, isotropic crystals with cubic or triangular morphology (Fig. 3E). Some zunyite crystals are fresh and pristine, whereas others are corroded and poikilitic, containing numerous minute inclusions, suggesting formation early in the alteration paragenesis. Pyrite is prominent and also most abundant in pyrophyllite-rich areas. Rutile is scattered throughout as small brown crystals, some with characteristic knee-shaped twinning, and also as skeletal crystals replacing ilmenite. Minor kaolinite and diasporite are also present.

Although relict plagioclase phenocrysts survive, many are pseudomorphed by coarser-grained quartz, alunite family minerals or pyrophyllite (Fig. 3B,D). Vugs and cavities are commonly lined with coarse-grained, euhedral, drusy quartz and may contain large crystals of native sulphur, euhedral pyrite and coarse aggregates of alunite or pyrophyllite.

Chemistry of alunite group minerals in the advanced argillic alteration zone

Introduction and analytical procedure. Alunite group minerals have the general structural formula $\text{AB}_3(\text{XO}_4)_2(\text{OH})_6$; where the A site may be occupied by K^+ , Na^+ , Ca^{2+} , Ba^{2+} , Sr^{2+} , Pb^{2+} , Ag^+ , NH_4^+ , H_3O^+ or Ce^{3+} , the B site is usually Al^{3+} or Fe^{3+} , and the anion $(\text{XO}_4)^{y-}$ may be SO_4^{2-} , PO_4^{3-} or AsO_4^{3-} (Parker, 1962; Wise, 1975; Botinelly, 1976; Scott, 1987; Stoffregen and Alpers, 1987). Substitution of divalent or trivalent cations in the A site is commonly accompanied by a concomitant increase in PO_4^{3-} in the $(\text{XO}_4)^{y-}$ site to maintain neutrality, as in the hinsdalite group (Scott, 1987; Stoffregen and Alpers, 1987), but substitution may also be compensated for by vacancies in the A site as in the Ca-bearing mineral minamiite and the Ca end-member huangite (Ossaka *et al.*, 1982; Li *et al.*, 1992).

Although alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) and natroalunite ($\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$) were reported in the advanced argillic alteration assemblage on Barton

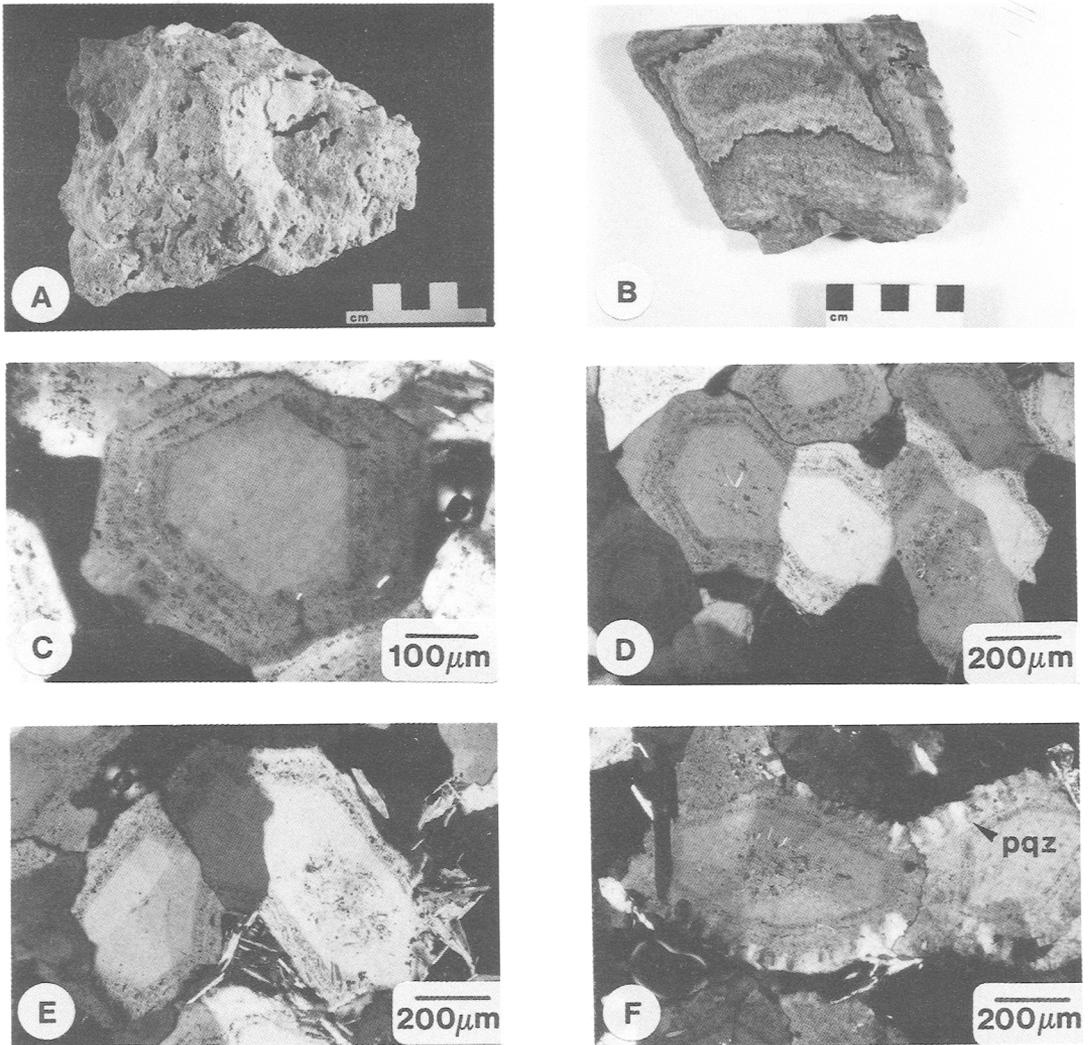


FIG. 2A-F. A. Hand specimen of 'vuggy silica', advanced argillic alteration zone; specimen P.2109.12. B. Hand specimen of chalcedonic silica with light and dark concentric banding, advanced argillic alteration zone; specimen P.2109.7. C. Photomicrograph of quartz crystal, cut perpendicular to c axis, containing euhedral fluid inclusion-rich zones; specimen P.2109.12, transmitted light, crossed polars. D. Photomicrograph of quartz crystals with fluid inclusion-rich zones cutting across grain boundaries; specimen P.2109.12, transmitted light, crossed polars. E. Photomicrograph of quartz crystals with fluid inclusion-rich zones cutting across grain boundaries; specimen P.2109.12, transmitted light, crossed polars. F. Photomicrograph of quartz crystals with plumose textures; pqz = plumose quartz, specimen P.2109.12, transmitted light, crossed polars.

Peninsula (Littlefair, 1978*a,b*), no detailed information on the mineral compositions exists.

Alunite group minerals from the advanced argillic alteration zone were analysed at the Department of Earth Sciences, Cambridge University, using a

Cameca SX50 electron microprobe, with an accelerating voltage of 20 kV and a beam current of 10 μA. Barium, lead and strontium were analysed using a wavelength-dispersive system, and all other elements were analysed using a Link energy-

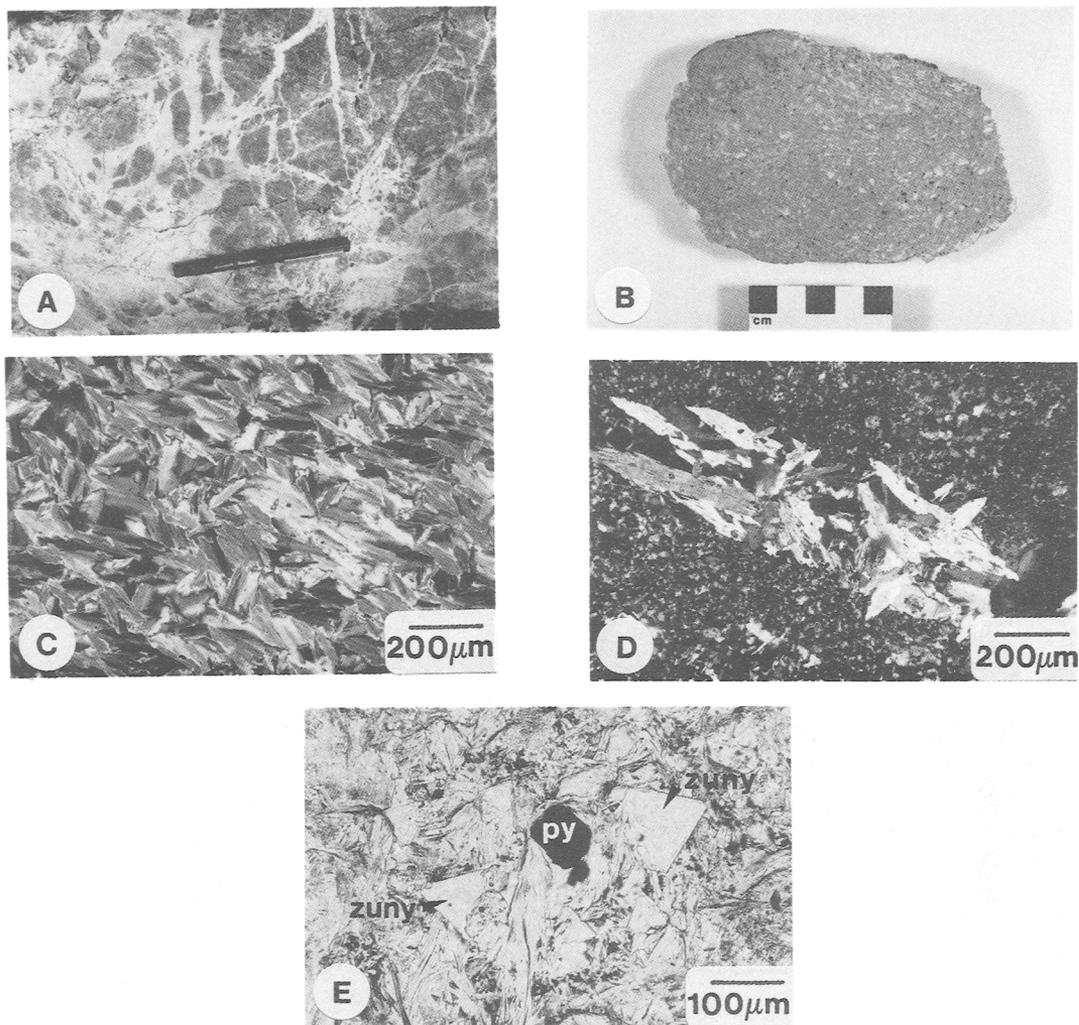


FIG. 3 A-E. A Alunite group mineral veins cementing chalcedonic silica clasts, advanced argillic alteration zone; station P.2110, pen is 13 cm long. B. Hand specimen of andesitic lava containing alunite group minerals pseudomorphing plagioclase phenocrysts, advanced argillic alteration zone; specimen P.2110.10. C. Photomicrograph of alunite group minerals; specimen P.2109.15, transmitted light, crossed polars. D. Photomicrograph of a plagioclase phenocryst replaced by alunite group minerals; specimen P.2109.8, transmitted light, crossed polars. E. Photomicrograph of euhedral zunyite crystals in a fibrous aggregate of pyrophyllite; zuny = zunyite, py = pyrite, specimen P.2110.3, transmitted light, plane polarized.

dispersive system. Alunite group minerals analysed comprised those dispersed throughout the advanced argillically altered rock matrix and those forming cross-cutting monomineralic veins and breccia cements, to determine differences in mineral chemistry which may reflect different origins.

Analytical results. Microprobe analyses confirm the presence of alunite (*sensu stricto*) and natroalu-

nite, but also indicate that significant quantities of Ca, Ba and Sr are present in many alunite group minerals from Barton Peninsula (Table 2). However, the low PO_4 contents and lack of a concurrent increase of PO_4^{3-} with divalent cation content suggests that cation substitution is compensated for by A site vacancies. The Na-dominant, Ca-bearing mineral minamiite (Ossaka *et al.*, 1982), which has A

TABLE 2. Selected representative electron microprobe mineral analyses (in wt.%), advanced argillic alteration zone, Barton Peninsula

Sample Point No.	P.2110.3 36	P.2109.3 159	P.2109.18 131	P.2110.9 117	P.2109.10 178	P.2109.15 12	P.2110.4 221
Mineral	zunyite	alunite	alunite	alunite	alunite	alunite	alunite
Type	—	group matrix	group matrix	group matrix	group vein	group vein	group vein
SiO ₂	23.9	0.2	0.2	0.1	0.1	0.1	0.1
TiO ₂	0.0	0.1	0.0	0.1	0.0	0.0	0.0
Al ₂ O ₃	57.4	39.4	39.2	39.6	39.4	39.2	38.7
FeO	0.1	0.0	0.0	0.0	0.0	0.0	0.0
ZnO	0.0	0.0	0.0	0.0	0.0	0.0	0.1
MnO	0.0	0.0	0.0	0.0	0.0	0.0	0.1
MgO	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaO	0.0	3.3	0.4	2.6	1.6	1.5	1.2
Na ₂ O	0.1	1.5	1.6	2.0	1.5	1.5	1.4
K ₂ O	0.0	1.0	3.9	1.3	2.3	2.2	2.3
SrO	0.0	0.4	0.5	0.0	1.0	1.2	1.8
BaO	0.0	0.7	0.5	0.1	0.8	0.5	1.4
SO ₃	0.1	41.1	40.6	41.2	41.5	40.9	40.5
P ₂ O ₅	0.3	0.5	0.5	0.1	0.2	0.2	0.2
F	5.7	n/a	n/a	n/a	n/a	n/a	n/a
Cl	2.9	n/a	n/a	n/a	n/a	n/a	n/a
Total	87.2	88.2	87.4	87.1	88.4	87.3	87.8

n/a — not analysed

site vacancies, was subsequently confirmed by XRD analysis.

There is considerable variation in the composition of both matrix and vein alunite group minerals, from those containing almost all monovalent cations to those containing almost all divalent cations in the A site. Compositions change over tens of microns within a single crystal and backscattered electron images indicate that different compositional domains commonly occur within individual grains. It is, however, possible to discriminate matrix and vein samples on the basis of their cation compositions, with matrix samples generally having significantly lower Ba and Sr contents, similar to slightly lower K contents, similar to slightly higher Ca contents and significantly higher Na contents relative to vein samples (Table 3, Fig. 4). Barium and strontium values have least scatter and Ca, Na and K contents in matrix samples are more scattered, with higher variances, than those in vein samples (Table 3, Fig. 4).

Variation of cation compositions in the alunite group minerals also reveal several correlations (Fig. 4). Calcium and sodium have marked negative correlations with all the other cations and also with each other. In contrast, K, Ba and Sr all have positive correlations with each other. Generally, correlations

between the cations in matrix alunite group minerals are not as good as those between cations in vein alunite group minerals, although the negative correlation between Ca and Na is more obvious in matrix samples.

Discussion of alunite mineral chemistry. Most acid sulphate systems occur in rhyolitic to dacitic host rocks and usually contain only the potassic and sodic end members of the alunite family (alunite and natroalunite, respectively) (Hayba *et al.*, 1985; Heald *et al.*, 1987). Alunite in these rocks results from *in-situ* leaching and replacement of alkali feldspars (Knight, 1977; Stoffregen, 1987). Barton Peninsula is located in an andesitic terrain and calcic plagioclase is the dominant phenocryst phase in host volcanic rocks. Petrographic study demonstrates that alunite group minerals in the advanced argillic alteration zone replace plagioclase phenocrysts (Fig. 3B,D) and consequently the resultant alunite assemblage is dominated by Ca and Na rather than K. It is interesting to note that the first, and best documented, occurrence of minamiite, at Okumanza, Japan, is also in hydrothermally altered, labradorite-bearing andesite (Ossaka *et al.*, 1982).

The presence of veins and breccia cements consisting entirely of alunite group minerals indicates transport of alunite-forming elements. The signifi-

TABLE 3. Descriptive statistics for cation compositions (in atomic percent) of alunite group minerals, advanced argillic alteration zone, Barton Peninsula

	vein Ca	matrix Ca
Mean	1.9	2.1
Standard Deviation	1.3	2.3
Variance	1.6	5.2
Minimum	0.1	0.0
Maximum	5.8	7.1
	vein Na	matrix Na
Mean	3.4	3.9
Standard Deviation	1.1	1.4
Variance	1.3	2.0
Minimum	0.9	0.9
Maximum	5.7	7.0
	vein K	matrix K
Mean	3.6	3.0
Standard Deviation	1.5	2.0
Variance	2.2	3.9
Minimum	1.0	0.1
Maximum	7.0	8.9
	vein Ba	matrix Ba
Mean	0.5	0.3
Standard Deviation	0.4	0.4
Variance	0.2	0.1
Minimum	0.0	0.0
Maximum	1.7	2.5
	vein Sr	matrix Sr
Mean	0.9	0.3
Standard Deviation	0.6	0.3
Variance	0.4	0.1
Minimum	0.1	0.0
Maximum	2.7	1.0
Number of analyses	103	54

cantly higher amounts of Ba and Sr in vein alunite minerals suggests these elements were derived from an external source and introduced by the hydrothermal fluid. However, as the hydrothermal fluid flushed through the host rock it also scavenged Ca and Na from rock feldspars, explaining why vein alunite minerals have similar to lower contents of Ca and Na compared to matrix ones. The source of the K is not clear but it is likely that it was also scavenged from adjacent wall rocks. The more uniform composition of vein alunite minerals reflects the chemistry of the hydrothermal fluid and availability of cations in solution, whereas greater variation of cation compositions in matrix alunite minerals is

related to greater original compositional variation in precursor feldspars.

The inverse relationship between Ca and Na in all alunite group minerals analysed is due to lattice spacing and cation size. Alunite group minerals with divalent cations in the A site have a superlattice with *c* spacing double that of alunite (*sensu stricto*), due to ordering of the cations and vacancies in the A site (Ossaka *et al.*, 1982; Li *et al.*, 1992). The relatively large K⁺ cation occupies the A(1) site and the relatively small Ca²⁺ cation occupies the A(2) site, but Na⁺ can occupy both sites. It therefore follows that as Ca²⁺ occupancy of the A(2) site increases, the amount of Na⁺ that can be accommodated in the mineral lattice must decrease.

Environment of advanced argillic alteration on Barton Peninsula

The Barton Peninsula advanced argillic alteration assemblage of chalcedonic silica, alunite family minerals, pyrophyllite, pyrite, native sulphur, zunyite and rutile is diagnostic of extreme base-leaching of host rocks by acidic fluids in an acid sulphate-type epithermal system (Hemley and Jones, 1964; Meyer and Hemley, 1967; Hemley *et al.*, 1969; Knight, 1977; Hayba *et al.*, 1985; Heald *et al.*, 1987).

The acid sulphate alteration occurs in a structurally controlled depression probably representing a volcanic crater or small caldera structure located on the summit or flank of an andesitic stratovolcano. The relationship between acid sulphate epithermal systems and calderas is well-documented (Sillitoe and Bonham, 1984; Heald *et al.*, 1987), with the role of caldera faulting being one of ground preparation and development of a permeable plumbing system for incoming hydrothermal fluids (Lipman *et al.*, 1976).

The areas of coarse-grained quartz containing fluid inclusion-rich zones and plumose quartz textures described in this paper (Fig. 2C,D,E,F) are similar to those documented by Sander and Black (1988) for the Rawhide and Round Mountain epithermal systems in Nevada. Previous work suggests these textures are restricted to, and are characteristic of, the epithermal environment (Adams, 1920), and that they are the product of postdepositional recrystallization of a metastable, hydrous, silica phase to quartz (Sander and Black, 1988). The zones represent chalcedony coatings deposited on a hydrothermal quartz substrate, hence reflecting primary deposition, but the fluid inclusions contained within them formed during later recrystallization of the precursor metastable silica phase (Sander and Black, 1988). If quartz textures in the acid sulphate alteration zone on Barton Peninsula are the result of similar processes then the fluid inclusions contained in them are not

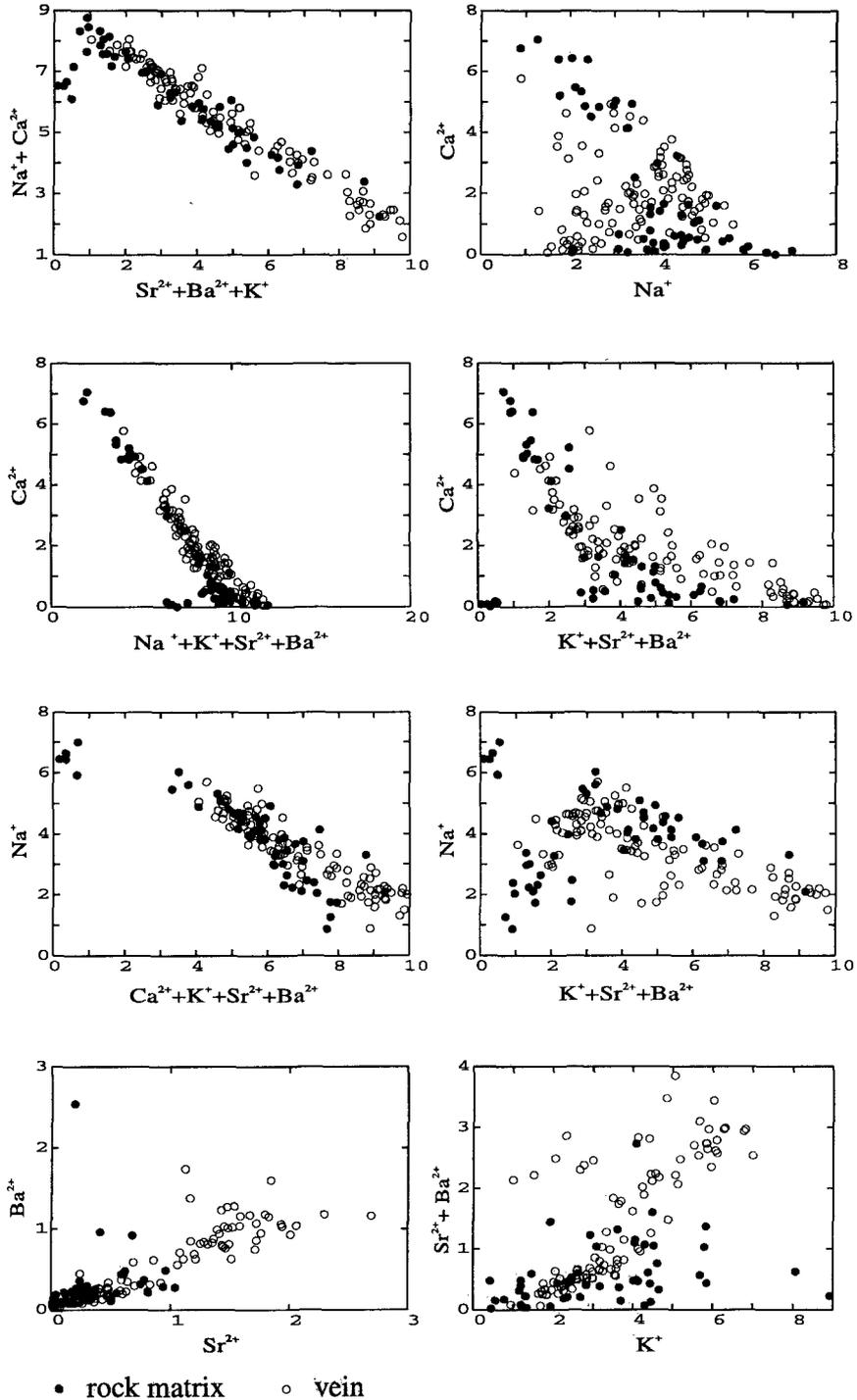


FIG. 4. X-Y scatter plots of cation compositions (in atomic percent) of alunite group minerals in vein and rock matrix samples, advanced argillic alteration zone, Barton Peninsula.

primary and cannot provide reliable microthermometric information about conditions of primary silica deposition. Hence, previous fluid inclusion observations used as evidence of boiling (Park, 1991) are erroneous. If much of the silica was deposited initially as chalcedony, then temperatures of formation were no greater than 200°C (Fournier, 1985) and depths of formation less than 100 m (Hedenquist and Henley, 1985).

Morphological characteristics of some quartz-rich parts of the Barton Peninsula acid sulphate zone are similar to the 'vuggy silica' zone described from Summitville, Colorado (Stoffregen, 1987). The Summitville vuggy silica zone contains large voids produced by removal of feldspar phenocrysts, and is interpreted to be the result of extreme acid dissolution that occurred at a maximum depth of 300 m (Stoffregen, 1987). The similar vuggy, friable nature of rock in the Barton Peninsula acid sulphate zone (Fig. 2A) supports near-surface alteration.

Pyrophyllite is usually indicative of formational temperatures above 270°C, but it will form at temperatures below 250°C from silica-supersaturated hydrothermal solutions (Knight, 1977). Hence, the presence of pyrophyllite in equilibrium with chalcedony in the Barton Peninsula acid sulphate assemblage is not incompatible with low formation temperatures. Zunyite is another mineral diagnostic of acid sulphate alteration (Meyer and Hemley, 1967) and suggests that the hydrothermal fluid was rich in fluorine and chlorine in addition to sulphur. Pyrite and zunyite are most abundant in pyrophyllite-rich areas, probably representing deeper parts of the alteration zone. Rutile occurs as a residual mineral derived from decomposition of ferro-magnesium minerals (Hemley *et al.*, 1969). Abundant native sulphur in cavities probably represents late-stage sublimates deposited by high-temperature fumaroles venting to the palaeosurface during the final stages of hydrothermal activity.

Large quantities of low-pH solutions are required to produce acid sulphate alteration and requisite acid fluids can be generated by several mechanisms in supergene, steam-heated and magmatic hydrothermal environments (Rye *et al.*, 1992). Supergene acid sulphate alteration is the result of weathering of sulphide-rich rocks and commonly results in a topographically controlled alteration blanket. In steam-heated environments, sulphuric acid is produced by oxidation, above the water table, of H₂S distilled off the underlying hydrothermal system (Schoen *et al.*, 1974) and the resultant alteration assemblage is similar to that produced in the supergene environment (Rye *et al.*, 1992). The absence of secondary iron hydroxide minerals such as limonite, goethite and jarosite, and the fracture-controlled morphology, suggest acid sulphate altera-

tion on Barton Peninsula is not of supergene or steam-heated origin.

Magmatic hydrothermal acid sulphate systems are driven by magmatic heat and have a significant magmatic fluid component, with sulphuric acid being produced by disproportionation of magmatic SO₂ with decreasing temperature (Holland, 1965). Acid sulphate alteration in these systems is generally fracture-controlled and characterised by extreme base-leaching resulting in vuggy silica zones, replacement of feldspar phenocrysts by alunite and large amounts of pyrite in the assemblage (Rye *et al.*, 1992). The minerals zunyite and pyrophyllite are also considered to be unique to acid sulphate alteration assemblages produced in magmatic hydrothermal environments (Rye *et al.*, 1992). Moreover, native sulphur is commonly considered to be a surface manifestation of an underlying magmatic hydrothermal system (Sillitoe, 1973). Thus the mineralogical and textural characteristics of the Barton Peninsula acid sulphate alteration appear most similar to magmatic hydrothermal systems.

Alunite group minerals also occur in monomineralic veins and breccia cements cutting, and hence postdating, the main matrix acid sulphate alteration (Fig. 3A). These vein alunite minerals have demonstrably different chemical compositions to those in the rock matrix suggesting they may have formed by a different mechanism. Alunite of magmatic steam origin is precipitated directly from the vapour phase and characteristically occurs in monomineralic veins and brecciation zones (Cunningham *et al.*, 1984). It is possible that the alunite veins transecting the acid sulphate alteration zone on Barton Peninsula were produced in a magmatic steam environment which encroached on the earlier magmatic hydrothermal system during waning stages of hydrothermal activity.

The source for the hydrothermal system is unclear, but possibilities include the nearby Noel Hill stock, its parent magma or another pluton underlying the alteration at depth. If the Noel Hill magma was the source, then the lack of appreciable height difference between it and the alteration can be readily explained if the pluton was intruded at shallow depths in the volcanic pile (~1 km), followed by telescoping of the hydrothermal system as a result of sector or caldera collapse.

Conclusion

It is concluded that acid sulphate alteration of early Tertiary andesite rocks on Barton Peninsula occurred in a magmatic hydrothermal environment, possibly with a magmatic steam component, rather than in a supergene or steam-heated environment. The alteration is typical of subaerial, high-level, vent-proximal

epithermal systems and is the first example recognized in the Antarctic Peninsula magmatic arc. The alteration assemblage clearly indicates that large volumes of acidic fluids were generated at shallow depths and there is good evidence that sulphurous fumaroles were venting to the palaeosurface during the lifespan of the hydrothermal system. Red Mountain, Lake City, Colorado, although hosted by dacitic volcanic rocks, is probably the closest analogue to Barton Peninsula in that it occurs in a caldera setting and contains superposed magmatic hydrothermal and later magmatic steam acid sulphate alteration (Bove *et al.*, 1990; Rye *et al.*, 1992).

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