

## Epithermal Alteration and Mineralization Zoning within the Stratovolcano, Barton Peninsula, King George Island

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**Abstract :** Epithermal ore deposits hosted by volcanic rocks and formed by volcanic-related hydrothermal alteration are increasing as important precious metal producers in the world with many recent discoveries. Exploring for these types of deposits can be greatly aided by detailed mapping of hydrothermal alteration.

A stratified volcanic-arc type Barton Peninsula succession is divided into three tectonic units. The volcanics are mainly represented by andesitic pyroclastic flow and surge deposits. Hypabyssal intrusions and pluton were impregnated into these rock in the Eocene (Park, 1989). Volcanism, accompanied and followed by faulting, continued beyond the Eocene.

The hydrothermal alteration and some metal mineralization were predicted in the Barton Peninsula. The alteration-mineralization system is considered to be centered on a fault structure which was associated with explosive volcanism and subvolcanic intrusive activity. Hydrothermal wall rock alteration occurs with the iron oxide-cemented breccias and as envelopes of altered rock adjacent to vein and fault of the Barton Peninsula epithermal system.

Four types of wallrock alteration are recognized in the epithermal system: prophyllitic, sericitic, argillic and advanced argillic alteration. Prophyllitic alteration by base cation metasomatism is the most widespread type. The main products of prophyllitic alteration are chlorite, epidote and quartz. Sericitic alteration forms linear areas around fracture zones and borders the vein system. Argillic alteration is characterized by the bleaching of the wall rock and appears to grade outward into sericitically or prophyllitically altered rocks. Advanced argillic alteration is exposed on the north-west part of the Barton Peninsula. The wide expanse of the advanced argillic alteration is a result of abundant acid-sulfuric fluids attacking the rock close to their source.

Near surface oxidation of effluent sulfur gases in upper zone produces sulfuric acid which attacks the host rocks resulting in an assemblage of kaolinite, alunite, pyrophyllite, diaspore, native sulfur and silica minerals. The advanced argillic alteration is the result of condensation of H<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub>S from ascending boiling water. Very acidic waters of acid-sulfate composition are generated from the oxidation of sulfidic gas by atmospheric oxygen. Vertical zoning in alteration mineralogy appears to be related to gradual decrease in kaolinite, alunite (and/or pyrophyllite) and sericite. The wide expanse of shallow argillic alteration in the Barton Peninsula is probably a result of abundant acidic fluids attacking the rock close to their source.

Sulfide and silver mineralization occurs with the alteration zone. The mineralized zone occurs as irregular pockets. It consists of silicified rocks and contains kaolinite, silica and native sulfur veinlet. Fine grained pyrites (or marcasites) are the principal sulfides. Fine grained sphalerites and silver sulfosalts occur as disseminations in the silicified rocks.

A lead-zinc bearing quartz vein is observed in the south-west part of the Barton Peninsula. Limited fluid inclusion data are obtained from the quartz vein. Two types of primary fluid inclusions are recognized in this study, ranging from less than 10 to greater 30  $\mu\text{m}$  in size. Primary liquid rich type fluid inclusion homogenize 194° - 345°C in quartz and 184°C in sphalerite.

**Key words :** epithermal alteration, epithermal mineralization, alteration zoning

## Introduction

Although the logistic and climatic problems of large-scale mining in Antarctica are enormous today, the discovery of metal sulfide focuses attention on that region as a potential source of metals. Mineralized and hydrothermally altered rocks in the Antarctic Peninsula have been reported by many workers (Wright and Williams, 1974). The quartz-pyrite rocks of the South Shetland Island have been described as lodes (Barton, 1964) that formed along Shatter zones as mineralized breccia in Pre-Tertiary faults. Littlefair (1978) supposed that the deposits are surface expression of ore deposits by low-temperature epithermal solfataric derivation.

King George Island is built largely of calc-alkaline volcanic rocks. The volcanics are mainly represented by andesitic pyroclastic flow and surge deposits. Hypabyssal intrusions and pluton were impregnated into these rock in the Eocene (Park, 1989). Volcanism, accompanied and followed by faulting, continued beyond the Eocene. Hydrothermal alteration and some metal mineralization were predicted in the Barton Peninsula. The alteration-mineralization system is considered to be centered on a fault structure which was related to explosive volcanism and subvolcanic intrusive activity.

Epithermal ore deposits hosted by volcanic rocks and formed by volcanic-related hydrother-

mal alteration are increasing as important precious metal producers in the world with many recent discoveries. Exploring for these type of deposits can be greatly aided by detailed mapping of hydrothermal alteration. Epithermal deposits are often formed as vein, replacement, dissemination, stockwork, and breccia in Barton Peninsula.

This article describes the result of epithermal alteration and sulfide and native sulfur mineralization of the Barton Peninsula. The inter-relationship between epithermal alterations and mineralization is considered to be one of the most important situations for ore depositions in the igneous activity. It is greatly aided to understand epithermal environment.

## Geology

Barton Peninsula comprises a stratified sequence of volcanic and volcanogenic rocks pierced by intrusions and a volcanic plug. The stratified volcanic-arc type succession is divided into three tectonic units. The volcanics are mainly represented by andesitic to basaltic pyroclastic flow and surge deposits. The volcanics and plutonic rocks from the Barton Peninsula are Tertiary in age (Table 1). However, Jurassic age was assigned by Davies (1982) and Kang and Jin (1989). Three tectonic units have been distinguished by different episodes of volcanic activity (Fig. 1).

Table 1. Radiometric Ages of Rocks and Lodes in the Barton Peninsula.

Unit	Mineral	Method	Age(Ma)	Source
Andesite	Whole-rock	K-Ar	48.5±4.0	Park (1989)
Altered Basalt	Whole-rock	K-Ar	35.5±3.4	Park (1989)
Andesite				
Lapilli Tuff	Whole-rock	K-Ar	44.2±2.4	Park (1989)
Granodiorite	Whole-rock	K-Ar	45.2±1.9	Park (1989)
Granodiorite	Whole-rock	K-Ar	42.1±1.9	Park (1989)
Quartz-Diorite	Whole-rock	K-Ar	45.2±2.4	Park (1989)
Granodiorite 1	Whole-rock	K-Ar	46.0±0.7	Watts (1982)
Granodiorite 2	Whole-rock	K-Ar	50.2±0.6	Watts (1982)
Granodiorite	Whole-rock	K-Ar	46.0±1	Smellie et al. (1987)
Quartz Diorite	Whole-rock	K-Ar	55	Grikurov (1977)

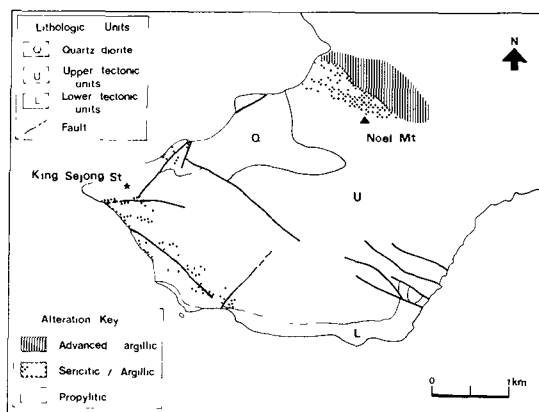


Fig 1. Geologic Map of Barton Peninsula showing granodiorite intrusion, hydrothermal alteration and the mineralized area. Lower tectonic unit includes lower unit and intermediate unit.

**Lower unit:** The lower volcanic member is exposed in some restricted area. It comprises red, flat-lying (about  $20^\circ$  to south), well stratified lapillistone and agglomerate. Locally hornfels and clotted texture containing quartz and chlorite are developed in the stratified rock.

**Intermediate unit:** An angular unconformity separates the lower unit from the intermediate unit. It crops out in the coastal part of the Barton Peninsula. It comprises mostly green tuffs with subordinate agglomerate, lapillistone and thin lava flows. The rocks are steeply dipping, and poorly stratified prophyllitic alteration developed widely, and some phyllic alterations developed along the fault.

**Upper unit:** Angular unconformity separates the intermediate unit from the upper unit. It comprises a sequence of gently deeping green, black and red lava flows, lapillistones and agglomerates. The thickness of the unit in Noel Hill is about 500 m. A contact alteration aureole surrounds the Noel Hill granodioritic plugs. Wide epithermal alterations are developed near the Noel Hill and the Jiri Bong.

Vein, disseminated mineralization and

spatially associated sericitic, argillic and advanced argillic alteration envelopes crosscut all lithologic units and contact altered rocks.

The volcanic unit is intruded by a small granodiorite plug. The plug is divided into granodiorite and quartz gabbro (Kang and Jin, 1989). The general relations between the volcanic rocks are intrusions, contact alteration and breccia pipes. A detailed description of alteration exposed in the Barton Peninsula is in the next chapter.

### Hydrothermal Mineralization

In the Barton Peninsula, two types of hydrothermal mineralization can be differentiated by cutting relations and structure. Early mineralization consists of breccia pipe or lenses of disseminated sulfides. The breccia pipes are the result of hydrothermal activity that closely resembles a porphyry copper-style system. The breccias consist of equant to tabular clasts of bleached, sericitically altered rock that was cemented by quartz, pyrite and later iron oxides. The sericitically altered clasts consist of interlocking fine-grained quartz and sericite that replace the original rock texture.

The later epithermal veins and disseminated deposits cut volcanic units. The origin of the epithermal veins is indicated by vein texture that includes multiple brecciation, stockwork veining and vuggy silica.

Sillitoe and Sawkins (1971) propose that the formation of breccia is associated with porphyry copper mineralization. The sulfide mineralization consists of disseminated euhedral grains of pyrite and small amounts of chalcopyrite. The discrete pyrite mineralization that predates the epithermal system is located within or adjacent to breccia pipes. Quartz-pyrite replacement bodies, the largest of which is 2 km long and as much as 0.3 km wide, occur as brecciated rocks apparently along the fault zone. Disseminated pyrite occurs adjacent to

volcanic rocks over an area of several square kilometers. Some secondary sulfide placer are developed near the Noel Hill (Fig. 2), but detailed mineralogical study is not carried out. This style of mineralization is locally over-

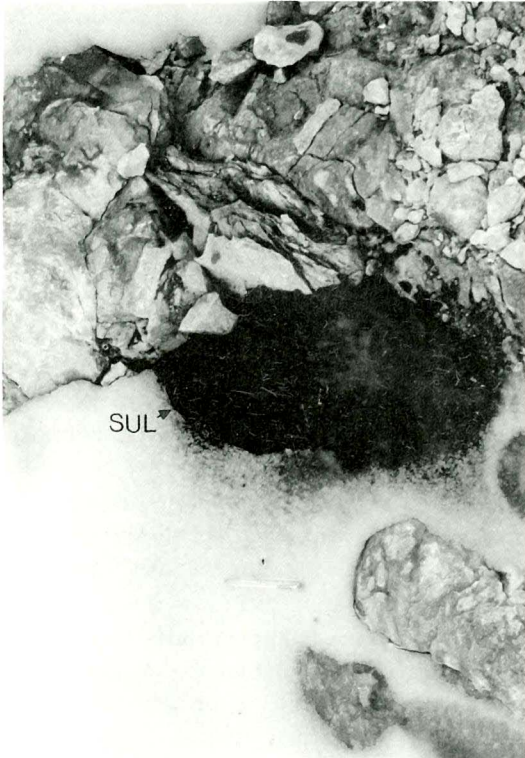


Fig. 2. Placer sulfide minerals near the Noel Hill.

printed by sericitic and argillic fracture-related alteration.

Au, Ag, As, Pb, Zn and Ga are present in significant amounts in the altered rocks and veins at Barton Peninsula (Table 2). Au, Ag, Pb, Zn, Sb, Cd and As are present mainly in vein. Sr, Ba, Se and Sc are present in acid-altered (argillic or advanced argillic) rock.

A lead-zinc bearing quartz vein is observed in south-west part of the Barton Peninsula (Fig. 3). Limited fluid inclusion data are obtained from the quartz vein. Two types of primary fluid inclusions are recognized in this study ranging from less than 10 to greater 30  $\mu\text{m}$  in size. Primary liquid-rich type fluid inclusion homogenizes 194° – 345°C in quartz and 184°C in sphalerite (Table 3). The trace metal distribution suggests that Au, Ag, Pb and Zn be associated with quartz vein.

Native sulfur is locally present as a dissemination or vein in the advanced argillic rock but forms irregular concentrations to the highest point in the alteration zone not far from the summit of a hill near the Noel Hill. This native sulfur is coarsely crystalline yellow in color and accompanied by chalcedonic silica and pyrite (Fig. 4).

Quartz-epidote veinlets cut the volcanic rocks near granodioritic intrusive contact. Some quartz-epidote veins are bordered by alteration

Table 2. Fluid inclusion homogenization temperature from sphalerite and galena bearing quartz vein in the Barton Peninsula.

Sample No.	Mineral	Type	Temp. (°C)
A1-1	Quartz	I	194-232
		II	259
A1-2	Sphalerite	I	184
A1-3	Quartz	I	230-293
		I	264-278
		II	308
A2-1	Quartz	I	189-249
A2-2	Quartz	I	173-268
A2-3	Quartz	I	218-298
A2-4	Quartz	I	281-345

\*Type I = Liquid-rich inclusion, Type II = Gas-rich inclusion

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Table 3. Analyses of altered zone and vein from the Barton Peninsula(ppm unless indicated)

	Au(ppb)	Ag	As	Pb	Zn	Fe(%)	Cu	Mn	Sb	Mo	Se	Co	Cr	Cd
P1	495	177.8	150	15195	710	0.32	193	18	1300	4	24	<1	75	60.19
S2	<5	0.3	84	20	147	12.1	517	47	10	4	13	24	120	0.9
S5	<5	0.1	6	18	20	9.03	101	48	0.9	2	37	33	130	<0.2
S6	<5	0.2	34	5	14	8.21	588	34	11	3	8	4	110	<0.2
152	<5	0.1	8	28	85	3.54	122	517	0.5	1	<3	16	160	<0.2
153	<5	0.1	2	10	6	0.17	6	5	2.6	1	<3	2	87	<0.2
154	<5	0.3	2	2	8	0.04	2	2	8.6	1	<3	<1	31	<0.2
157	<5	0.2	12	7	14	4.42	86	28	1.0	2	21	15	120	<0.2
158	6	0.1	4	4	9	0.13	6	2	11	1	<3	2	150	<0.2
	Hg	Cs	Sc	Ni	W	S	Sn	Bi	V	Br	P	Ba	La	Ce
P1	80	<0.5	0.4	29	<3	27245	<5	<2	2	11	0.003	<5	<0.5	<3
S2	<1	<0.5	21	58	7	38920	<5	<2	2	<1	0.001	349	57	120
S5	<1	<0.5	8.3	48	<3	19020	<5	5	3	<1	0.001	507	20.5	48
S6	<1	<0.5	8.2	32	<3	24630	<5	5	2	<1	0.004	847	34.6	67
152	<1	1.4	20	64	<3	5950	7	5	45	<1	0.75	393	6.6	23
153	<1	<0.5	9.9	31	<3	34370	7	<2	6	<1	0.003	1260	26.3	51
154	<1	<0.5	11	10	<3	2450	6	4	2	<1	0.003	226	27.2	64
157	<1	<0.5	8.3	46	<3	8235	6	5	2	<1	0.003	177	17.1	45
158	<1	<0.5	13	66	<3	22330	5	<2	3	<1	0.003	498	22.8	50
	Nd	Sm	Eu	Tb	Yb	Lu	Y	Th	U	Rb	Sr	Zr	Hf	Nb
P1	<5	<0.1	<0.2	<0.5	<0.2	<0.05	<2	21	<0.8	<2	37	880	19	<2
S2	66	11	2.8	0.8	2.1	0.43	20	22	4.1	<2	637	1453	32	14
S5	28	5.0	1.5	0.6	1.0	0.18	13	7.2	1.7	<2	1184	500	12	5
S6	25	5.1	1.2	0.7	0.6	0.10	12	14	1.5	<2	3023	49	4.5	5
152	14	3.1	0.8	<0.5	1.5	0.26	17	2.5	<0.5	43	584	313	8.0	2
153	15	1.0	0.4	<0.5	1.1	0.19	8	5.0	2.6	<2	883	888	22	6
154	32	6.1	1.3	<0.5	1.3	0.24	11	13	2.8	<2	535	351	10	6
157	26	4.1	1.1	<0.5	1.3	0.23	15	5	1.7	<2	643	297	7.6	5
158	20	1.8	0.4	<0.5	0.9	0.18	9	7.9	3.1	<2	791	482	13	7
	Ta	Ga	B	Be	Ir(ppb)	Na	Mg(%)	Ti(%)	Al(%)	K(%)				
P1	<1	37	11	0.1	<8	215	0.01	0.01	0.01	0.01				
S2	<1	<2	2	0.1	<5	5520	0.01	0.01	0.07	0.01				
S5	<1	41	4	0.1	<5	259	0.02	0.01	0.07	0.01				
S6	<1	7	4	0.1	<5	1420	0.01	0.01	0.05	0.01				
152	<1	31	5	0.1	<5	27900	0.85	0.01	3.05	0.19				
153	<1	26	4	0.1	<5	7460	0.01	0.01	0.38	0.02				
154	<1	28	5	0.1	<5	280	0.01	0.01	0.19	0.01				
157	<1	13	8	0.5	<5	335	0.01	0.01	0.08	0.01				
158	<1	25	10	0.1	<5	4330	0.01	0.01	0.21	0.01				

\*P1: Sampled from lead-zinc vein ; S2, S5, S6, 156, 157 and 158: Sampled from advanced argillic zone ; 154: Sampled from phyllic zone ; 152: Sampled from propylitic zone.

\*Au, As, Br, Co, Cr, Cs, Fe, Hf, Hg, Ir, Na, Sb, Sc, Se, Sr, Ta, Yb, U, V, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Analyzed by INAA. Mo, Cu, Pb, Zn, Ag, Ni, Mn, Cd, Bi, V, Ti, B, Al, K by ICP and Ga, Zr, Sr, Sn, Nb, Rb, S, Y, Ba by XRF.

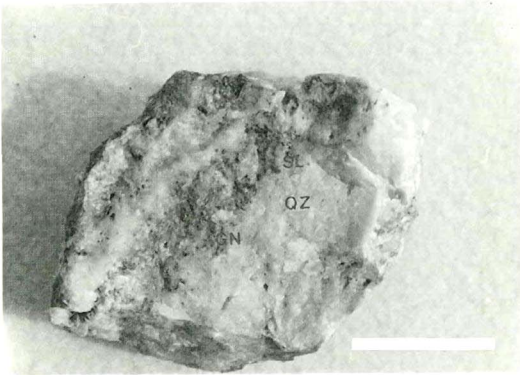


Fig. 3. Photograph showing sphalerite and galena sampled from galena-sphalerite-bearing hydrothermal vein. Scale bar is 5 cm. SL = sphalerite, GN = galena, QZ = quartz.

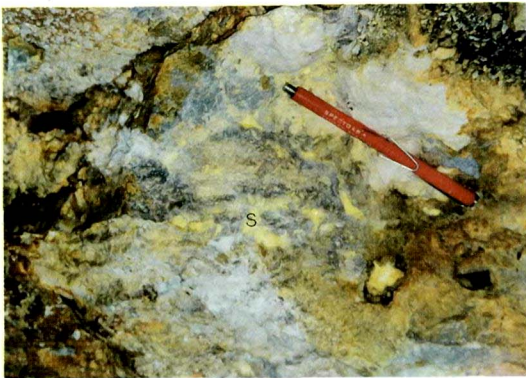


Fig. 4. Native sulfur in upper advanced argillic area. Pyrite is closely associated with the native sulfur. S = native sulfur.

envelopes that consist of alkali feldspar, sericite, quartz and small amounts of chlorite.

### Hydrothermal alteration

Alteration is important in the investigation of epithermal ore deposits for several reason (Hedenquist, 1984); 1) It provides a record of the physico-chemical conditions appropriate to the formation of the deposit (e.g. zones of boil-

ing, mixing, etc.). 2) It can provide evidence for the collapse of an epithermal system, or the overprinting of one system on another. 3) It provides data for position in a particular deposit, especially since hydrothermal alteration is generally more extensive than mineralization. The largest zone of hydrothermal alteration is observed on the west side of the Barton Peninsula. Hydrothermal wallrock alteration occurs with the breccias as broad zones that surround breccia pipes, and as envelopes of altered rock adjacent to faults and veins. Alteration envelopes adjacent to the fractures are superimposed on the pervasive sericitically and argillically altered rocks.

Four types of wall rock alteration are developed in the Barton Peninsula: propylitic, sericitic, argillic and advanced argillic alteration. Advanced argillic alteration grades downward into argillic and sericitic alteration in the north-west part of the peninsula. Advanced argillic alteration is observed in upper level near the Noel Hill. Propylitic alteration is the most common type, and other alteration would overprint it.

Contact alteration is developed adjacent to the granodiorite stock, and consists of replacement of feldspar by epidote, quartz, sericite and of pyroxenes by chlorite, magnetite and pyrite. Contact altered rocks commonly exhibit pervasive sericitization and silicification of the fine grained groundmass and matrix. The spatial distribution of contact alteration is a result of the intrusion. The original textures of clastic rocks are commonly obliterated and overprinted by fine grained aggregates of chlorite, epidote and magnetite (Fig. 5). The contact alteration grades outward into pervasive propylitic alteration.

#### 1. Propylitic Alteration

Propylitic alteration is observed in the relatively fresh rocks and forms a broad envelope around the epithermally altered area. It appears as red and green altered rock because of the



Fig. 5. Contact alteration. It formed clast by epidote, chlorite and quartz. QZ = quartz, EP = epidote.

epidot, chlorite and hematite. The alteration is characterized by epidote, chlorite and small amounts of pyrite assemblage. The propylitic alteration consists of epidotes replacing feldspars in association with sericites. Zoned plagioclase phenocrysts are selectively replaced by epidote (Fig. 6). Some mafic minerals are altered to chlorites with hematites. The development of propylitic alteration has been attributed to a broad hydrothermal system associated with the volcanic center and the cooling of sub-volcanic intrusion.

## 2. Phyllic (Sericitic) Alteration

This type of alteration forms linear areas around fracture zones. Large areas of sericitically altered rocks surround the breccia (Fig. 7). The sericitic alteration grades outward into sericitic-argillic alteration. The sericitic alteration would be later than propylitic alteration and overprint it. The sericitically altered rocks contain feldspars replaced by sericites with silicified groundmass. Euhedral pyrite cubes are scattered through the sericitic rocks, replacing original mafic minerals (Fig. 8).

## 3. Argillic Alteration

The zone of argillic alteration surrounds the area of phyllic alteration and genetically

extends to the borders of the fault or breccia pipes. Altered rocks are characterized by pervasive and abundant, fine-grained, disseminated pyrite. Argillic alteration completes conversion of former feldspars to fine grained sericite, calcite and clay minerals. In argillically altered rocks, the phenocrysts are replaced by kaolinite, and ferromagnesian minerals by sericite and clay minerals (Fig. 9).

The area of quartz-sericite-pyrite assemblages on the southwestern part of the Barton Peninsula reflects hydrothermal alteration and min-

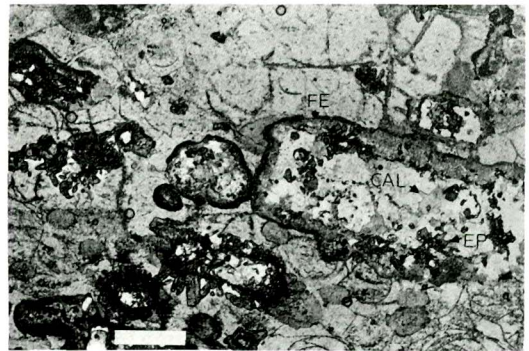


Fig. 6. Propylitized plagioclase units predominantly chloritized with epidote and calcite. Cross nicol. Scale bar is 10 $\mu$ m. FE = iron oxide, EP = epidote, CAL = calcite.



Fig. 7. Hydrothermal vein breccia cemented by silica and pyrite. QZ = quartz, BR = breccia.

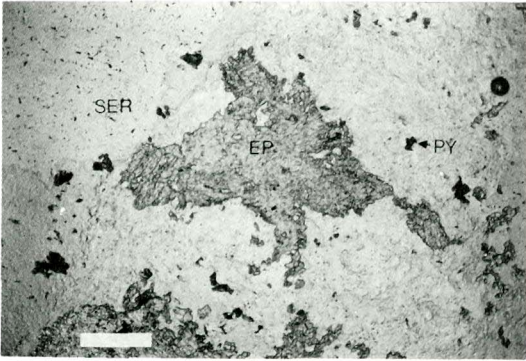


Fig. 8. Phyllic alteration of basaltic andesite. Plagioclase converts to sericite and pyrite. Open nicol. Scale bar is 10 $\mu$ m. EP = epidote, SER = sericite, PY = pyrite.

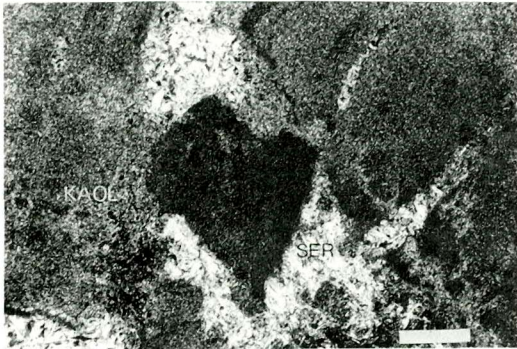


Fig. 9. Microphotograph of argillized tuff showing complete conversion to kaolinite. Open nicol. Scale bar is 10 $\mu$ m. SER = sericite, KAOL = kaolinite.

eralization of porphyry copper type. A lead-zinc vein is observed in the alteration zone.

#### 4. Advanced Argillic Alteration

Wide zones of advanced argillic altered rocks are developed in the upper level of north-west Barton Peninsula. In the field, these altered rocks consist of a quartz rich groundmass in which are lath-shaped voids partly filled with native sulfur.

A concentric banding of light and dark silica occurs in these zones (Fig. 10). In the advanced

alteration envelopes, the rock is replaced by kaolinite, pyrophyllite, alunite and diaspore. The altered rock is bleached off white in color and contains minor disseminated fine grained pyrite. Euhedral pyrite crystals and fine grained pyrite aggregates are scattered through the altered rock, and narrow fractures are filled with fine grained quartz with pyrite and native sulfur. In the alteration zone, particularly in the silicified patches, small circular bodies of hydrothermal replacement breccia were observed.

The most strongly altered areas are veinlike or irregular patches with the zone of advanced argillic alteration that have undergone silicification. A lot of pyrites are associated with these alteration. The hydrothermal minerals identified are chiefly quartz, kaolinite, (nature) alunite, pyrite and native sulfur with small amounts of diaspore and gypsum. Some vuggy silica and quartz-alunite are cut by late stage of veins and fractures filled by near-surface alteration. The quartz crystallites show zoned growth that indicates boiling environment (Fig. 11). Vertical zoning in alteration mineralogy appears to be related to a gradual decrease in kaolinite and alunite, and increase in pyrophyllite and sericite.

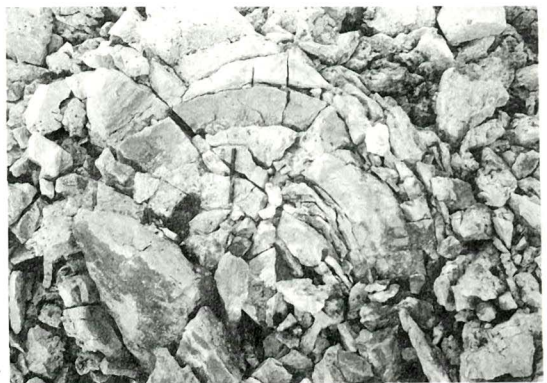


Fig.10. Concentric banding of quartz and kaolinite assemblage in advanced argillic zone.



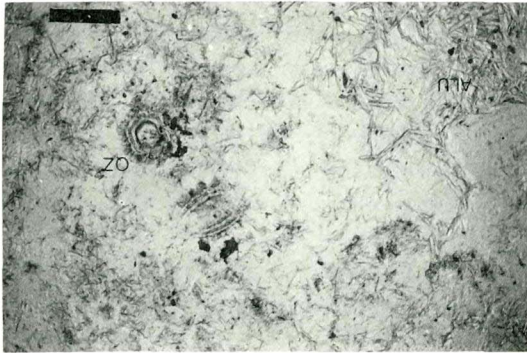


Fig.11. Microphotograph showing zoned quartzes in fibrous alunite and fine grained quartz matrix. Open nicol. Scale bar is 10µm.

### Geochemical Conditions of Wall Rock Alteration

Brown(1979) summarized the factors affecting the formation of hydrothermal minerals and showed that the alteration suite depended on temperature, pressure, rock type, permeability, fluid composition and duration of activity. A classic discussion of this type of alteration is that of Meyer and Hemley (1967). In these cases, alteration refers to metasomatic changes in the wall rock mineral assemblage adjacent to the site of ore deposition. The common types of such alteration include: a) Hydrogen ion metasomatism, which produces sericitic, argillic and advanced argillic assemblages, b) base cation metasomatism, such as K<sup>+</sup>, Na<sup>+</sup> or Mg<sup>2+</sup> metasomatism, which produce potassic (K-feldspar, biotite), albitic and chloritic assemblages, and c) anionic metasomatism, particularly carbonatization and sulfidation by CO<sub>2</sub> (HCO<sub>3</sub><sup>-</sup>) and H<sub>2</sub>S, respectively.

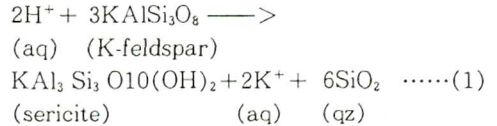
Many ore-related natural waters are chemically active because they are acidic. The sources of acidity of natural waters are 1) magmatic gas production of hydrochloric and sulfuric acid, 2) oxidation of hydrogen sulfide gas, 3) base exchange, 4) carbonation, 5) oxi-

dation of ferrous iron and hydrolysis by ferric iron in weathering, and 6) oxidation of sulfide minerals in weathering (Mann, 1983).

There are many secondary mechanisms in geochemical systems that cause pH to increase including boiling, silicate wall rock reaction and fluid-fluid mixing reactions (Reed and Spycher, 1985). Reaction of acidic waters with silicate wall rock is cause of pH increase and consequent sulfide precipitation by which disseminated sulfides occur in wall rock.

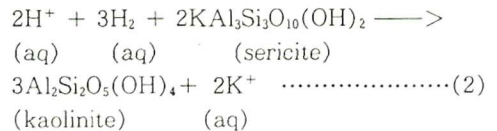
H<sup>+</sup> metasomatism occurs in acidic environment and yields aluminous phyllosilicates and quartz. Hydrogen ion metasomatism involves the addition of H<sup>+</sup> to the rock, ordinarily producing hydrated alteration minerals. For example the sericitic to advanced argillic alteration series of Meyer and Hemley (1967) include the following reactions, starting with K-feldspar:

1) Acid attack of K-feldspar producing sericite.



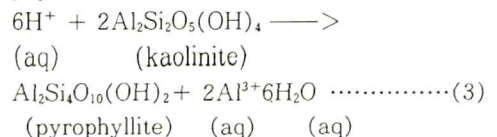
In this reaction, H<sup>+</sup> is exchanged for K<sup>+</sup> as feldspar is converted to a mineral with a larger ratio of Al to K.

2) If, in a given alteration zone, the K-feldspar is consumed by reaction (1), the H<sup>+</sup> attacks sericite, producing kaolinite:



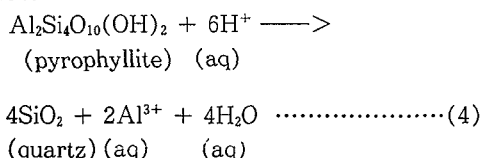
Again, H<sup>+</sup> is exchanged for K<sup>+</sup> and the product mineral has a larger ratio of Al to K than the reactant.

3) Further H<sup>+</sup> attack converts kaolinite to pyrophyllite:



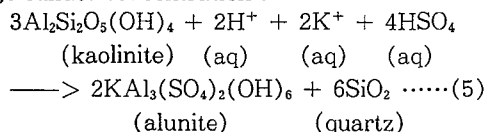
In this reaction  $H^+$  ion is exchanged for  $Al^{3+}$  ion, which is significantly soluble only at low pH, and the product mineral is more silicious than the reactant.

4) Silicification by acid attack (Meyer and Hemley, 1967) may occur if additional  $Al^{3+}$  is liberated:



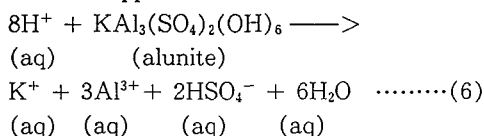
Again,  $H^+$  is exchanged for  $Al^{3+}$ , producing pure quartz as the alteration product.

5) Acid sulfate spring waters or volcanic gas condensates may produce alunite from kaolinite by acid attack in the presence of  $K^+$  ion and a large sulfate concentration :



Stoffregen (1985) suggests that this reaction may be significant at Summitville at the interface between the kaolinite zone and the veinward quartz-alunite zone.

6) Innermost alteration zone at Summitville consists of quartz alone. Acid attack of the alunite in the quartz-alunite assemblage could produce such apparent silicification:



These reaction represents examples of extreme hydrogen ion metasomatism by hydrothermal waters. Similarly intense metasomatism may take place in weathering where oxidation of sulfides produces acid.

Intense argillic alteration is observed in modern geothermal systems (White et al., 1971), and is the result of condensation of  $H_2$ ,  $CO_2$  and  $H_2S$  from ascending boiling waters, and their subsequent oxidation by atmospheric oxygen. Reed and Spycher (1985) calculate the effects

of condensation and oxidation from the boiling gas component in the shallow levels of an epithermal system (above the water table). They determine that the condensation of  $CO_2$  will produce a mildly acidic (pH=4.5) fluid that contains carbonic acid at low temperatures (95°C). This fluid is acidic enough to produce the argillic alteration of feldspars to kaolinite, as shown by experimental data on kaolinite (Van Oosterwycke and Gustache, 1977).

### Interpretation of Advanced Argillic Alteration

Figure 12 shows the typical environment in which epithermal advanced argillic alteration forms. The advanced argillic assemblage is characterized by extreme hydrolysis and cation leaching, relatively high total sulphur, and oxidizing conditions. Therefore, the sulphur is oxidized, and the sulphuric acid carries out the cation leaching, leaving an aluminium-silicate and/or sulphate assemblage. Depending on the temperature, and related metal concentrations (e.g. Cu, As), various assemblages characterize this alteration.

Figure 12 is slightly modified from Hemley et al. (1969), and demonstrates the relative stabilities of alunite, kaolinite and K-mica. At low pH values, caused by sulfuric acid, kaolinite becomes unstable with respect to alunite; if the  $K^+$  concentration in the fluid is high enough, the kaolinite stability between alunite and K-mica is eliminated.

At high temperatures (280°C; Hemley et al., 1980) in equilibrium with quartz, pyrophyllite replaces kaolinite. However, under acid conditions the existing silica polymorph is often cristobalite or even amorphous silica, allowing kaolinite-pyrophyllite to coexist at temperature as low as 160°C. If diaspore is present with pyrophyllite, the experimental data indicate minimum coexistence temperatures of 280°C (Hemley et al., 1980). Although these minerals

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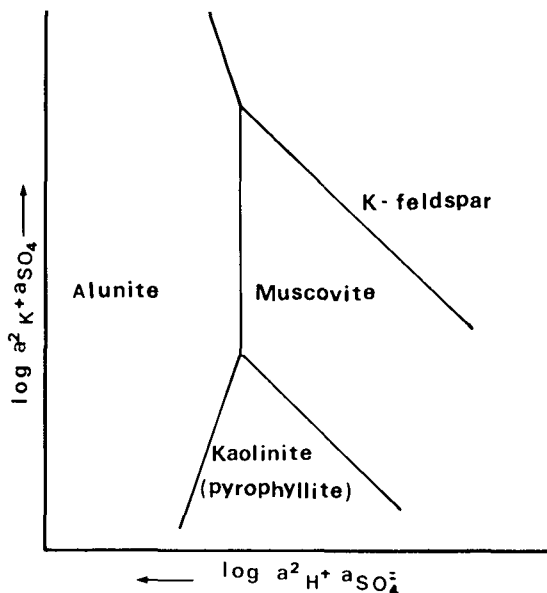
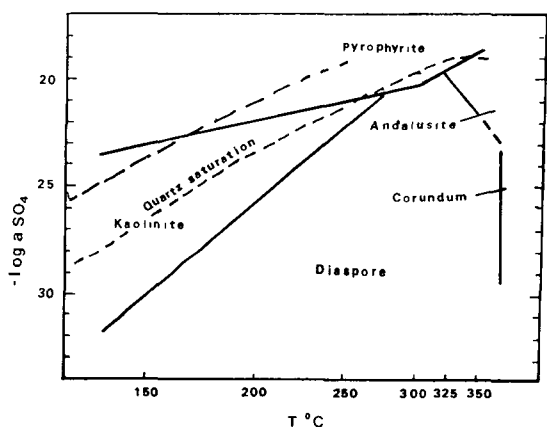


Fig. 12. A : Generalized illustration of stability relationships of alteration products as a function of  $K_2SO_4$  and  $H_2SO_4$  activities. Kaolinite is stable rather than pyrophyllite below  $250^\circ C$ . Quartz is present, temperature and pressure being constant. Diagram and phase relationships after Hemley, et al., 1969. B: Stability relationships in the system  $Al_2O_3-SiO_2-H_2O$  along the liquid-vapour curve. Note position of cristobalite solubility curve. from Hemley, et al., 1980.

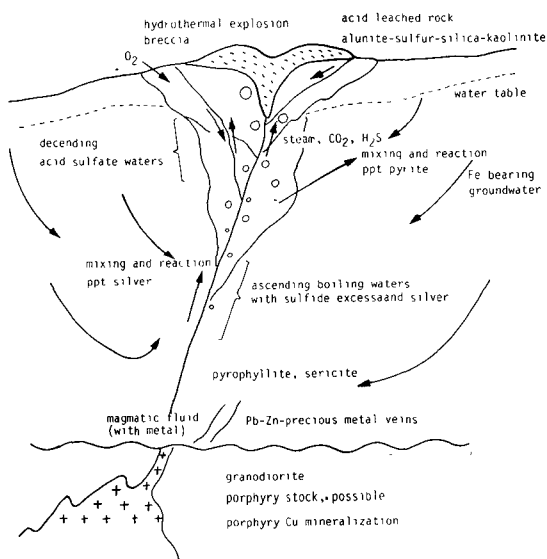


Fig.13. Epithermal Model. The acid-sulfate fluids interact with the previously altered rocks in a zone coincident with the observed sulfide mineralization.

are present together at temperatures as low as  $200^\circ C$  in acid zones in the Bacon-Manito geothermal system, Luzon (Reyes, 1985), fluid inclusion data indicate they were probably formed at somewhat higher temperatures, supporting in general the experimental data.

Very acidic waters ( $pH < 3.0$ ) of acid-sulfate composition are generated from the oxidation of sulfidic gas by atmospheric oxygen above the water table (White, 1957). Reed and Spycher (1985) calculate the effects of oxidizing a condensate and gas, derived from the boiling of a hydrothermal fluid, that has an original composition similar to a Broadlands water. Sulfuric acid is produced as  $H_2S$  (in gas and condensate) is oxidized by atmospheric oxygen, and the calculated pH changes from 4.5 to 2.06 as acid is produced (Reed and Spycher, 1985). A fluid of this composition can also carry elevated levels (4–30 ppm) of Al. It would precipitate kaolinite if it mixed with an ascending silica-bearing fluid. The pH of this fluid is low enough to produce the intense argillic alteration.

Figure 14, a pH- $f_{O_2}$  diagram, inferred stability field of the advanced argillic alteration in the Barton Peninsula. Kaolinite-alunite-pyrite assemblage is used to provide a pH environment. The upper bound for the alteration environment is provided by the boundary between kaolinite and alunite. Sulfur stability is also used to provide a minimum pH. The wide expanse of shallow argillic alteration in the Barton Peninsula is probably a result of abundant acidic fluids attacking the rock close to their source.

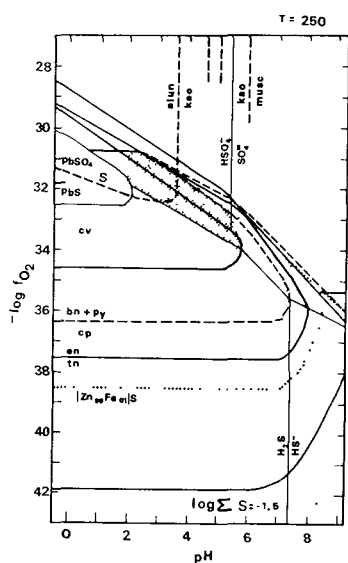


Fig.14. A pH- $f_{O_2}$  diagram at 250°C and vapor saturation pressure showing the fields of silica, quartz-alunite and native sulfur mineralization(modified from Barton et al., 1977). This figure indicates highly oxidizing and acidic conditions required for the silica and quartz-alunite in the Barton Peninsula.

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