Hydrothermal Alteration and Mineralization in the Granodioritic Stock of the Barton Peninsula, King George Island, Antarctica

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ABSTRACT : Early Tertiary volcanics, volcanoclastics and granodiorite occur in the Barton Peninsula, King George Island, Antarctica. In the granodioritic stock and volcanic rocks, propylitic alteration characterized by actinolite, epidote, chlorite and calcite is widespread, and disseminations and veinlets of sulfide minerals such as pyrite, chalcopyrite and bornite are ubiquitous. The study on the hydrothermal alteration near granodioritic stock can be summarized as follows; (1) granodiorite intrusion is a small, high level stock associated with calc-alkaline volcanism, and have high copper content, (2) high temperature type of propylitic alteration and common occurrence of copper sulfides in and around granodiorite intrusion, (3) low $\delta^{34}S$ values of pyrites by oxidational conditions of sulfide deposition, (4) low $\delta^{18}O$ values of quartz and feldspar in the granodiorite, and isotopic non-equilibrium by hydrothermal alteration. It suggest that hyrothermal alteration and mineralization near granodioritc stock should be genetically related to granodiorite intrusion in the Barton Peninsula.

INTRODUCTION

The Antarctic Peninsula is considered to be a particularly favorable geologic environment for formation of mineral deposits because its geologic and tectonic settings are similar to those of the Andean belt of South America, one of the world's major mineralized belt. Thus, the Antarctic Peninsula belongs to the Andean metallogenic province which is the southward extension of the province in western South America (Ericksen, 1976).

The South Shetland Islands is mainly calc-alkaline island arc, separated from the Antarctic Peninsula by the young marginal basin of the Bransfield Strait. In this region, widespread hydrothermal alteration and mineralization are associated mainly with Tertiary volcanic and plutonic rocks. Many workers (e.g., Wright, Williams, 1974; Cox et al., 1980) have pointed out that the ages and characteristics of plutons in the South Shetland Islands are similar to those in the Chilean Andes of South America in which porphyry-type and related mineralizations are dominant.

Hydrothermally altered rocks and related quartz veins are scattered on King George Island of the South Shetland Islands. On the hydrothermally altered rocks of the island, Littlefair (1978) and Hawkes

(1982) considered that it is low temperature hot spring type alteration that may represent the surface expression of porphyry-type mineralization at deeper depth on the island. According to Cox (1981), the alteration and mineralization may not be porphyry-type in character but due to the devolatilization of diorite and granodiorite-quartz diorite magmas as they crystallized. Willan (1987) considered that the mineralization could have been volcanogenic or high level epithermal in origin related to gabbroic or granodioritic intrusions. These previously studies suggest that the mineralization in King George Island is likely to be closely associated with granitic magmatism and could be a potential region as the site of porphyry-type and related metal mineralization.

The mineralogy and geochemistry of quartz veins hosted in altered volcanic rocks of the Barton Peninsula, King George Island, were studied by Littlefair (1978), Park (1991) and So et al. (1995). However there has been no detailed work on hydrothermally altered rocks in and around the granitic pluton. In this study, we first describe hydrothermal alteration and mineralization in and around granitic pluton, and then discuss the genesis of metal mineralization on the basis of mineralogy, geochemistry and stable isotope of hydrothermally altered rocks.

GENERAL GEOLOGY

King George Island is situated in the middle of the South Shetland Islands. The stratigraphic sequence of

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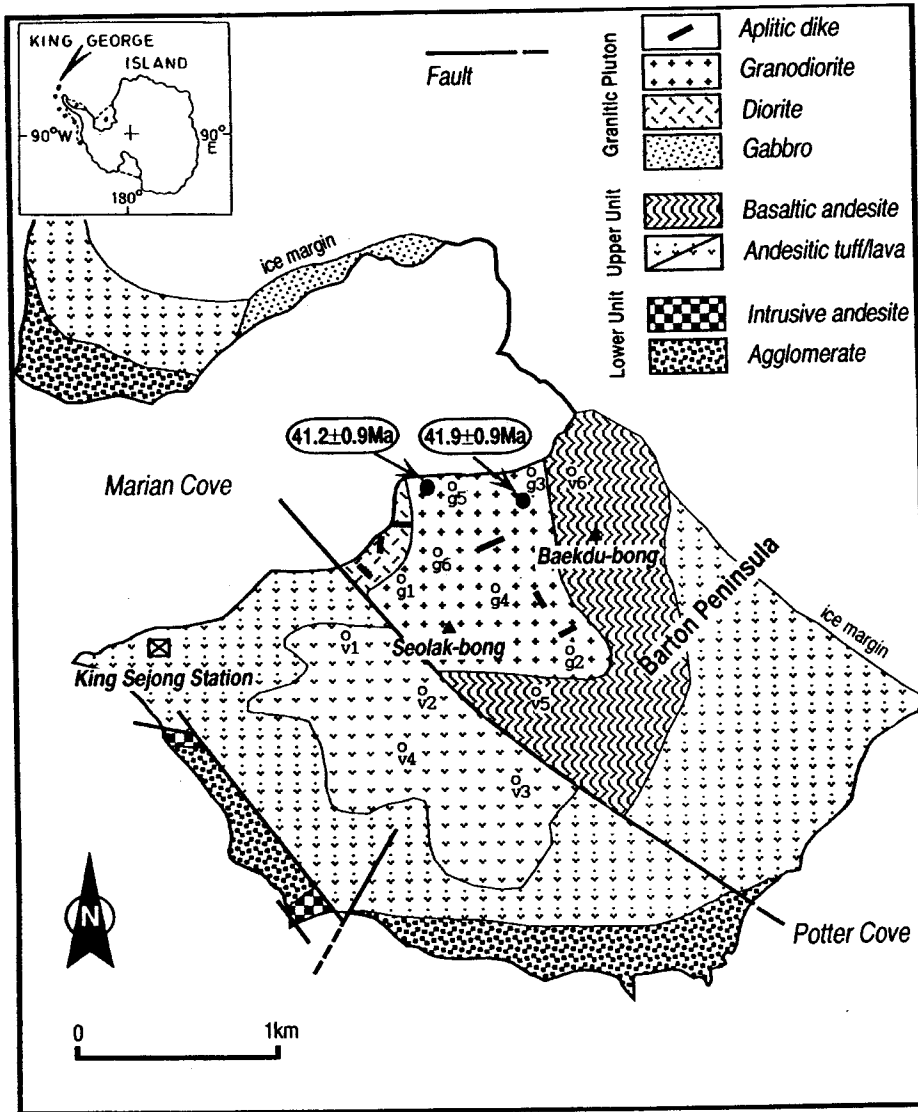** Polar Research Center, Korea Ocean Research & Development Institute, Ansan 425-600, Korea

Fig. 1. Geological map of the Barton Peninsula. Location and K-Ar biotite ages of granodiorite determined by the authors are shown. Sampling sites are listed as follows; g1-g6 (granodiorite), v1-v6 (volcanic rock).

the Barton Peninsula includes upper Cretaceous to lower Miocene, mostly calc-alkaline and predominantly subaerial volcanic and volcanoclastic rocks. They were intruded by medium-sized granitic rocks (Fig. 1). The southern Barton Peninsula is composed of volcanoclastic succession of mainly andesitic composition. Along the southern coast, poorly-sorted agglomerate, subordinate tuffaceous sandstone and purple or pale green sandstone/siltstone occupy the lower unit of volcanoclastic succession. Lots of plant fossils indicating late Paleocene to Eocene and tropical to subtropical environment were found in the purple or pale green sandstone/siltstone (Chun *et al.*,

1994). The upper unit of southern peninsula consists of andesitic tuff and lava. The northern peninsula, which also belongs to the upper unit and is separated from southern peninsula by NW-stretching fault, comprises andesitic tuff, basaltic andesite flow and granitic rocks. The granitic rocks, which intruded into basaltic andesite on the north and bounded by andesitic tuff and lava on the south, is composed of gabbro, diorite, granodiorite and aplitic dikes. Two K-Ar biotite ages of granodiorite determined by Lee *et al.* (1996) are 41.9±0.9 Ma and 41.2±0.9 Ma, respectively. In conjunction with previous results (Pankhurst, Smellie, 1983; Jin *et al.*, 1991; Park,

1989), these ages suggest that the granitic rocks have intruded in Eocene time.

PETROLOGY OF GRANITIC ROCKS

Triangular plot of modal quartz, alkali feldspar and plagioclase illustrates that the granitic rocks have wide compositional range from gabbro to granite, but is mainly composed of granodiorite (Fig. 2). Medium-grained gabbro in the Weaver Peninsula is characterized by cumulate texture. Fine-grained diorite along the southern coast of Marian Cove consists of plagioclase, quartz, pyroxene, hornblende, biotite and Fe-Ti oxides with minor apatite. Chlorite and epidote are the common secondary minerals. Medium-grained granodiorite is mainly composed of plagioclase, quartz, alkali feld-

spar, hornblende, biotite and Fe-Ti oxides. Minor phases are pyroxene, zircon and apatite. Common altered minerals are chlorite, epidote and calcite. Hornblende and biotite variable in modes mostly coexist with magnetite. Small amounts of clinopyroxene are commonly alter to biotite and magnetite. Frequently observed miarolitic cavities and microgaphic intergrowth of alkali feldspar and quartz support that the magma was saturated with water near its solidus and decompressed to a certain degree. Equigranular aplitic dikes, a few centimeter in width, has intruded into diorite and granodiorite. It is composed of alkali feldspar, quartz, plagioclase with subordinate hornblende, biotite, zircon and Fe-Ti oxides. Abundant miarolitic cavities are filled with secondary quartz, alkali feldspar and epidote. Micrographic textures are also observed in some samples.
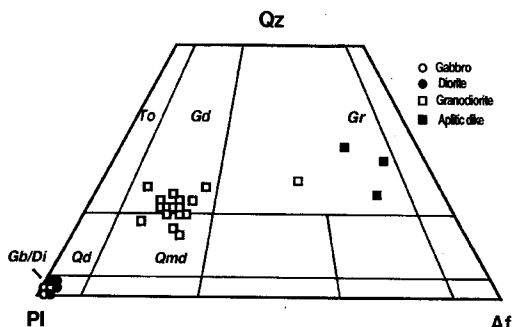

Fig. 2. Modal classification of the granitic rocks plotted on the Streckeisen's (1976) Q-A-P diagram. Abbreviation; quartz (Qz), plagioclase (Pl), alkali feldspar (Af), diorite (Di), quartz diorite (Qd), quartz monzodiorite (Qmd), tonalite (Tol), granodiorite (Gd), granite (Gr)
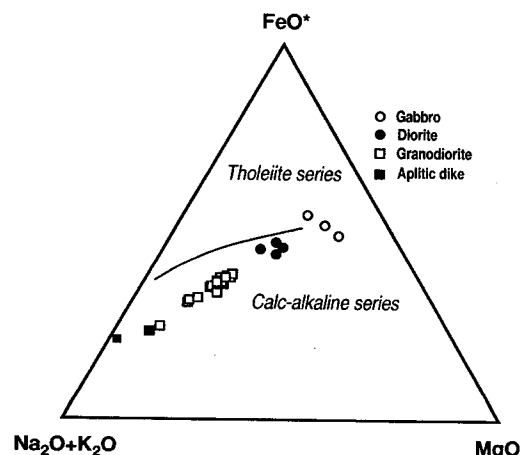

Fig. 3. AFM diagram of the granitic rock shows that it were formed by differentiation of calc-alkaline series (Petro et al., 1979). Symboles are the same as in Fig. 2.
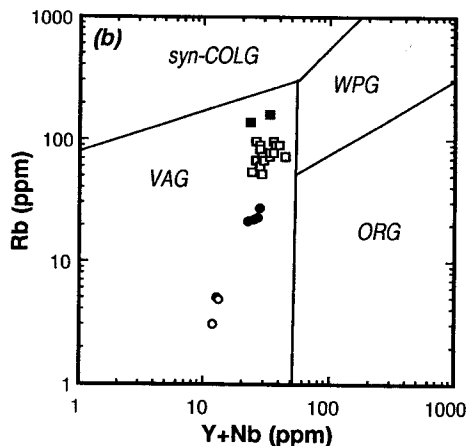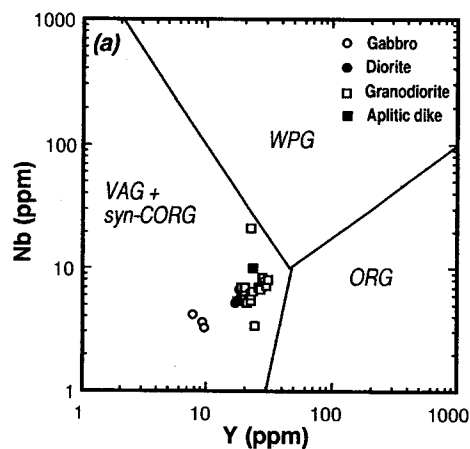

Fig. 4. Tectonic discrimination diagram for VAG (volcanic arc granite), syn-CORG (syncollision granite), WPG (within plate granite) and ORG (ocean ridge granite) of Pearce et al. (1984).
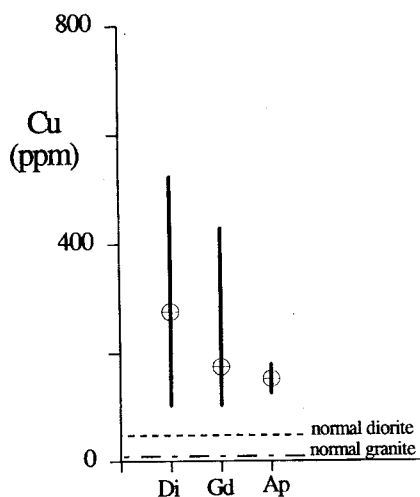
Fig. 5. The copper contents of the granitic rocks. They are higher than average granitic rocks (Taylor, 1965). Circle is average content of the granitic rock in the Barton Peninsula. Data from Hwang et al. (1995). Abbreviation; diorite (Di), granodiorite (Gd), aplite (Ap).

The whole-rock analyses of major and trace elements (Lee et al., 1996) suggest that the subunits of the pluton were formed by differentiation of calc-alkaline series (Fig. 3). Low concentrations of Nb and Y (Fig. 4a) and relatively low concentration of Rb compared to typical syn-collision granites in all subunits (Fig. 4b) demonstrate that the pluton was formed under volcanic arc environment (Pearce et al., 1984). Copper concentrations of all subunits are anomalously high although other metal elements such as zinc, lead and molybdenum are also present. The average copper concentrations of four diorites, seventeen granodiorites and two aplites are 276 ppm, 174 ppm and 152 ppm, respectively (Fig. 5). The average abundances of normal diorite and granite are 40ppm and 10ppm, respectively (Taylor, 1965). These copper contents of the studied pluton are higher than the average granitic rocks.

In this study, as gabbro occur only in the Weaver Peninsula and majority of the granitic rocks in the Barton Peninsula is granodiorite, we describe hydrothermal alteration in and around the granodiorite stock to discuss the geochemical condition and genesis of hydrothermal alteration and mineralization.

HYDROTHERMAL ALTERATION

Hydrothermally altered rocks, which are widespread in the Barton Peninsula, have been studied by many workers (Hawkes, 1961; Barton, 1964; Littlefair, 1978; Davies, 1982; Park, 1991; Kim et al.,

1995). In the previous works, many alteration minerals and four hydrothermal alteration types are recognized; propylitic, phyllic, argillic, and advanced argillic. Propylitic alteration characterized by epidote+chlorite±calcite assemblage is most widespread in granitic and volcanic rocks. The phyllic and argillic alterations which are characterized by sericite, illite and kaolinite with minor propylitic alteration assemblage, are developed in the northeastern and southwestern parts of the peninsula. The advanced argillic alteration containing microcrystalline quartz, kaolinite, alunite and native sulfur are developed in high level near the Baekdu-bong. Propylitic alteration is widely distributed in the Barton Peninsula, but the other alterations are confined to the vicinity of fault-related fracture zones in propylitized volcanic rocks. Park (1991) and So et al. (1995) reported that the phyllic and argillic alterations were superimposed on the early propylitic alteration zone along the fault zone. However, we could not find the field evidences of phyllic alteration in the fault zone on the southeastern part of the Barton Peninsula, though minor sericitization was found near the contact between granodiorite and volcanic rocks.

In the granodiorite, pyroxene and hornblende are replaced by actinolite+chlorite+calcite assemblage. Biotite is replaced by chlorite and actinolite with or without epidote (Fig. 6a). Plagioclase is replaced by epidote±calcite assemblage. The common alte- red mineral assemblage is chlorite+actinolite+epi- dote± calcite, and the most common altered mineral is chlorite (Fig. 6b). The aggregates of fine-grained magnetite commonly occur in chlorite. The chemical compositions of amphibole and chlorite determined by EPMA are listed in Table 1 and Table 2, respectively. The composition of amphiboles is actinolite, while some amphiboles are magnesio-hornblende (Fig. 7). The composition of chlorites is pychnochlorite (Fig. 8). Fine-grained secondary biotites associated with magnetite and epidote are observed along grain boundaries and twin planes of plagioclase.

The volcanic rocks suffered from propylitic alteration are reddish or greenish in color because of the presence of epidote, chlorite and hematite. Mafic minerals altered to chlorite and actinolite. Plagioclase phenocrysts are selectively replaced by calcite and epidote with or without chlorite. Chlorite, epidote and opaque minerals occur throughout the tuffaceous matrix. The amygdules of volcanic rocks are filled with aggregates of chlorite, chlorite+epidote+quartz and chlorite+epidote+calcite (Fig. 6c). The actinolite veinlets associated with chlorite and opaque minerals are ubiquitous in volcanic rocks (Fig. 6d).
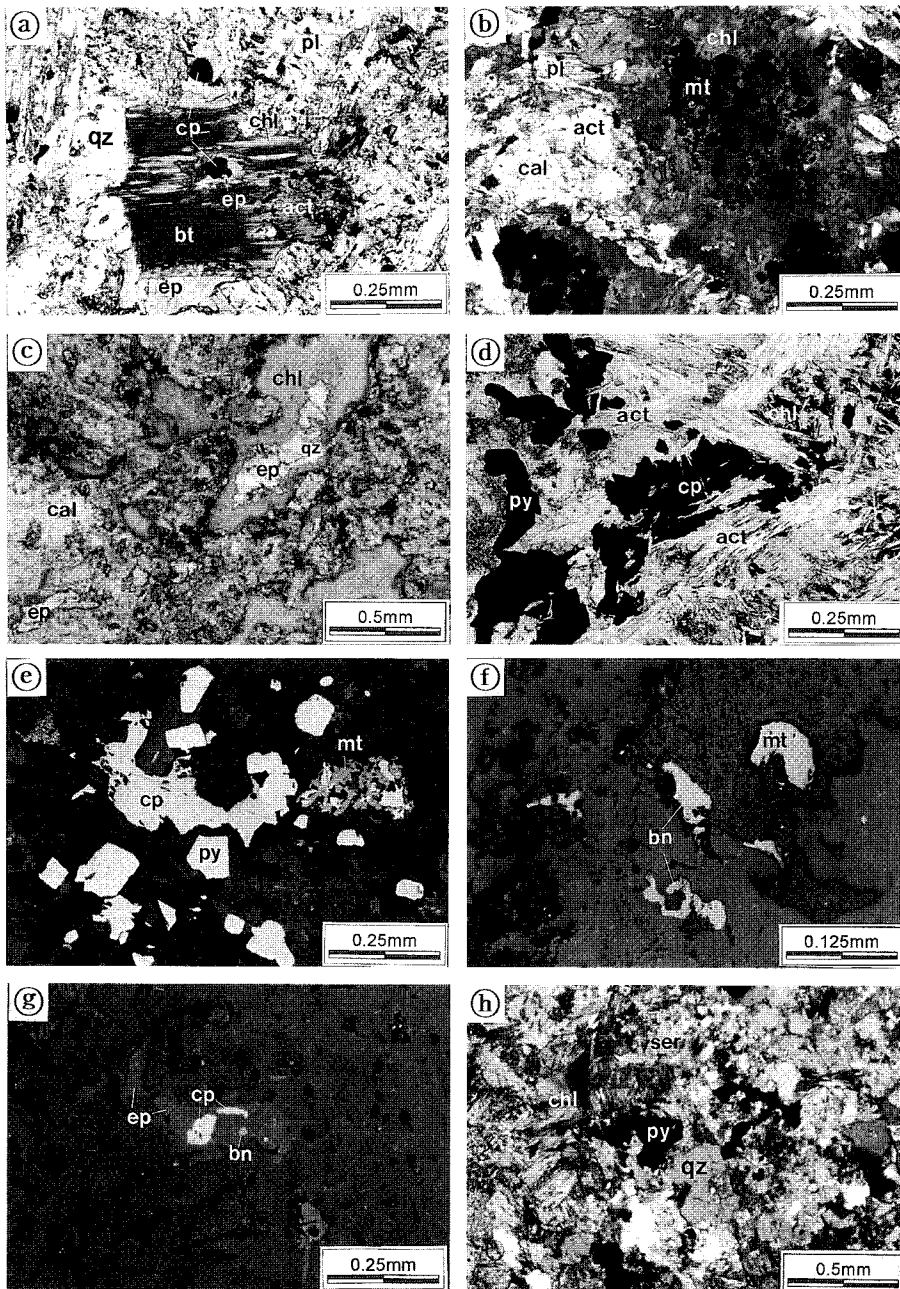
Fig. 6. Microphotographs of alteration and ore minerals. (a) Biotite is altered to chlorite, epidote and actinolite. Chalcopyrite is associated with alteration minerals; crossed nicol, in granodiorite. (b) The mineral assemblage of chlorite+actinolite+calcite is common. Fine-grained magnetites commonly occur in chlorite; crossed nicol, in granodiorites. (c) The amygdules are filled with chlorite, epidote, calcite and quartz; crossed nicol, in volcanic rocks. (d) Acicular actinolites with chlorite are closely associated with chalcopyrite and pyrite; crossed nicol, in volcanic rocks. (e) Sulfide veinlet is consist of pyrite, chalcopyrite and magnetite; reflected light, in volcanic rocks. (f) Bornite is disseminated in propylitized granodiorite; reflected light. (g) Bornite and chalcopyrite are associated with epidote in propylitized granodiorite; reflected light. (h) Pyrite and quartz are associated with sericite and chlorite. Highly sericitization develops in the contact between granodiorite and volcanic rocks; crossed nicol, in granodiorite. Abbreviation; pyrite (py), chalcopyrite (cp), bornite (bn), magnetite (mt), chlorite (chl), epidote (ep), actinolite (act), sericite (ser), calcite (cal), biotite (bt), quartz (qz), plagioclase (pl).

Table 1. Electron microprobe analyses of amphibole in granodiorite and volcanic rocks of the Barton Peninsula.

Rock type	granodiorite											volcanic rocks										
Sample No.	g1			g2			g3			g4		v1		v3			v5			v6		
SiO₂	55.81	54.80	55.61	53.83	51.72	51.33	47.45	47.49	47.40	47.64	49.55	54.42	53.09	55.89	56.59	55.79	52.60	55.60	54.04	54.78	54.53	55.87
Al₂O₃	1.41	1.58	1.80	1.83	2.08	2.88	5.59	5.34	5.35	5.10	3.95	2.06	2.95	0.80	1.09	1.85	3.85	2.32	3.65	2.44	2.56	2.04
TiO₂	0.28	0.50	0.37	0.53	0.56	0.22	1.42	1.32	1.32	1.18	0.56	0.46	0.76	0.00	0.11	0.12	0.41	0.11	0.36	0.21	0.10	0.16
FeO	7.60	7.89	8.72	10.75	12.45	13.86	13.67	13.65	13.66	13.98	10.50	8.86	8.68	6.25	3.75	5.06	5.63	8.08	5.47	4.81	6.13	5.81
MgO	20.61	20.04	19.10	17.51	16.43	14.34	15.28	15.03	15.11	14.88	17.44	19.40	18.63	18.25	22.77	21.35	20.24	22.20	20.83	21.73	21.56	22.66
MnO	0.92	0.75	0.84	0.63	0.63	0.66	0.36	0.38	0.44	0.39	0.34	0.61	0.49	3.77	1.20	2.03	2.08	3.33	2.05	2.25	2.27	2.11
CaO	11.48	11.70	11.68	12.65	11.36	12.30	11.30	11.20	11.37	11.25	11.62	11.50	11.78	13.00	12.36	11.12	11.12	6.82	10.98	10.38	9.91	9.84
Na₂O	0.33	0.43	0.43	0.44	0.68	0.31	1.55	1.49	1.39	1.28	1.22	0.75	0.86	0.00	0.01	0.05	0.32	0.21	0.35	0.19	0.14	0.10
K₂O	0.06	0.15	0.16	0.16	0.26	0.15	0.62	0.57	0.54	0.55	0.43	0.24	0.28	0.02	0.01	0.02	0.01	0.01	0.01	0.03	0.02	0.08
Total	98.60	97.90	98.84	98.38	96.23	96.14	97.32	96.54	96.68	96.35	95.71	98.42	97.63	98.07	97.96	97.44	96.34	98.74	97.83	96.87	97.26	98.73
23 oxygen base																						
Si	7.78	7.72	7.78	7.67	7.61	7.61	7.02	7.08	7.06	7.12	7.31	7.67	7.56	7.90	7.81	7.79	7.49	7.72	7.55	7.69	7.66	7.71
Al(IV)	0.22	0.26	0.22	0.31	0.36	0.39	0.98	0.92	0.94	0.88	0.69	0.33	0.44	0.10	0.18	0.21	0.51	0.28	0.45	0.31	0.34	0.29
Al(VI)	0.01	0.00	0.07	0.00	0.00	0.11	0.00	0.02	0.00	0.02	0.00	0.01	0.05	0.03	0.00	0.09	0.14	0.10	0.15	0.09	0.09	0.04
Ti	0.03	0.05	0.04	0.06	0.06	0.02	0.16	0.15	0.15	0.13	0.06	0.05	0.08	0.00	0.01	0.01	0.04	0.01	0.04	0.02	0.01	0.02
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.89	0.93	1.02	1.28	1.53	1.72	1.69	1.70	1.70	1.75	1.30	1.04	1.03	0.74	0.43	0.59	0.67	0.94	0.64	0.56	0.72	0.67
Mg	4.28	4.21	3.98	3.72	3.60	3.17	3.37	3.34	3.35	3.31	3.83	4.08	3.95	3.84	4.69	4.44	4.30	4.59	4.34	4.55	4.52	4.66
Ma	0.11	0.09	0.10	0.08	0.08	0.08	0.04	0.05	0.05	0.05	0.04	0.07	0.06	0.45	0.14	0.24	0.25	0.39	0.24	0.27	0.27	0.25
Na	0.09	0.12	0.12	0.12	0.19	0.09	0.44	0.43	0.40	0.37	0.35	0.21	0.24	0.00	0.00	0.01	0.09	0.06	0.10	0.05	0.04	0.03
Ca	0.71	1.77	1.75	1.93	1.79	1.95	1.79	1.79	1.81	1.80	1.84	1.74	1.80	1.97	1.83	1.66	1.70	1.01	1.64	1.56	1.49	1.45
K	0.01	0.03	0.03	0.03	0.05	0.03	0.12	0.11	0.10	0.11	0.08	0.04	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01
Mg/(Mg+Fe)	0.83	0.82	0.80	0.74	0.70	0.65	0.67	0.66	0.66	0.65	0.75	0.80	0.79	0.84	0.92	0.88	0.87	0.83	0.87	0.89	0.86	0.87

Table 2. Electron microprobe analyses of chlorite in granodiorite and volcanic rocks of the Barton Peninsula

Rock type: granodiorite (g1–g4), volcanic rocks (v1, v5, v6)

| Sample No.	g1	g1	g1	g1	g1	g2	g2	g2	g2	g3	g3	g3	g3	g3	g3	g4	g4	g4	g4	v1	v1	v5	v5	v6	v6
SiO_2	31.09	29.33	29.15	29.10	27.77	29.34	28.74	28.83	27.69	28.35	27.85	28.64	28.64	28.39	28.25	28.42	28.82	29.00	29.86	30.03	29.21	28.81	28.81	28.58	29.00
Al_2O_3	14.34	15.75	23.18	23.53	22.91	18.42	18.54	18.95	19.40	19.62	20.12	17.50	17.38	16.60	16.94	17.02	18.24	17.18	17.12	19.68	20.16	18.27	17.66	18.45	17.19
TiO_2	0.01	0.03	0.00	0.00	0.04	0.02	0.00	0.02	0.03	0.05	0.02	0.00	0.00	0.03	0.00	0.00	0.09	0.01	0.00	0.03	0.06	0.01	0.00	0.02	0.23
FeO	22.65	23.66	12.89	11.64	15.48	17.37	18.23	19.01	19.24	19.27	18.38	17.93	18.69	18.51	19.05	18.29	18.50	17.20	16.15	7.75	6.89	20.46	20.42	20.57	20.30
MgO	18.78	18.10	22.76	23.65	21.97	22.64	21.31	21.42	20.08	20.83	20.34	21.54	21.23	22.15	21.34	21.82	21.96	23.47	24.77	27.94	29.25	20.30	20.01	19.73	19.98
MnO	0.32	0.46	0.61	0.28	0.54	0.54	0.40	0.39	0.85	0.96	0.76	0.65	0.53	0.58	0.63	0.54	0.32	0.39	0.44	1.17	0.69	0.49	0.39	0.38	0.29
CaO	0.80	0.25	0.11	0.06	0.03	0.09	0.04	0.02	0.04	0.04	0.05	0.11	0.12	0.11	0.10	0.10	0.05	0.03	0.08	0.08	0.07	0.10	0.11	0.11	0.15
Na_2O	0.08	0.01	0.00	0.00	0.00	0.01	0.04	0.02	0.00	0.01	0.00	0.00	0.07	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.02
K_2O	0.05	0.00	0.04	0.02	0.00	0.00	0.01	0.01	0.00	0.02	0.02	0.00	0.00	0.01	0.01	0.01	0.02	0.00	0.00	0.03	0.04	0.01	0.00	0.03	0.05
Total	88.12	87.56	88.74	88.27	88.74	88.43	87.32	88.67	98.34	89.15	87.53	87.21	85.87	86.37	86.31	86.21	88.02	87.30	88.43	86.71	86.37	88.45	87.43	87.87	87.22
28 oxygen base																									
Si	6.414	6.131	5.643	5.616	5.465	5.863	5.844	5.791	5.680	5.691	5.663	5.866	5.930	5.877	5.867	5.880	5.824	5.879	5.935	5.834	5.672	5.853	5.922	5.847	5.973
Al(IV)	1.586	1.869	2.357	2.384	2.535	2.137	2.156	2.209	2.320	2.309	2.337	2.134	2.070	2.123	2.133	2.120	2.176	2.121	2.065	2.166	2.328	2.147	2.078	2.153	2.027
Al(VI)	1.901	2.010	2.930	2.967	2.547	2.202	2.288	2.277	2.369	2.331	2.485	2.091	2.169	1.925	2.012	2.031	2.167	1.984	1.945	2.340	2.285	2.226	2.200	2.294	2.145
Ti	0.001	0.004	0.000	0.000	0.006	0.003	0.000	0.003	0.004	0.007	0.003	0.000	0.000	0.004	0.000	0.000	0.014	0.001	0.000	0.005	0.009	0.001	0.000	0.003	0.035
Fe	3.908	4.135	2.087	1.878	2.777	2.903	3.100	3.193	3.301	3.235	3.126	3.104	3.202	3.203	3.308	3.164	3.127	2.917	2.685	1.259	1.118	3.476	3.509	3.518	3.496
Mg	5.777	5.639	6.569	6.803	6.446	6.742	6.460	6.415	6.141	6.232	6.167	6.576	6.550	6.835	6.607	6.729	6.615	7.092	7.339	8.092	8.467	6.148	6.132	6.018	6.134
Mn	0.056	0.081	0.100	0.045	0.090	0.092	0.069	0.067	0.147	0.164	0.132	0.112	0.093	0.102	0.111	0.094	0.055	0.067	0.074	0.192	0.113	0.083	0.067	0.066	0.050
Ca	0.177	0.056	0.022	0.012	0.006	0.020	0.008	0.005	0.009	0.009	0.010	0.026	0.025	0.025	0.022	0.023	0.011	0.007	0.016	0.017	0.015	0.023	0.023	0.025	0.034
Na	0.032	0.003	0.000	0.000	0.000	0.004	0.015	0.007	0.000	0.005	0.000	0.000	0.028	0.000	0.000	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.014	0.000	0.006
K	0.012	0.000	0.010	0.006	0.000	0.000	0.004	0.002	0.000	0.004	0.004	0.000	0.000	0.001	0.003	0.001	0.005	0.000	0.001	0.007	0.010	0.004	0.000	0.008	0.014
Formation Temperature(°C)	186	216	268	271	287	244	246	252	264	263	266	244	237	243	244	243	249	243	237	247	265	245	238	246	233
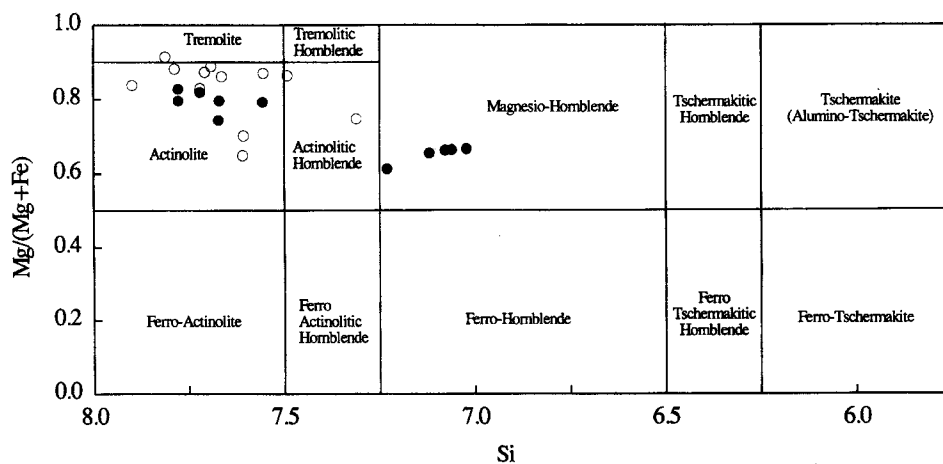
Fig. 7. Mg/(Mg+Fe) atomic ratio versus number of Si atoms in the unit cell formula of amphiboles based on Leake (1978). full circle; granodiorite rocks, open circle; volcanic rocks.
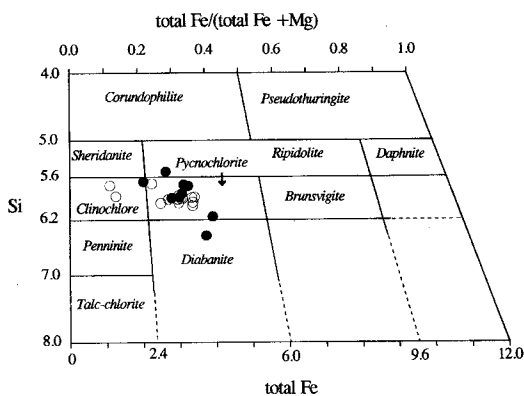

Fig. 8. Composition of the analyzed chlorite plotted on the Hey's (1954) diagram. open circle; granodiorite rocks, full circle; volcanic rocks.

METAL MINERALIZATION

The disseminations and veinlets of ore minerals are common in propylitic alteration zone. Ore minerals include pyrite, chalcopyrite, bornite, magnetite, hematite and rutile. Pyrite, chlacopyrite, and magnetite are common ore minerals, and the majority of these minerals is found within veinlets in volcanic rocks (Fig. 6e). The dissemination of pyrite, chalcopyrite and minor bornite is common in propylitized granitic rocks which are characterized by chlorite+actinolite±calcite assemblage (Fig. 6f, g). Pyrite and quartz coexist with chlorite in highly sericitized rocks around the contact between granodiorite intrusion and volcanic rocks (Fig. 6h). In propylitized volcanic rocks, disseminations and veinlets of ore minerals are ubiquitous. Euhedral pyrite

crystals, which have minute inclusions of plagioclase, are closely associated with epidote and chlorite. Chalcopyrite+pyrite±bornite are disseminated with or without magnetite and hematite. In hand specimens, two types of veinlets are recognized: (1) actinolite veinlets consisting of acicular actinolite, chalcopyrite, pyrite and minor amount of chlorite (Fig. 6d); (2) sulfide veinlets consisting of pyrite, chalcopyrite and magnetite (Fig. 6e). The aggregates of actinolite always occur as major alteration minerals in highly altered volcanic rocks, and are preferentially associated with chalcopyrite (Fig. 6d).

Cathelineau and Nieva (1985) found that the relationship, $X_{Al}^{IV}=4.71\times10^{-3}$ T - 8.26×10^{-2}, is valid for chlorite forming in the temperature range 130 to 310°C, and it would be extrapolated to lower and higher temperature. The calculated formation temperature of chlorite in granodiorite rocks is 186~287°C, and that in volcanic rocks is 233~265°C (Table 2). So et al. (1995) have reported that primary fluid inclusions from void-filling calcite in altered andesite homogenize at 223~269°C. The consistence between chlorite and fluid inclusion geothermometer data in altered volcanic rocks suggests that the main reaction producing propylitic alteration occurred at 250°C. Thus we assumed that the reaction producing propylitic alteration occurred arround 250°C. Sulfur and oxygen fugacites can be estimated from the stability relations of characteristic mineral assemblages (Fig. 9). As mentioned above, chalcopyrite and pyrite commonly coexist with magnetite and hematite with or without bornite. A possible fs_2-fo_2 condition for copper mineralization can be determined by the pyrite+chalcopyrite+magnetite+hematite±bornite assemblage, hence the estimated log fs_2 and log fo_2 values are about -11
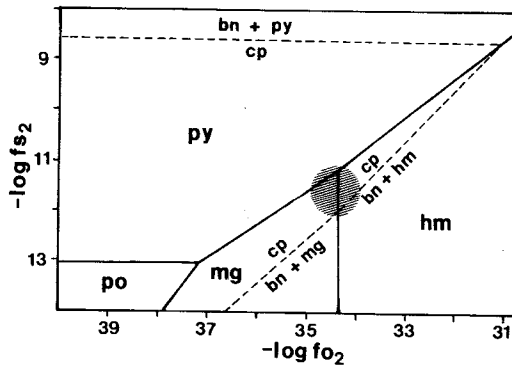
Fig. 9. The log fs_2-log fo_2 diagram showing the mineral stability fields at 250°C. The hatched area show the depositional condition of sulfide minerals in the Barton Peninsula. Sulfidation curves are from Barton, Skinner (1979).

Table 3. Sulfur isotope data of pyrites in the hydrothermally altered rocks of the Barton Peninsula.

Mineral	Sample no.	$\delta^{34}S$ (‰)	Occurrence	Host Rock
pyrite	g1	-0.6	dissemination	granodiorite
pyrite	g3	+1.0	dissemination	granodiorite
pyrite	v1	-6.9	dissemination	andesitic tuff
pyrite	v1	-6.8	veinlet	andesitic tuff
pyrite	v2	-6.4	veinlet	andesitic tuff
pyrite	v3	-7.4	veinlet	andesitic tuff
pyrite	v3	-7.9	dissemination	andesitic tuff
pyrite	v4	-4.0	dissemination	andesitic tuff
pyrite	v5	-1.8	veinlet	basaltic andesite
pyrite	v6	-9.6	dissemination	basaltic andesite

atm. and -34 atm., respectively. Although these estimated T, fs_2, and fo_2 do not represent the whole range of ore depositonal conditions, the main mineralization in propylitic alteration zone should have occurred on these conditions.

STABLE ISOTOPES

Sulfur and oxygen isotopic compositions of sulfide and silicate minerals separated from altered rocks were measured in order to clarify the composition of ore forming fluid. SO_2 gas, prepared by combustion with CuO+sulfides powder at 1000°C (Thode *et al*, 1961), was analyzed to determine the sulfur isotopic composition of sulfides. Oxygen was extracted from silicate minerals by fluorine extraction procedure (Taylor and Epstein, 1962), then was converted to CO_2 by reaction with hot carbon. The measurement of isotopic ratio was performed using a VG Prism II stable isotope ratio mass spectrometer at Korea Basic Science Institute. The analytical results are reported in standard δ notation; $\delta = (R_{sample}/R_{standard}-1) \times 1000$. The sulfur isotope data are expressed relative to CDT, and oxygen isotope to SMOW. The standard errors are approximately ± 0.2‰ for S and O.

Sulfur Isotope

The sulfur isotope data of pyrite are listed in Table 3. Disseminated pyrite in altered granodiorite have $\delta^{34}S$ values of -0.6 to 1‰, while the $\delta^{34}S$ values of disseminated and veinleted pyrite in altered volcanic rocks are relatively low, ranging from -9.6 to -1.8‰. The sulfur isotopic composition of sulfide minerals can be used to determine the sulfur isotope com-

posititon of ore fluid ($\delta^{34}S_{\Sigma S}$) and source of sulfur only when the temperature, fo_2, and pH conditions of ore-forming fluids are known (Ohmoto, 1972). Fig. 10. is a pH-fo_2 diagram that combines stability fields of iron sulfides and $\delta^{34}S_{py}$ value at 250°C from a solution which contains 0.001 m of ΣS and 0‰ of $\delta^{34}S_{\Sigma S}$. Sericite occurs as altered mineral adjacent to

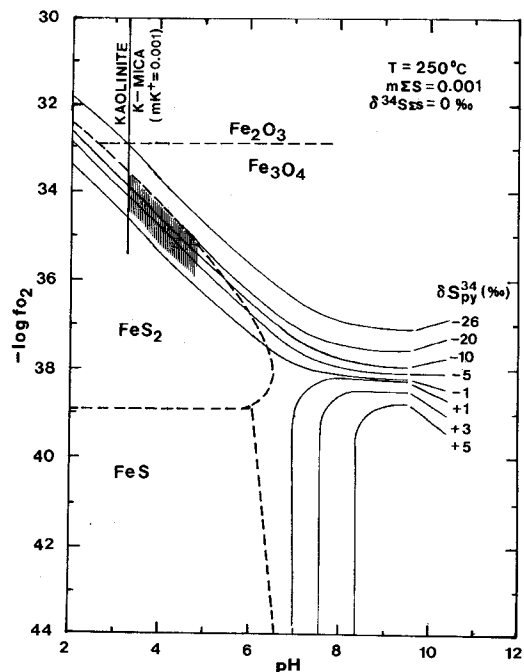**Fig. 10.** The log fo_2-pH diagram showing the relationships among the $\delta^{34}S_{py}$ contours and the stability fields of Fe-S-O minerals. A slight variation of fo_2 and/or pH values can cause drastic variation in the sulfur isotopic composition of pyrite. The condition of hatched area which is estimated in Fig. 9. is suitable to explain the $\delta^{34}S_{py}$ values in the Barton Peninsula. Diagram from Ohomoto (1972).

the contact between granodiorite and volcanic rocks. Some kaolinite occur in advanced argillic zone (Park, 1991), but kaolinite does not occur in propylitic zone. This implies that the lower limit of pH of ore fluids were controlled by the following reaction:

$$2KAl_3Si_3O_{10}(OH)_2+3H_2O+2H^+=3Al_2Si_2O_5(OH)_4+2K^+$$
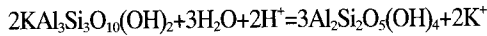
At 250°C and m_{K+} of 0.001, stability field of sericite limits the pH to the value higher than 3.2 (Helgeson et al., 1978). The analyzed $\delta^{34}S_{py}$ values agree with above-mentioned depositional condition of pyrite at the $\delta^{34}S_{\Sigma S}$ value of about 0‰ (Fig. 10). The $\Delta^{34}S_{\Sigma S}$ value of about 0‰ indicates that the sulfur source is an igneous origin. As shown in Fig. 10, pyrites coexisted with magnetite and/or hematite can show much lower $\Delta^{34}S_{py}$ values than the $\Delta^{34}S_{\Sigma S}$ value, and a slight variation of fo_2 and/or pH in the ore fluids can cause drastic variation of $\delta^{34}S_{py}$ value. So the low $\delta^{34}S_{py}$ values in propylitic zone can be explained by high oxidational condition of ore fluids (Ohmoto and Rye, 1979). The $\delta^{34}S_{py}$ values between granodiorite and volcanic rocks are similar, but it is noted that $\delta^{34}S_{py}$ in granodiorite are slightly higher than those of volcanic rocks. This difference is probably due to the slightly higher oxidational condition when pyrites were deposited in altered volcanic rocks than in altered granodiorite.

Oxygen Isotope

The oxygen isotope data of quartz and feldspar in the Barton Peninsula granodiorite are summarized in Table 4. The $\delta^{18}O$ values of quartz are 2.1 to 5.1‰. The $\delta^{18}O$ values of feldspar vary between 0.7 and

4.5‰, having an average of about 2.8‰. These oxygen values are lower than those of average granitic rocks elsewhere in the world (Taylor, 1978).

The normal fractionation between quartz and alkali feldspar $(\Delta=\delta^{18}O_{qz}-\delta^{18}O_{fd})$ in granodiorite rocks is about 0.8 to 1.5‰ and that between quartz and plagioclase is 1.0 to 2.5‰ (Taylor, 1978). Fig. 11. shows $\delta^{18}O$ relation of coexisting quartz and feldspar of the granodiorite in the Barton Peninsula. Two quartz-feldspar pairs display normal Δ_{qz-fd} values, but the four other pairs show abnormal negative Δ_{qz-fd} values. These negative Δ_{qz-fd} values are interpreted as isotopic non-equilibrium between quartz and feldspar.

If we assumed that the two of normal fractionation values between quartz and feldspar are equilibriated oxygen isotope values of fresh granodiorite, the low $\delta^{18}O$ values of quartz and feldspar suggest that major magma source is mantle which had low initial $\delta^{18}O$ vlaue. The reason why $\delta^{18}O_{fd}$ values are higher than $\delta^{18}O_{qz}$ values in the four of quartz-feldspar fairs is considered as follows. The granodiorite of the Barton Peninsula is pervasively propylitized, suggesting that granodiorite had interacted with hydrothermal fluids. So et al. (1995) calculated $\delta^{18}O_{fl}$ of hydrothermal fluids as -6.0 to 0.8‰ from quartz veins on the Barton Peninsula. Assuming that the oxygen isotope value of hydrothermal fluids interacted with granodiorite was about -6.0‰ which is the lowest limit
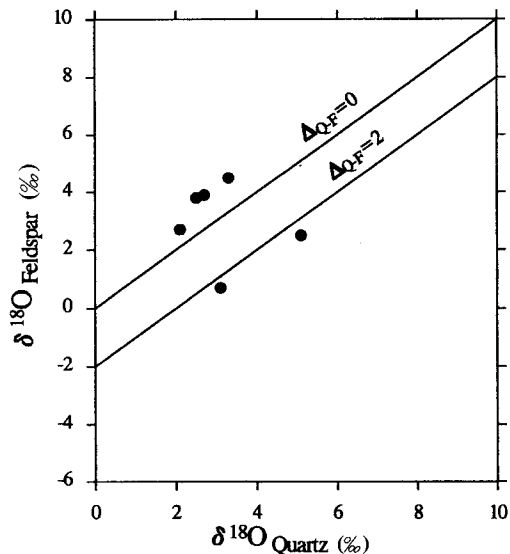
Table 4. Oxygen isotope data of quartz and feldspar in the granodiorite of the Barton Peninsula.

sample no.	$\delta^{18}O_{qz}$ (‰)	$\delta^{18}O_{fd}$ (‰)	calculated $\delta^{18}O_{fd}$ reacted with fluid ($\delta^{18}O_{fl}$=-6‰) at indicated temperature*			
			150°C	200°C	250°C	300°C
g1	3.3	4.5				
g3	2.6	3.8				
g5	3.1	0.7				
g6	5.1	2.5	6.5	3.5	1.0	-0.5
g3	2.1	2.7				
g4	2.7	3.9				

* Based on fractionation factors from O'Neil and Taylor (1967). Sodium and potassium feldspar have identical isotopic properties within the limits of analytical uncertainty. $\delta^{18}O_{qz}$; oxygen isotope value of quartz, $\delta^{18}O_{fd}$; oxygen isotope value of feldspar, $\delta^{18}O_{fl}$; oxygen isotope value of ore fluid (So. et al., 1995).

Fig. 11. $\delta^{18}O$ relations of coexisting quartz and feldspar in granodiorite of the Barton Peninsula. Fresh granodiorite have relatively normal quartz-feldspar fractionation (Δ_{Q-F}) of about 2‰, but hydrothermally altered granodiorite have negative or non-equilibrium quartz-feldspar fractionation.

of $\delta^{18}O_{fl}$ calculated by So et al. (1995), we can calculate $\delta^{18}O_{fd}$ values which were isotopically re-equilibriated with hydrothermal fluids at various temperature. Calculated $\delta^{18}O_{fd}$ values between 150 to 300°C are well consistent with measured $\delta^{18}O_{fd}$ values (Table 4). This temperature agree with formation temperature of chlorite in granodiorite (186~287°C) and include assumed temperature of propylitic alteration (250°C) as mentioned above. The $\delta^{18}O$ enrichment of feldspar result from oxygen isotope exchange at low temperature with water having $\delta^{18}O$ value about -6‰. When isotopic fractionations occur in hydrothermally altered rocks, isotopic exchange rate of feldspar is much faster than that of quartz (Criss, Taylor, 1983). Feldspar is more susceptible to such alteration because they exchange oxygen more rapidly than do quartz. Thus, feldspar typically undergoes significant $\delta^{18}O$ change during hydrothermal alteration. It is concluded that hydrothermal alteration at low temperature is responsible for higher $\delta^{18}O_{fd}$ rather than $\delta^{18}O_{qz}$ of the grano-diorite in the Barton Peninsula.

DISCUSSION

Propylitic alteration is widespread in th Barton peninsula. The common altered minerals are actinolite, chlorite, epidote and calcite. Kim et al. (1995) report that the mineral assemblage of epidote-chlorite-calcite change to actinolite-chlorite-epidote from south to north of the Barton Peninsula, suggesting that the volcanic and plutonic rocks have experienced greenschist to amphibolite facies of low pressure thermal metamorphism. However, the altered minerals are closely associated with ore minerals characterized by pyrite, chalcopyrite and bornite. Moreover actinolite, major alteration minerals in highly altered rocks, is preferentially associated with chalcopyrite. This suggest that the granodiorite and volcanic rocks have experienced hydrothermal alteration rather than thermal metamorphism. Eaton, Setterfield (1993) point out that actinolite-bearing alteration mineral assemblage is interpreted to be the highest temperature type in the propylitc alteration. The development of high temperature type alteration in and around the granodiorite means that the hydrothermal alteration and mineralization are genetically related to the granodiorite intrusion in the nothern part of the Barton Peninsula.

Ore deposits of the igneous (hydrothermal) origin may have a wide range of $\delta^{34}S$ values because of the presence of several generations of minerals deposited sequentially under different conditions. Moreover, the $\delta^{34}S$ values if sulfide minerals depend not only on the

isotopic composition of the total S in the system but also on the environmental conditions at the site of deposition (Ohmoto, 1972). The general range of sulfide $\delta^{34}S$ values in island arc volcanic rock is -1 to 5‰ (Taylor, 1987). The sulfide $\delta^{34}S$ values in altered volcanic rocks of the Barton Peninsula is -9.6 to -1.8‰, which is isotopically lighter than that of typical island-arc volcanic rock sulfides. Low $\delta^{34}S$ values for sulfides in some ore deposits may mean that the oxidation state of the fluids was high or that they incorporated some sedimentary sulfides. As normal sedimentary sulfides have a $\delta^{34}S$-value between -30 and -10‰(Hoefs, 1987), this suggest that sulfur should be derived either by hydrothermal solution or by remobilization of volcanic sulfide in high oxidational condition during the hydrothermal alteration.

The $\delta^{18}O$-values of normal granitic rocks is 6 to 10‰(Taylor, 1978). However in the Barton Peninsula, the $\delta^{18}O$-values of quartz and feldspar in the granodiorite is 0.7 to 5.1‰, and the isotopic fractional values of $\delta^{18}O$ between quartz and feldspar are negative. The low $\delta^{18}O$ values of quartz and feldspar suggest that major magma source is mantle which had low initial $\delta^{18}O$ vlaue. And isotopic non-equilibrium between quartz and feldspar of granodiorite can be attributed to the interaction at low temperature with meteoric-hydrothermal fluids.

In this study, we can summary the result as follows; (1) granodiorite intrusion is a small, high level stock associated with calc-alkaline volcanism, and have high copper contents, (2) high temperature type of propylitic alteration and common occurrence of copper sulfides in and around granodiorite intrusion, (3) low $\delta^{34}S$ values of pyrite by oxidational conditions of sulfide deposition, (4) low $\delta^{18}O$ values of quartz and feldspar in the granodiorite, and isotopic non-equilibrium by hydrothermal alteration. It suggest that hyrothermal alteration and mineralization should be genetically related to granodiorite intrusion in the Barton Peninsula. Due to the similarities in subaerial intrusive depth of pluton, age of intrusion and tectonic setting, hydrothermal alteration and occurrence of ore minerals, this area can be compared to surface expression of the porphyry copper deposits of the Chilean Andes. However, detailed field studies, accompanied by district zoning of alteration and mineralogy, and fluid inclusion studies are critical to further constrain the hydrothermal mineralization of the Barton peninsula, King George Island, Antarctica.

CONCLUSION

1. Granodiorite is a small and high level stock asso-

ciated with calc-alkaline volcanism, and have higher copper contents than average granitic rocks.

2. Propylitic alteration charaterized by actinolite, epidote, chlorite and calcite is widespread in grano- diorite and volcanic rocks. The dessiminations and veinlets of ore minerals such as pyrite, chalcopyrite and bornite are common in propylitic alteration zone.

3. Actinolite-bearing mineral asemblage, which is high temperature-type of propylitic alteration, is more common in and around granodioritic stock. It suggest that hydrothermal alteration should be genetically rela- ted to the granodiorite intrusion.

4. The main sulfide depositional conditions of temperature, sulfur and oxygen fugacity, estimated by mineral assemblages, are $250°C$, 10^{-11} atm. and 10^{-34} atm., respectively.

5. The $\delta^{34}S$ values of pyrites are -9.6 to 1‰ and estimated sulfur isotope composition of ore fluid indicate that the sulfur is igneous origin. The low $\delta^{34}S$ values of pyrites can be explained by oxidational condition of sufide deposition.

6. The $\delta^{18}O$ values of quartz and feldspar in the granodiorite are 0.7 to 5.1‰ which are lighter iso- topic composition than normal granitic rocks, and the non-equilibriated fractionational values of $\delta^{18}O$ be- tween quartz and feldspar result from hydrothermal alteration at low temperature.

ACKNOWLEDGMENTS

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남극 킹죠지섬 바톤반도 화강섬록암의 열수변질과 광화작용

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요   약 : 남극 킹죠지섬 바톤반도에는 신생대 제3기의 화산암류, 화산성 쇄설암류, 그리고 이들을 관입한 화강섬록암이 분포한다. 화강섬록암과 주변 화산암류에는 양기석, 녹염석, 녹니석, 방해석으로 특징지워지는 프로필리틱 열수변질대가 광범위하게 발달하며, 변질대에서는 황철석, 황동석, 반동석 등의 황화광물이 산점상 혹은 세맥상으로 산출된다. 화강섬록암 주변 열수변질작용의 특성에 관한 연구결과를 요약하면 다음과 같다; (1) 화강섬록암은 칼크-알칼리 계열의 천소관입 암상이며 동 함유량이 높다. (2) 화강섬록암의 주변을 중심으로한 상대적으로 높은 온도 유형의 프로필리틱 변질대가 발달하며 동-황화광물의 산출이 흔하다. (3) 황화광물은 산화환경 조건의 광화작용으로 가벼운 황동위원소 조성을 보인다. (4) 화강섬록암내 석영과 장석은 가벼운 산소동위원소 조성을 보이며 열수변질작용으로 비평형적인 동위원소 조성을 보인다. 이는 바톤반도 열수변질작용 및 광화작용이 화강섬록암체의 관입과 성인적으로 밀접한 관련이 있음을 시사한다.