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Hydrothermal alteration and isotopic variations of igneous rocks in Barton Peninsula, King George Island, Antarctica

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ABSTRACT: O, H, S and Sr isotopes were investigated to characterize the nature of hydrothermal fluids and alteration processes in volcanic and intrusive rocks in Barton Peninsula, King George Island. The oxygen and hydrogen isotope compositions of altered basaltic andesite and granodiorite are similar to each other. The δ^{18}O and δD values gradually decrease from altered basaltic andesite to altered dyke and quartz-veined volcaniclastic rock. The genetic linkage between hydrothermal fluid and granodiorite intrusion accounts for similar δ^{34}S values among sulfide minerals, both in the granodiorite stock and in nearby altered basaltic andesite. Broadly positive correlations of δ^{18}O-SiO_2, δ^{18}O-$(^{87}Sr/^{86}Sr)_i$, and $^{87}Sr/^{86}Sr$-SiO_2 can be established by siliceous fluids enriched in ^{18}O as well as ^{87}Sr. In addition, a positive relationship between $(^{87}Sr/^{86}Sr)_i$ values and 1/Sr contents in basaltic andesites can result from mixing between fresh rocks and infiltrating fluids with different end-member $^{87}Sr/^{86}Sr$ values and Sr contents. The hyperbolic variation of $(^{87}Sr/^{86}Sr)_i$-K/Rb suggests that meteoric water participated in hydrothermal activities via mixing with magmatic water, and the contribution of seawater was insignificant. All of the above results indicate that hydrothermal alteration was influenced by fluids related to granodiorite intrusion, and ^{18}O- and ^{87}Sr-rich meteoric water circulating in the upper crust significantly contributed to hydrothermal activities in Barton Peninsula.

Key words: isotope, volcanic rock, hydrothermal alteration, Barton Peninsula, Antarctica

1. INTRODUCTION

The South Shetland Islands represent a volcanic arc that formed during Cretaceous and Tertiary times, prior to the opening of the Drake Passage between Antarctica and the Southern Andes (Storey and Garrett, 1985). They are separated from the Antarctic Peninsula by the Bransfield Strait. King George Island is the largest island in the South Shetland Islands, and consists mainly of volcanic and plutonic rocks of the calc-alkaline series from Paleocene to Eocene epoch.

The geology and petrography of King George Island have been documented by several previous studies (Barton, 1965; Birkenmajer 1983; Smellie et al., 1984; Tokarski, 1988). Trace element and radiogenic isotope studies were conducted to constrain the timing of igneous activities, to discuss the magma source, and to investigate the evolutionary processes of the South Shetland Arc area (Lee et al., 1996; Kim et al., 2000, 2002; Yeo et al., 2004; Machado et al., 2005).

Numerous studies on hydrothermal alteration of the volcanic and intrusive rocks in the South Shetland Islands have also been carried out (Littlefair, 1978; Smellie et al., 1984; Birkenmajer et al., 1986; Park, 1991; So et al., 1995; Hur et al., 2001; Willan and Armstrong, 2002). Four types of wall-rock alteration were recognized and described by Littlefair (1978) and Park (1991): propylitic, phyllic (sericitic), argillic, and advanced argillic. Park (1991) suggested a model for the alteration zoning and genesis of the epithermal system at Barton Peninsula. Hur et al. (2001) described the mineral assemblage of altered rocks, and published age data for the hydrothermal alteration of different rock types. Based on petrographic evidence, most workers have related the alteration to the nearby Noel Hill pluton (e.g., Davies, 1982; Tokarski, 1988; So et al., 1995; Hur et al., 2001), and they regarded the alteration event as a post-granodiorite product. Willan and Armstrong (2002) suggested the additional possible role of a hidden igneous body, preceding the Noel Hill pluton found by petrographic and geochemical studies.

Though the nature of hydrothermal fluids has been discussed in previous studies (So et al., 1995; Hwang and Lee, 1998; Willan and Armstrong, 2002), it still remains unclear what types of igneous activities were related to hydrothermal fluids, and how the fluids evolved through fluid-rock interaction during hydrothermal processes. No systematic isotope study has yet been performed to discuss these problems. Thus, the present study aims to document the oxygen, hydrogen, sulfur, and strontium isotopic composition of volcanic and intrusive rocks, and to discuss the nature of hydrothermal fluids and alteration processes in accordance with isotope variation. The results will help us better understand the relationship between igneous activity and hydrothermal alteration.

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2. GEOLOGY

The South Shetland Islands were formed in a typical island arc setting around the northern Antarctic Peninsula and are dominated by volcanic rocks of the late Cretaceous to Miocene, in four stratigraphic/structural blocks younging in a southeast direction. The lithology of Barton Peninsula consists mainly of lavas, pyroclastic, and plutonic rocks (Fig. 1). The lowermost Sejong Formation (Yoo et al., 2001), formerly the Lower Volcanic Member (Davies, 1982), is distributed along the southern and southwestern coasts of Barton Peninsula. It is largely composed of volcaniclastic sediments with a maximum thickness of approximately 100 m, and gently dips to the south or southwest. Plant fossil leaves in fine-grained sandstones are suggestive of Late Paleocene to Eocene deposition (Chun et al., 1994).

Volcanic rocks are widespread in the peninsula, and mainly consist of basalt and basaltic andesite. They show

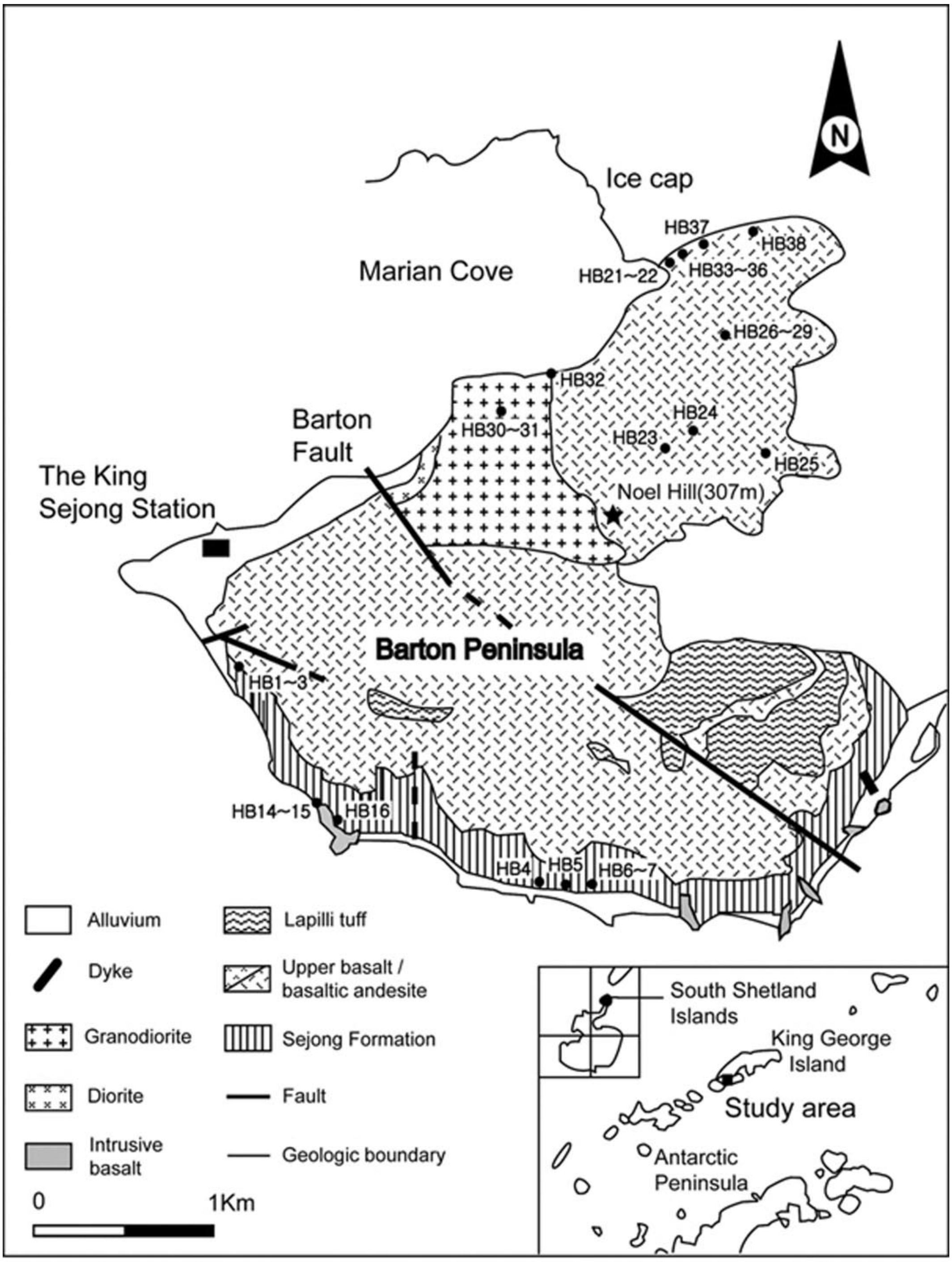

Fig. 1. Geologic map of Barton Peninsula in King George Island, Antarctica (after Kim et al., 2000). Sample locations are also shown.

porphyritic textures, in which plagioclase occurs as phenocrysts, together with minor proportions of clinopyroxene and orthopyroxene. Several units of thick-bedded lapilli tuffs are intercalated and occur in the eastern part of the peninsula, to the north of the Barton Fault and locally to the south. Secondary minerals such as hornblende, actinolite, epidote, chlorite, calcite, mica, quartz, and opaque minerals are common in these volcanic rocks (Kim et al., 2002). The volcanic sequence is transitional between tholeiitic and calc-alkaline and is probably derived from a single fractionating magma (Willan and Armstrong, 2002).

Several basaltic plugs and dikes trending north or northwest have intruded the Sejong Formation along the southern coast of the peninsula. They are generally plagioclase-phyric or massive basaltic andesites, and they commonly show microscopic flow structures (Willan and Armstrong, 2002).

In western King George Island, calc-alkaline granodiorite and diorite plutons occur exclusively in Barton Peninsula. Granodiorite forms a stock in association with minor fine-grained diorite at Noel Hill, in the northern part of the peninsula. The southwestern boundary between the Noel Hill pluton and the volcanic rocks is partly defined by a fault, although the exact relationship is difficult to determine due to the lack of exposure. The ubiquitous occurrence of miarolitic cavities indicates a relatively shallow emplacement near the surface (Kim et al., 2002).

Most of the rocks in Barton Peninsula have been exposed to extensive hydrothermal alteration. Hur et al. (2001) and Willan and Armstrong (2002) argued that propylitic alteration was dominant over the entire range of Barton Peninsula, especially in the northern part by enclosing the advanced argillic alteration zone. However, because of the multiplicity of hydrothermal episodes, it is difficult to unravel the alteration affinities or boundaries, and to constrain the precise eruption or alteration ages. However, most ages are concentrated at two modes: the early Cretaceous period and the Paleocene to Eocene epochs (Smellie et al., 1984; Tokarski, 1988; Lee et al., 1996; Kim et al., 2000; Hur et al., 2001).

Kim et al. (2000) published Ar-Ar ages of basaltic andesites, which are defined as two distinct plateau ages of 52-53 Ma and 119-120 Ma. The latter is interpreted to represent the primary cooling age of basaltic andesites, while the former is regarded as thermally-reset age caused by the intrusion of Tertiary granitic pluton. K-Ar ages of granodiorite reported by Watts (1982), Smellie et al. (1984), Park (1989), and Lee et al. (1996) range from 41 to 50 Ma, slightly younger than Ar-Ar ages. In regard to the timing of hydrothermal activities, Hur et al. (2001) published several K-Ar ages of various altered rocks, 28-35 Ma, which are younger than the granodiorite intrusion age.

3. ANALYTICAL METHODS

All the samples for isotope analyses were the residual splits of bulk rock powders used for geochemical analyses by Hur et al. (2001). Sample locations are provided in Figure 1. Oxygen, hydrogen, sulfur and strontium isotopic compositions were analyzed for four less altered basaltic andesites. (These samples are petrographically fresh, but show a rather variable range of oxygen isotope compositions and LOI (Loss On Ignition) contents.) Also analyzed were eighteen altered basaltic andesites, six quartz-veined volcaniclastic rocks, three altered dykes, and three granodiorite samples.

For oxygen isotope analysis, the samples were treated with HCl to dissolve the carbonate fraction, and oxygen was extracted using the BrF_5 method of Clayton and Mayeda (1963). The CO_2 gas was analyzed on the Finnigan MAT 252 with a dual-inlet mass spectrometer at Indiana University. The data were calibrated with respect to NBS-28 quartz of 9.6‰, and the sample reproducibility was better than ±0.25‰.

Hydrogen isotope compositions were analyzed using a high-temperature-elemental analyzer-continuous flow method similar to that reported by Sharp et al. (2001). Samples were loaded into silver cups and combusted at 1400 °C in a glassy carbon column. Hydrogen was analyzed using a Finnigan Delta Plus-XP stable isotope mass spectrometer at Indiana University. Internal standards, including actinolite (-69‰), hornblende (-80‰) and serpentine (-100‰) were run for each series of the analysis, and they were calibrated relative to NBS-30 biotite (-65‰). The sample reproducibility was within ±2.0‰. Both oxygen and hydrogen are reported in delta notation with respect to VSMOW (Vienna Standard Mean Ocean Water).

For sulfur isotope measurements, whole-rock powders were analyzed using elemental analyzer-continuous flow isotope ratio mass spectrometry (Studley et al., 2002). Sample powders (1 mg to 150 mg) were placed in tin cups with 1 to 5 mg of V_2O_5 and combusted at ~1800 °C, with a reactor column temperature of 1010 °C. Analyses of SO_2 were made using a Finnigan MAT 252 stable isotope ratio mass spectrometer at Indiana University, with the results reported in standard delta notation relative to CDT (Canyon Diablo Troilite). The instrumental uncertainty for each analysis was less than ±0.05‰, and sample reproducibility was within ±0.3‰.

Sr isotopic compositions of whole-rock powders were analyzed at Korea Basic Science Institute. For the analysis, 10 mg of the powders were mixed with highly enriched ^{84}Sr spikes and then dissolved with a mixed acid ($HF:HClO_4$ = 10:1) in Teflon vessels. Sr fractions were separated by conventional carbon column chemistry (Dowex AG50W-X8, H^+ form) in HCl medium. Isotopic ratios were measured using a VG54-30 thermal ionization mass spectrometer equipped with nine Faraday cups. Instrumental fractionation was normalized to $^{86}Sr/^{88}Sr = 0.1194$, and the measured $^{87}Sr/^{86}Sr$ ratio was further corrected for the added spikes. Total procedural blank levels were around 60 pg.

4. RESULTS

The oxygen, hydrogen, sulfur and strontium isotope compositions are listed in Table 1. Oxygen isotope compositions vary from 4.1 to 9.8‰ in basaltic andesite. The $\delta^{18}O$ values of quartz-veined volcaniclastic rocks vary considerably from 1.6 to 13.6‰. In contrast, altered dykes are relatively depleted in ^{18}O ranging from 1.1 to 2.5‰. Two fresh granodiorite samples show 4.9 and 5.8‰, while one altered granodiorite in contact with basaltic andesite has a comparatively high $\delta^{18}O$ value of 10.9‰.

The δD values of less altered basaltic andesite span relatively narrow range from -86 to -82‰, while those of altered basaltic andesite became heavier and scattered from -82 to -71‰. The latter is similar to those of granodiorite, which are from -79 to -74‰. The δD values of quartz-veined vol-

Table 1. Oxygen, hydrogen, sulfur and strontium isotope data for igneous rocks from Barton Penninsula

Sample No.	$\delta^{18}O$	δD	$\delta^{34}S$	Age (Ma)1)	Rb (ppm)	Sr (ppm)	$(^{87}Sr/^{86}Sr)m$	Error (ppm)	$^{87}Rb/^{86}Sr$	$(^{87}Sr/^{86}Sr)i$2)	K/Rb3)	SiO_2 (wt.%)3)	LOI (wt.%)3)
less altered basaltic andesite													
HB25	7.7	-84	No peak	52	14	478	0.703546	12	0.086194	0.703483	926	55.77	3.39
HB26	4.9	-86	No peak	52	7	552	0.703454	11	0.036250	0.703427	722	54.87	3.36
HB37	6.0	-83	No peak	52	11	572	0.703320	14	0.053212	0.703280	998	57.77	0.23
HB38	8.3	-82	No peak	52	1	590	0.703218	10	0.003945	0.703215	2486	53.99	2.53
altered basaltic andesite													
HB02	9.5	-81	No peak	34	94	36	0.708166	11	7.535835	0.704527	494	77.28	0.64
HB03	6.6	-78	-6.3	34	63	178	0.704188	12	1.023803	0.703694	516	70.93	1.75
HB21	5.8	-76	-0.6	34	5	358	0.703507	11	0.038901	0.703488	956	56.54	2.71
HB22-1	8.6	-74	-1.5	34	5	231	0.703494	10	0.057184	0.703466	1204	57.55	2.28
HB23	4.1	-76	-7.9	34	23	364	0.703603	11	0.179352	0.703516	492	68.95	0.55
HB24	4.7	-76	No peak	34	53	503	0.703567	15	0.305245	0.703420	367	55.14	2.76
HB27	8.9	-76	-7.3	34	1	864	0.703430	20	0.003231	0.703428	56690	76.16	0.18
HB28	7.9	-82	-10.6	34	13	655	0.703554	22	0.055992	0.703527	686	57.78	2.79
HB29	8.4	-74	-3.4	34	-	-	-	-	-		-	60.64	4.29
HB32-2	5.2	-81	-1.0	34	18	289	0.703578	10	0.177993	0.703492	355	55.02	2.46
HB32-3	7.4	-81	-2.1	34	49	97	0.704341	6	1.454296	0.703639	477	69.66	2.81
HB32-4	7.3	-79	-2.4	34	58	478	0.703536	11	0.215966	0.703432	482	53.92	2.57
HB32-5	8.2	-78	1.2	34	94	148	0.704620	50	1.841346	0.703731	334	73.07	0.74
HB32-6	8.1	-80	0.6	34	54	380	0.703826	19	0.410418	0.703628	414	60.23	2.23
HB32-7	6.6	-71	0.4	34	24	452	0.703517	12	0.152719	0.703443	478	63.03	0.21
HB33	7.5	-79	-6.6	34	26	468	0.703554	14	0.161267	0.703476	410	68.57	1.38
HB35	6.5	-75	-4.3	34	1	611	0.703447	19	0.006563	0.703444	1010	48.96	2.80
HB36	9.8	-75	No peak	34	2	133	0.703419	11	0.044000	0.703397	544	78.29	1.44
quartz-veined volcaniclastic rock													
HB04-2	13.6	-79	-	31	3	12	0.704035	12	0.588513	0.703776	1077	92.68	1.56
HB05	9.3	-79	-10.4	31	17	56	0.704227	11	0.876757	0.703841	652	68.44	2.89
HB06	7.9	-88	-7.7	31	17	166	0.703711	12	0.299122	0.703579	680	56.91	3.17
HB07	6.2	-83	-6.1	31	7	165	0.703791	12	0.117264	0.703740	643	66.72	3.21
HB16A	3.4	-80	-	31	17	391	0.703541	14	0.127065	0.703485	611	55.86	2.32
HB16B	1.6	-83	-	31	6	784	0.703491	12	0.020637	0.703482	644	48.20	2.03
altered dyke													
HB01	1.1	-91	No peak	34	2	596	0.703554	12	0.010014	0.703549	678	47.01	2.54
HB14	2.1	-83	-7.6	34	79	367	0.703835	14	0.619070	0.703536	412	59.66	2.19
HB15	2.5	-83	-7.0	34	29	354	0.703598	12	0.239044	0.703483	574	57.81	0.28
granodiorite													
HB30	4.9	-75	No peak	42	52	416	0.703709	11	0.359736	0.703443	479	60.57	1.66
HB31	5.8	-79	No peak	42	48	349	0.703682	10	0.398981	0.703387	504	62.00	1.63
HB32-1	10.9	-76	-0.9	42	74	327	0.703850	12	0.652446	0.703368	433	65.20	0.24

-: not analyzed, 1) see text, 2) Initial Sr isotopic composition based on the data of 1) except granodiorite, which was corrected to 52Ma, the thermally-reset ^{40}Ar-^{39}Ar age of basaltic andesite caused by the granodiorite intrusion (Kim et al., 2000), 3) from Hur et al. (2001)

caniclastic rock, -88 to -79‰, and altered dyke, -91 to -83‰, are generally lower than those of altered basaltic andesite.

The $\delta^{34}S$ values of various rock types differ from each other according to their localities. Most $\delta^{34}S$ values of altered basaltic andesites range from -7.9 to +1.2‰, except one specimen (HB28: -10.6‰). Among them, the HB32 series samples (HB32-2 to 32-7) in contact with granodiorite are concentrated in heavy isotopes ranging from -2.4 to 1.2‰. The $\delta^{34}S$ values of the samples from the southern coast of the peninsula are typically low, -10.4 to -6.1‰ in quartz-veined volcaniclastic rock and -7.6 to -7.0‰ in altered dyke. These are lower than those of altered basaltic andesite. The amounts of sulfur present in less altered basaltic andesite and granodiorite were below the detection limit for isotope measurement, but one altered granodiorite produced a $\delta^{34}S$ value of -0.9‰.

Initial Sr isotopic compositions of less altered basaltic andesite span relatively a narrow range from 0.703215 to 0.703483. In other rock types, $(^{87}Sr/^{86}Sr)_i$ ratios are generally higher than those of less altered basaltic andesite. The $(^{87}Sr/^{86}Sr)_i$ ratio of granodiorite ranges from 0.703387 to 0.703443, and in altered basaltic andesite from 0.703397 to 0.704527. In quartz-veined volcaniclastic rock, $(^{87}Sr/^{86}Sr)_i$ ratios range from 0.703482 to 0.703841, and in altered dyke from 0.703483 to 0.703549, which are similar to those of granodiorite.

5. DISCUSSION

5.1. Oxygen and Hydrogen Isotopes

Though the $\delta^{18}O$ values for less altered basaltic andesite belong to the oxygen isotope range of common primary andesitic rocks in arc environments (Macpherson et al., 1998; Bindeman et al., 2004), they are relatively wide to be classified as magmatic and primary. It has been reported that hydrothermal differentiation and alteration could overlap magmatic differentiation processes to a large extent, producing wide range of $\delta^{18}O$ values in igneous rocks (Vroon et al., 2001; Goll et al., 2003). Similarly, the wide range of $\delta^{18}O$ values of altered basaltic andesite could result from high- and low- temperature exchange with meteoric waters, and isotopic disequilibrium during the alteration process.

The low $\delta^{18}O$ values of granodiorite, 4.9 to 5.8‰, belong to the group of low ^{18}O granitic rocks ($\delta^{18}O < 6.0‰$), according to Taylor (1978). Granitic rocks with $\delta^{18}O$ values lower than 6‰ cannot be derived by any differentiation process from basaltic magmas, excluding those that have exchanged with ^{18}O-depleted meteoric-hydrothermal fluids under subsolidus conditions at high temperatures (Taylor, 1987). On the contrary, one slightly altered granodiorite (HB32-1), consisting mostly of quartz and plagioclase with a minor phase of halloysite at the contact with basaltic andesite, has an anomalously high $\delta^{18}O$ value of 10.9‰. This enrichment could result from non-equilibrated isotopic exchange with infiltrating fluids, as evidenced by the isotopic relation between the quartz-feldspar pairs of Hwang and Lee (1998), where feldspar typically underwent significant $\delta^{18}O$ change during hydrothermal alteration (Criss and Taylor, 1983; Goll et al., 2003).

As for quartz-veined volcaniclastic rocks, two high $\delta^{18}O$ values, 13.6 and 9.3‰, were measured for the samples, HB04 and HB05, respectively, consisting mostly of large quartz crystals. Other smaller quartz-veined volcaniclastic rocks, consisting of quartz, plagioclase, chlorite and calcite, have lower values of 1.6 to 7.9‰. This leads us to suggest that mineralogical variation of the rocks was closely coupled to their isotopic alteration.

The H_2O contents of the samples analyzed for stable isotope were not measured in this study, but only LOI values were provided by Hur et al. (2001). Since propylitized volcanic rocks contain calcite, besides chlorite and epidote, to a certain degree, the LOI values would be different from their H_2O contents. However, the LOI values of the HB32 series samples, which were collected at intervals of about 1 m from the intrusive rock contact and appear to be free from carbonate minerals, may approximate the H_2O contents. Thus, if δD and LOI values of HB32 samples are plotted on a diagram, they show a trend of increasing δD with decreasing LOI content (Fig. 2). This negative slope can be established by low temperature hydration or by loss of H_2O (Kyser and O'Neil, 1984). Because the δD values of minerals may vary depending on the water composition involved in hydrothermal alterations, this negative trend could be caused by the infiltration of meteoric water with low δD values around the cooling pluton.

In summary, the δD values of altered basaltic andesite

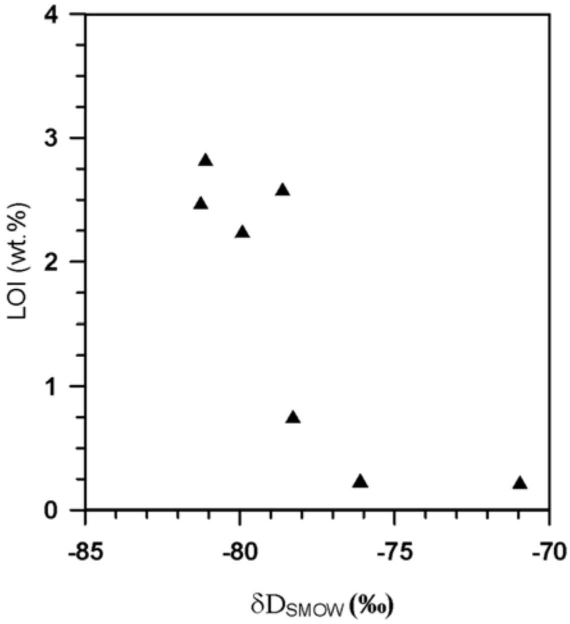

Fig. 2. Plot of LOI (Loss On Ignition) vs. δD for HB32 series rocks.

rock increased in comparison to those of less altered basaltic andesite with a relatively constant oxygen composition. Considering the similarities of the hydrogen and oxygen isotope compositions between altered basaltic andesite and granodiorite, the alteration of basaltic andesites would have been influenced by hydrothermal fluids related to granodiorite intrusion. Quartz-veined volcaniclastic rocks and dyke rocks, which intruded basaltic andesite, have lower δD values than other rock types (Table 1). The variation implies that the decrease in δ^{18}O and δD values, consecutively from altered basaltic andesite to altered dyke and quartz-veined volcaniclastic rocks, could be related to the growing effect of meteoric water in the hydrothermal fluid system (So et al., 1995; Hwang and Lee, 1998; Hur et al., 2001; Willan and Armstrong, 2002). During the process the pluton may have acted as a passive heat source driving groundwater circulation through nearby faults.

In view of the geographic position of the study area, the H-isotope composition of meteoric water during the time of hydrothermal activities could be extremely low. It is necessary, however, to consider paleoclimate data to estimate the isotope composition of meteoric water when the alteration took place. The mean annual temperature of King George Island during the Middle Eocene was generally between 12 ºC and 13.3 ºC (Poole et al., 2005), much higher than the present average -2.8 ºC (Ferron et al., 2004). Thus, this suggests that the isotopic composition of meteoric water during the alteration process would have not been so low as that of the present time.

5.2. Sulfur Isotopes

It has been reported that sulfur from the volcanic arc systems commonly has δ^{34}S values higher than 0‰ (Alt et al., 1993; Hoog et al., 2001; Hoefs, 2004). Most of the δ^{34}S values in the study area, however, are below 0‰. The highest values are those of the HB32 series, -2.4 to 1.2‰, which are in contact with granodiorite. They are much higher than those of other altered basaltic andesite, -10.6 to -0.6‰, showing propylitic or advanced argillic alteration zones.

Generally low sulfur isotope compositions in Barton Peninsula could be ascribed to higher oxidational conditions, when sulfide minerals were precipitated in altered volcanic rocks rather than in altered granodiorite (Hwang and Lee, 1998). In addition, previous studies (Tokarski et al., 1987; Chun et al., 1994) reporting the presence of purple or black shale along the southern coast, where plant remains have been found, raise a possibility that the δ^{34}S values in this area could have been affected by biogenic sulfur from sedimentary rocks in a high oxidational state of precipitating fluids. Nevertheless, the input of biogenic sulfur, which commonly has δ^{34}S value between -30 and -10‰ (Ohmoto and Goldhaber, 1997; Shen et al., 2001), does not seem to be strong, as the resultant δ^{34}S values are mostly higher than -10‰.

The low concentration of sulfur in less altered basaltic andesite and granodiorite suggests that most sulfur present in the altered rocks was introduced after their primary formation. This harmonizes with the age data, indicating that hydrothermal alterations accompanying sulfide mineralization occurred during the cooling stage after granodiorite intrusion (Hur et al., 2001).

An alternative interpretation has been raised that the heat source of the hydrothermal system is a hidden pluton underlying the alteration zone (Armstrong, 1995; Kim et al., 2002). However, in view of the mineralogical and stable isotopic evidence, it is still probable that hydrothermal alteration was genetically related to granodiorite intrusion. This suggestion is based mainly on two observations: (1) high temperature-types of propylitic alteration and actinolite-bearing mineral assemblages are more common near granodiorite stock; and (2) the δ^{34}S values of sulfide minerals in and around the stock are similar to each other, -0.9 to +1.0‰ in the stock body (Hwang and Lee, 1998; this study) and -2.4 to +1.2‰ in the neighboring altered basaltic andesite (HB32 series).

5.3. Fluid Evolution and Isotopic Variation

5.3.1. Variation of δ^{18}O vs. SiO_2 concentration

In Figure 3, the δ^{18}O values of volcanic rocks are plotted as a function of SiO_2 content, in order to test whether the isotopic range could be generated by fractional crystalliza-

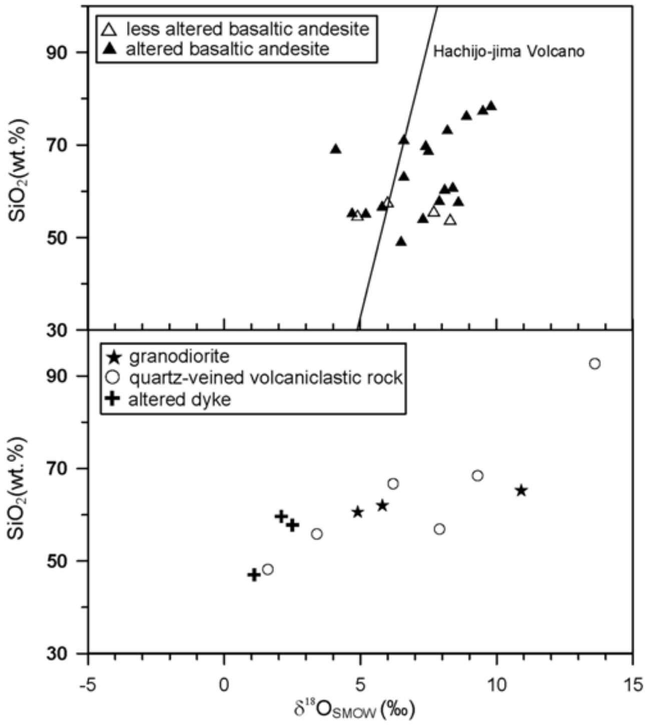

Fig. 3. Plot of SiO_2 vs. δ^{18}O for the analyzed samples. The Hachijo-jima volcanic trend of Matsuhisa (1979) is shown for reference.

tion alone, or in combination with other processes. The data array for basaltic andesites shows a broad tendency of positive correlation with some outliers. This trend could be explained by contamination with an ^{18}O-rich crust during intracrustal differentiation. However, this explanation could be wrong if the overall positive correlation is ascribed to such magmatic processes. Instead, for this trend, the effect of post-eruptive hydrothermal processes should be considered, as evidenced by mineralogical and geochemical characteristics indicating extensive hydrothermal alteration in the volcanic rocks (So et al., 1995; Hur et al., 2001; Willan and Armstrong, 2002). As given in Table 1, the SiO_2 content of less altered basaltic andesites is between 54 and 58 wt%, while that of the altered basaltic andesite is mostly much higher, even up to 78 wt%. This difference seems to be the result of hydrothermal alteration characterized by intensive silicification of volcanic rocks, as evidenced by the common development of quartz veins and silicic aureole around the igneous body (Hur et al., 2001; Willan and Armstrong, 2002).

The positive correlation is evident, especially, in quartz-veined volcaniclastic rocks (Fig. 3). One of them, HB04-2, having the highest SiO_2 concentration of as much as 93 wt%, shows the highest $\delta^{18}O$ value, 13.6‰. This implies that the enrichment of ^{18}O in the altered rock types is strongly controlled by silicification during the hydrothermal process.

5.3.2. Variation of $\delta^{18}O$ vs. $(^{87}Sr/^{86}Sr)_i$

In contrast to the well-defined $\delta^{18}O$-SiO_2 variations, the $\delta^{18}O$-$(^{87}Sr/^{86}Sr)_i$ data do not show a clear trend, and are less impressive (Fig. 4). This may in part be due to the use of whole rocks rather than mineral separates, and probably due to hydrothermal alteration after volcanic eruption. The data for basaltic andesites form a steep or slightly positive trend at a characteristic, relatively uniform $^{87}Sr/^{86}Sr$ ratio. The samples, which form a slightly positive trend, belong to the highest SiO_2 (70-77 wt%) group. It seems likely that basaltic andesites, which originally show a vertical variation, became enriched in ^{87}Sr by the reacting fluids during hydrothermal alteration.

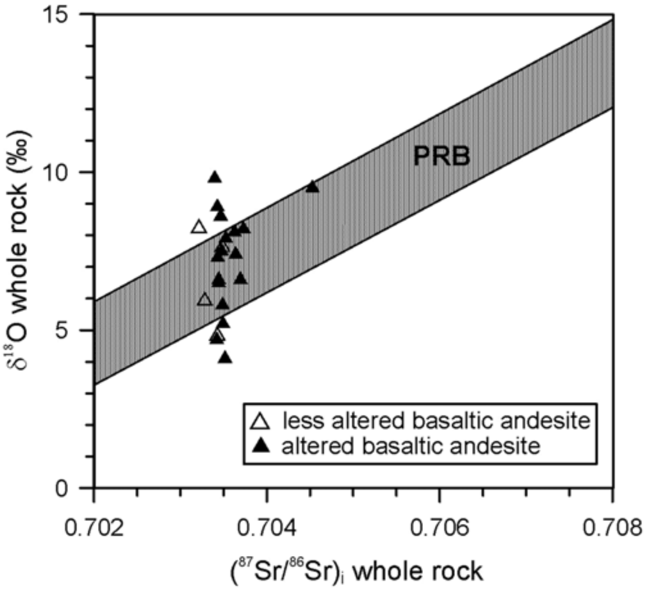

Fig. 4. Plot of $\delta^{18}O$ vs. $(^{87}Sr/^{86}Sr)_i$ for basaltic andesites. The PRB (Peninsula Ranges Batholith) trend is shown for comparison (Taylor and Silver, 1978).

5.3.3. Variation of $^{87}Sr/^{86}Sr$ vs. SiO_2 concentration

It has been known that fractional crystallization could produce nearly uniform $^{87}Sr/^{86}Sr$ ratios with variable SiO_2 content, as exemplified by Santorini, Greece (Barton et al., 1983) and the Lesser Antilles (Davidson, 1986). However, a positive correlation between the $^{87}Sr/^{86}Sr$ ratio and the SiO_2 content of volcanic rocks from subduction-related regions has been reported in many cases, and commonly attributed to crustal contamination (e.g., St Lucia: Davidson, 1987; Monte Arcuentu: Downes et al., 2001).

The plot of $^{87}Sr/^{86}Sr$ vs. SiO_2 for volcanic rocks from Barton Peninsula forms a weak and gentle positive correlation, especially for the HB32 series rocks (Fig. 5). This trend, however, cannot be attributed only to crustal contamination during magma ascent. It is mostly likely, as discussed above, that primary geochemical signatures including $^{87}Sr/^{86}Sr$ ratios were significantly affected by siliceous fluids during the alteration process.

5.3.4. Variation of $(^{87}Sr/^{86}Sr)_i$ vs. 1/Sr

The $(^{87}Sr/^{86}Sr)_i$ values of less altered basaltic andesites belong to the range of the present MORB (Mid-Oceanic Ridge Basalt) (0.702-0.704) (Dickin, 2005). The measured data are the lowest values, as a group, among several South Shetland islands, and are similar to those of King George Islands reported by Machado et al. (2005) (Fig. 6). The Sr isotope compositions of altered basaltic andesite, however, increase over those of less altered basaltic andesite, while Sr

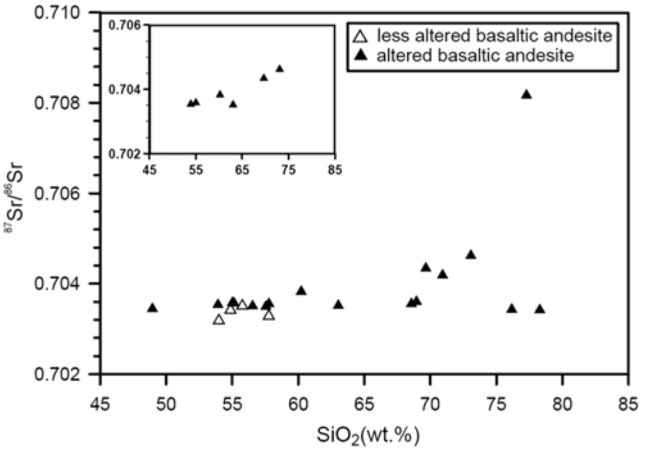

Fig. 5. Plot of $^{87}Sr/^{86}Sr$ vs. SiO_2 for basaltic andesites. Inset diagram is for the HB32 series rocks.

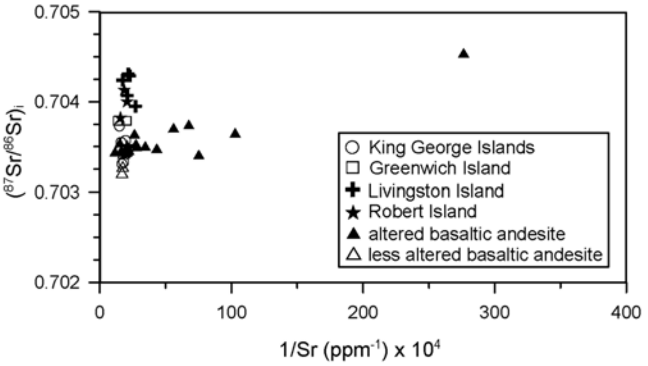

Fig. 6. Plot of $(^{87}Sr/^{86}Sr)_i$ vs. 1/Sr for igneous rocks in Barton Peninsula (this study) and other islands in South Shetland Islands (Machado et al., 2005).

concentrations decrease from less altered basaltic andesite (548 ppm in average) to altered basaltic andesites (367 ppm in average). Thus, $(^{87}Sr/^{86}Sr)_i$-1/Sr diagram shows a positive correlation (Fig. 6). This relationship can be derived from a process similar to the hydrothermal alteration given for the $\delta^{18}O$-SiO_2 variation: a mixing between original fresh rocks with low $(^{87}Sr/^{86}Sr)_i$ and high Sr content and infiltrating fluids with high $(^{87}Sr/^{86}Sr)_i$ and low Sr content.

5.4. Seawater vs. Meteoric Water

In volcanic rocks, Sr isotope compositions vs. K/Rb ratios commonly fit a hyperbolic curve, as the result of mixing of two components: one with high K/Rb and low $(^{87}Sr/^{86}Sr)_i$ (mantle source), and the other with low K/Rb and high $(^{87}Sr/^{86}Sr)_i$ (crustal source) (Davidson, 1986). Most K/Rb values of basaltic andesites in Barton Peninsula are much lower than those of seawater (K/Rb=3000) (Staudigel et al., 1981), and the data form a “L-type” correlation with $(^{87}Sr/^{86}Sr)_i$ values, similarly to common volcanic rocks (Fig. 7). An andesite (HB02) has a high $(^{87}Sr/^{86}Sr)_i$ value (=0.7045), but retains a K/Rb ratio below 500. In contrast, a less altered basaltic andesite (HB38) has a high K/Rb value (=2486) while its Sr isotopic composition ranks the lowest among the analyzed samples. One altered basaltic andesite, HB27, not plotted in Figure 7, has an extraordinarily high K/Rb ratio (=56690) with a low Sr isotope value (Table 1). Thus, no specimens are plotted near or towards the K/Rb and $^{87}Sr/^{86}Sr$ ratios (0.70907; Hess et al., 1986) of seawater. This suggests that seawater participation during the hydrothermal alteration in basaltic andesite was insignificant.

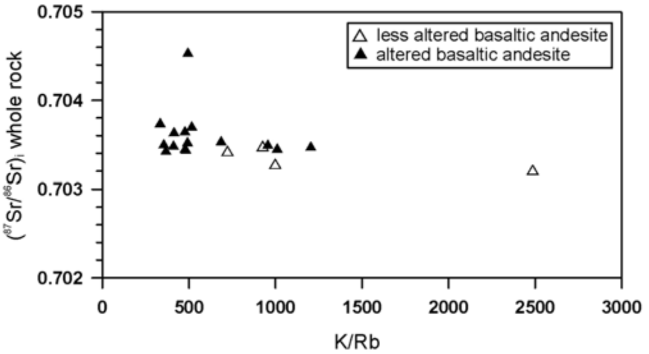

Fig. 7. Plot of $(^{87}Sr/^{86}Sr)_i$ vs. K/Rb for basaltic andesites.

A similar conclusion can be drawn from the $\delta^{18}O$-$(^{87}Sr/^{86}Sr)_i$ variation (Fig. 4). It has been shown that pervasive hydrothermal circulation changed the $\delta^{18}O$ values of whole rock and minerals profoundly (Goll et al., 2003). If equilibrium was established through the exchange with seawater, $\delta^{18}O$ values should approach 0‰ and $^{87}Sr/^{86}Sr$ values might be expected to be elevated towards the value of seawater (0.70907), producing a negative sense. The correlation described in Figure 4, however, is not negative at all.

6. CONCLUSIONS

(1) The similarities between altered basaltic andesite and granodiorite, in both oxygen and hydrogen isotope compositions, imply that alteration of basaltic andesites was influenced by hydrothermal fluids related to granodiorite intrusion.

(2) The gradual decrease in $\delta^{18}O$ and δD values from altered basaltic andesite to altered dyke and quartz-veined volcaniclastic rock could be related to the effect of meteoric water in the hydrothermal system. The hyperbolic variation between Sr isotope compositions and K/Rb ratios also implies that meteoric water participated in hydrothermal activities via mixing with magmatic water, and the contribution of seawater was insignificant.

(3) Hydrothermal alteration genetically related to granodiorite intrusion produced similar $\delta^{34}S$ values among sulfide minerals both in and around the granodiorite stock, ranging from -0.9 to +1.0‰ in the stock body, and from -2.4 to +1.2‰ in altered basaltic andesite near the stock. Low $\delta^{34}S$ values, ranging from -10.6 to -0.6‰, for the volcanic rocks could be caused mainly by a high oxidational state of precipitating fluids with little influence of biogenic sulfur from sedimentary rocks.

(4) Broadly positive correlation of $\delta^{18}O$-SiO_2, $\delta^{18}O$-$(^{87}Sr/^{86}Sr)_i$, $^{87}Sr/^{86}Sr$-SiO_2, and $(^{87}Sr/^{86}Sr)_i$-1/Sr in basaltic andesite and other igneous rock types can be attributed to the infiltration of siliceous fluids enriched in ^{18}O as well as ^{87}Sr with low Sr content.

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