

Isotope Geochemistry of Volcanic Rocks from the Barton Peninsula, King George Island, Antarctica

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ABSTRACT: C, O, H, S and Sr isotopes were investigated to characterize the isotopic composition of the Paleocene–Eocene volcanic rocks in Barton Peninsula, King George Island, Antarctica. The analyzed samples of volcanic rocks cover a range from basalt to andesite. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of calcite in volcanic rocks range from -7.5‰ to -3.2‰ and 0.4‰ to 5.1‰ , respectively. The homogenous $\delta^{13}\text{C}_{\text{cal}}$ and depleted $\delta^{18}\text{O}_{\text{cal}}$ values relative to primary magmatic values reflect the effect of high temperature alteration of volcanic rocks. The $\delta^{18}\text{O}$ of volcanic rocks ranges from -1.1‰ to 7.2‰ , and the majority of values are significantly lower than those of primary magmatic values. The low $\delta^{18}\text{O}_{\text{WR}}$ values are compatible with high temperature alteration. The initial values of $^{87}\text{Sr}/^{86}\text{Sr}$ of volcanic rocks span a narrow range from 0.703 312 to 0.703 504 which belong to the present mid-oceanic ridge basalt. The values of $^{87}\text{Sr}/^{86}\text{Sr}$ of volcanics in the Barton Peninsula are similar to those determined in the Fildes Peninsula, King George Island. The $\delta\text{D}_{\text{WR}}$ and H_2O contents of volcanic rocks range from -74‰ to -66‰ and 0.67 wt.% to 2.74 wt.%, respectively. The higher $\delta\text{D}_{\text{WR}}$ and H_2O wt.% of volcanic rocks relative to fresh basalts also result from high temperature alteration. Sulfur isotope compositions of the volcanic rocks range from -12.5‰ to -7.0‰ ; these values may represent fractionation accompanying partial oxidation of magmatic S or incorporation of some bacteriogenic sulfide. The low S contents and negative correlation with C and H_2O reflect the formation of calcite and breakdown of sulfide as a result of high temperature water-rock interaction.

KEY WORDS: isotope, volcanic rock, high temperature alteration, Antarctica.

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INTRODUCTION

The South Shetland Islands form a 550-km-long archipelago at the southwestern end of the Scotia Ridge, and are separated from the Antarctic Peninsula by the Bransfield Strait, which is a marginal basin. The South Shetland Islands are an Early Cretaceous to Miocene volcanic arc system resulting from the sub-

duction of the Pacific plate under the Antarctic continent. King George Island is the largest island in the South Shetland Islands which were formed in a typical island arc setting around the northern Antarctic Peninsula (Fig. 1), and consists mainly of subalkaline volcanic and plutonic rocks of Paleocene to Eocene. The geology and petrography of King George Island have been documented in many previous studies (Park, 1989; Tokarski, 1988; Smellie et al., 1984; Birkenmajer, 1982). The contributions of subducted material to source magma have recently been evaluated by trace element and radiogenic isotope studies (Machado et al., 2005; Yeo et al., 2004; Birkenmajer et al., 1991).

Several studies have documented evidence for thermal or hydrothermal alteration throughout the altered volcanic sequences in the South Shetland Islands (Birkenmajer et al., 1986; Smellie et al., 1984). Vol-

canic rocks in the Barton Peninsula located in the southwestern part of King George Island are also altered and have been described by many workers. Smellie et al. (1984) and Armstrong (1995) reported albite-epidote hornfels or greenschist facies thermal metamorphism caused by a granodiorite intrusion near Noel Hill. Kim et al. (2002) reported thermal metamorphism up to the upper greenschist facies, and suggested that the Noel Hill pluton was not the major heat source for the metamorphism. On the other hand, So et al. (1995), Hwang and Lee (1998), and Willan and Armstrong (2002) reported that the altered volcanic rocks that contain secondary minerals such as epidote, chlorite, actinolite, alunite and calcite were formed by hydrothermal alteration. Willan and Armstrong (2002) reported at least three distinct fossil hydrothermal episodes and four types of alteration zones distributed

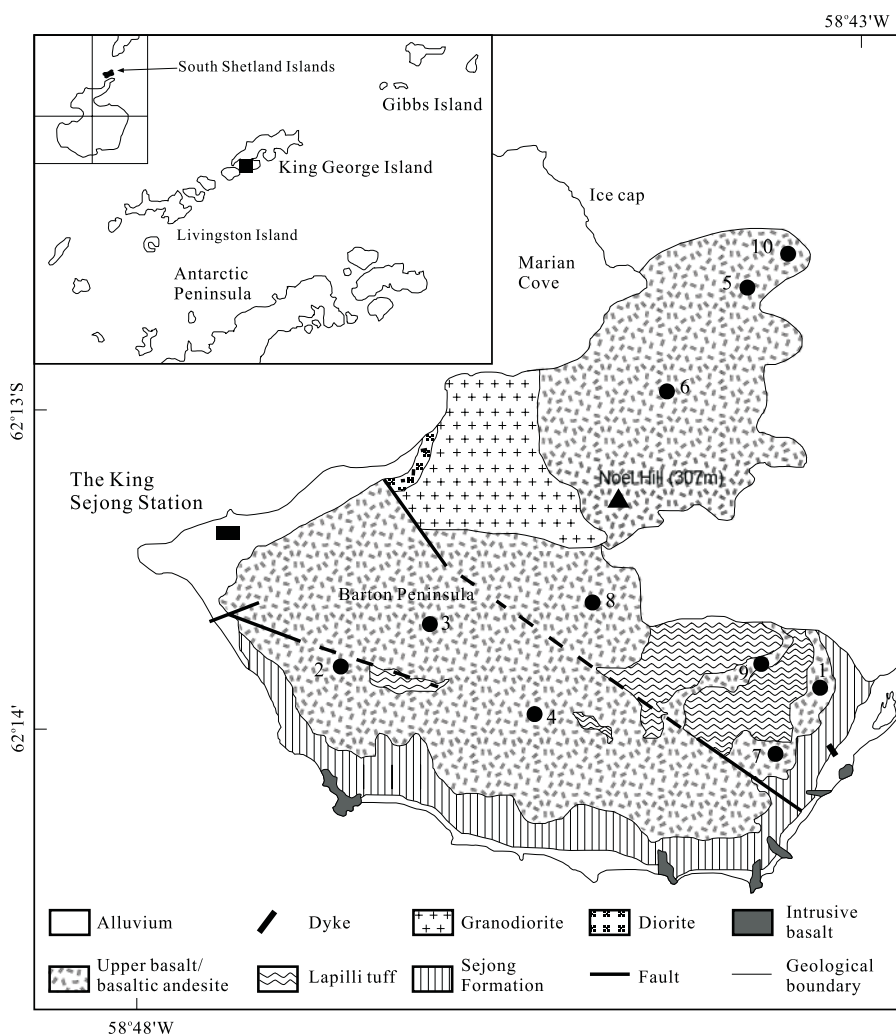


Figure 1. Geological map of the Barton Peninsula, King George Island, Antarctica (modified from Lee et al., 2002). The sample numbers are shown as filled circles.

linearly along fracture zones.

Many workers have related the alteration to the nearby Noel Hill pluton (Hur et al., 2001; Armstrong, 1995; So et al., 1995; Davies, 1982), and they regarded the alteration event as a post-granodiorite product. Some workers suggested the additional possible role of a hidden igneous body, preceding the Noel Hill pluton found by petrographic and geochemical studies (Kim et al., 2002; Willan and Armstrong, 2002). Although there have been many studies on the altered volcanic rocks in the study area, there still remains an uncertainty as to the source and extent of the thermal metamorphism and hydrothermal alteration. This uncertainty is caused by petrographic occurrences of volcanic rocks that indicate that metamorphosed volcanic lavas are overprinted by hydrothermal alteration with sulfide-bearing mineral assemblages along vein and fracture margins. Also, it is difficult to distinguish the thermal metamorphic event from the hydrothermal event on the Barton Peninsula because the mineral assemblages caused by thermal metamorphism and hydrothermal alteration are similar. Further studies are needed to establish the history of multiple thermal events. Numerous studies on altered volcanic rocks with sulfide mineralization have been performed, but a systematic isotope study on volcanic lavas that retain original mineralogy and texture has not yet been performed to discuss the processes of thermal events in accordance with isotopic variation.

The carbon, oxygen, hydrogen, sulfur and strontium isotope compositions of volcanic rocks were examined to characterize the isotopic compositions of volcanic lava that are fresh or the least altered in the Barton Peninsula. These isotope ratios are sensitive indicators of chemical exchange between rock and fluid; therefore, the results of this study are utilized to evaluate the nature of fluid-rock interaction. They will also help us better understand the history of igneous activity preceding the Noel Hill pluton in the Barton Peninsula and be added to the isotope database available for the South Shetland Island arc system.

GEOLOGY AND METAMORPHISM

General Geology

The lithology of the Barton Peninsula consists mainly of volcanic and plutonic rocks (Fig. 1). Vol-

canic rocks occupy most of the peninsula, and range in composition from basalt to andesite. Texturally they comprise mainly stratified lapilli tuffs, volcanic breccias and lava flows. The lowermost Sejong Formation (Yoo et al., 2001), formerly the Lower Volcanic Member (Davies, 1982), is distributed along the southern coasts of the Barton Peninsula. It is largely composed of lapilli tuffs and volcanic breccias with a maximum thickness of about 100 m and gently dips to the south or southwest. Mafic to intermediate volcanic lavas (basalt to andesite) overlying the Sejong Formation are widespread in the Barton Peninsula. These lavas mostly contain euhedral to subhedral phenocrysts of either plagioclase only or plagioclase and clinopyroxene. Modal contents of phenocrysts vary between 10% and 20% (Yeo et al., 2004). Plagioclase phenocrysts commonly show normal zoning. Although it is difficult to constrain the precise eruption ages due to alteration, most lavas seem to have erupted during the Paleocene to Eocene (Willan and Armstrong, 2002; Kim et al., 2000; Park, 1989).

Calc-alkaline granodiorite and diorite plutons intrude the volcanic rocks at Noel Hill in the northern Barton Peninsula. The occurrences of contact metamorphic minerals have been reported in the contact aureole close to the Noel Hill (Willan and Armstrong, 2002; Armstrong, 1995; Smellie et al., 1984). The southwestern boundary between the Noel Hill pluton and the volcanic country rocks is partly defined by a fault (Smellie et al., 1984), although the exact contact relationship is difficult to determine owing to a lack of exposure. This pluton is interpreted to have intruded in the Middle Eocene (Kim et al., 2000; Lee et al., 1996; Park, 1989).

Thermal Metamorphism

Previous studies reported thermal metamorphism in volcanic rocks on the Barton Peninsula. The volcanic rocks commonly contain secondary minerals such as hornblende, actinolite, epidote, chlorite, calcite and hematite, ilmenite and pyrite. Pyrite also occurs in fresh volcanic lava disseminated in the matrix between euhedral phenocryst of plagioclase and pyroxene. Pyrite may also occur along fractures in phenocrysts of plagioclase. Kim et al. (2002) reported that metavolcanic rocks underwent low grade meta-

morphism of greenschist and transitional greenschist-amphibolite facies characterized by the calcite-chlorite and the amphibole-chlorite mineral assemblages, respectively. They also suggested low-pressure conditions less than 1 kbar and metamorphic temperatures in the range of 250–300 °C based on mineral assemblages and geochemistry. Thermal metamorphism in the Barton Peninsula probably was associated with magmatic-arc plutons emplaced during the Tertiary subduction of the southeast Pacific plate under the Antarctic Peninsula (Kim et al., 2002; Armstrong, 1995; Birkenmajer et al., 1991).

METHODS

Selection of Samples

Volcanic rocks occurring in the Barton Peninsula can be broadly classified into (1) metamorphosed volcanics that retain original mineralogy and texture, and (2) hydrothermally altered volcanics in which sulfide minerals have been precipitated from hydrothermal fluids. For this study, volcanic rocks were collected at 10 outcrops. The original mineralogy has been partly changed, but the original textures and structures are preserved. The analyzed samples cover a range from basalt to andesite in chemical composition representative of the rock suites occurring in the Barton Peninsula. The sampling sites are shown in Fig. 1 as filled circles.

Analytical Methods

Carbon and oxygen isotope analyses

Carbon and oxygen isotope compositions of calcite in whole rock samples were determined using the conventional H_3PO_4 digestion method of McCrea (1950). To produce CO_2 , samples were reacted with phosphoric acid at 50 °C overnight. Whole rock samples that were treated with 10% HCl acid to remove calcite were analyzed by the conventional oxygen isotope technique at Indiana University. The samples were reacted with BrF_5 at 610 °C in nickel vessels to liberate oxygen following the method of Clayton and Mayeda (1963). Oxygen was converted to CO_2 by reaction with a hot graphite disk.

The $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of calcite and whole rock samples were measured with a Finnigan MAT 252 stable isotope ratio mass spectrometer and

the results are expressed in the δ notation relative to $\delta^{13}\text{C}$ (VPDB) and $\delta^{18}\text{O}$ (VSMOW). The $\delta^{18}\text{O}$ of calcite was calculated by using the fractionation factor (1.009 31) between the calcite and CO_2 gas (Swart et al., 1991). Analytical uncertainty of isotopic measurements was $\sim 0.05\text{‰}$, and sample reproducibility was within $\pm 0.25\text{‰}$ for all samples. The NBS-28 quartz and NBS-19 carbonate standards have values of 9.6‰ and 1.95‰, respectively, in the Stable Isotope Research Facility in Indiana University.

Hydrogen isotope analyses

Powders of whole rock samples for hydrogen isotope compositions and water contents 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 1 400 °C in a glassy carbon column. Hydrogen was analyzed using a Finnigan Delta Plus-XP stable isotope mass spectrometer. Several standards were run with each series of analyses. Internal standards included muscovite (-74‰), actinolite (-69‰), and two serpentines (-100‰, -65‰), all calibrated relative to an NBS-30 biotite value of -65‰. Results are reported in delta notation with respect to VSMOW. Instrumental reproducibility was within $\pm 0.2\text{‰}$ and sample reproducibility was $\pm 2\text{‰}$.

Sulfur isotope analytical method

Powders of whole rock samples were analyzed using elemental analyzer-continuous flow isotope ratio mass spectrometry (Studley et al., 2002). Sample powders (3 to 150 mg) were placed in tin cups with 1 to 1.5 mg of V_2O_5 and combusted at $\sim 1\ 800$ °C, with a reactor column temperature of 1 010 °C. Analyses of SO_2 were made using a Finnigan MAT252 stable isotope ratio mass spectrometer, with results reported in standard delta notation relative to VCDT. Instrumental uncertainty for each analysis was less than $\pm 0.05\text{‰}$, and sample reproducibility was within $\pm 0.3\text{‰}$. Sulfide standards utilized included IAEA S-1 (with a defined value of -0.3‰ VCDT), IAEA S-2 (21.7‰), IAEA S-3 (-31.3‰) and several Indiana University laboratory standards.

Sr isotope analytical method

Sr isotope analyses of all whole rock powder samples, including chemical separation and multicollector thermal ionization mass spectrometer (Isoprobe-T), were performed at Korea Basic Science Institute (KBSI). About 20 mg of whole rock powder samples was added mixed ^{87}Rb - ^{84}Sr spikes, and then dissolved with a mixed acid of $\text{HF}+\text{HClO}_4$ (10 : 1) for 24 h in a tightly closed Teflon vial at 120 °C on a hot plate. Rb and Sr were extracted by the conventional cation column chemistry (Dowex AG50W-X8, #200-400, H^+ form) using HCl media, and loaded on Ta filament with 1 M H_3PO_4 . The isotopic ratios were measured by a multi-collector thermal ionization mass spectrometer (TIMS) equipped with nine faraday cups. Measurement of Rb was performed with static mode, and Sr performed with dynamic mode. Rb and Sr contents were obtained by isotope dilution method. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were corrected for instrumental fractionation and spike contribution using $^{87}\text{Sr}/^{86}\text{Sr}=0.1194$. The replicate analyses of NBS987 standard gave a mean to $^{87}\text{Sr}/^{86}\text{Sr}=0.710168\pm0.000009$ ($n=15$, 2σ SE). Total procedural blank levels were less than 10 pg for Rb and 0.1 ng for Sr.

Sulfur and carbon concentrations

Total carbon and sulfur were determined using a C/S analyzer, model ELTRA CS-2000 with a resistance furnace. Bulk sample powders from 200 to 400 mg were combusted at 1450 °C in an oxygen atmosphere, converting organic and inorganic carbon to CO_2 and sulfur to SO_2 . These gases were measured using IR detectors against a calibration of standard reference materials and internal laboratory standards. Several standards were run with each series of analyses. Internal standards utilized included US Geological Survey Devonian Soil AR4019 ($\text{S}=0.100\%$, $\text{C}_{\text{tot}}=0.102\%$) from Alpha Resources, Inc.. The precision of these analyses is better than 1%–2% of the analyzed values of the standards.

RESULTS

The isotopic compositions of C, O, H, S and Sr and the contents of C, S and H_2O^+ of investigated rocks with SiO_2 content are listed in Table 1. Because of the small quantity of calcite in the whole rock sam-

ples, the carbon and oxygen isotope value of calcite ($\delta^{13}\text{C}_{\text{cal}}$, $\delta^{18}\text{O}_{\text{cal}}$) could be measured in only 4 samples. The $\delta^{13}\text{C}_{\text{cal}}$ and $\delta^{18}\text{O}_{\text{cal}}$ values range from -3.2‰ to -7.5‰ and 0.4‰ to 5.1‰, respectively (Fig. 2). The $\delta^{13}\text{C}_{\text{cal}}$ values are similar to those that are thought to be representative of magmatic values, but the $\delta^{18}\text{O}_{\text{cal}}$ values are lower than primary magmatic values (Taylor et al., 1967). The whole-rock oxygen isotopic compositions ($\delta^{18}\text{O}_{\text{WR}}$) for the basalt to andesite samples are in a range from -1.1‰ to 7.2‰ (Fig. 3a). The sample No. 1 with $\delta^{18}\text{O}_{\text{WR}}$ value of 5.8‰ appears to have retained a value similar to its initial magmatic value of island-arc basalts (average $\delta^{18}\text{O}_{\text{WR}}=(6.0\pm0.3)\%$) based on conventional oxygen isotope data (Harmon and Hoefs, 1995). Most of the volcanics have $\delta^{18}\text{O}_{\text{WR}}$ values that are significantly lower than their original magmatic values. Whole rock hydrogen isotope values ($\delta\text{D}_{\text{WR}}$) and water contents range from -74‰ to -66‰ (Fig. 3b) and from 0.67 wt.% to 2.74 wt.%, respectively. These values are higher than the average $\delta\text{D}_{\text{WR}}$ and H_2O wt.% of fresh basalt reported by Kyser and O'Neil (1984). The sulfur concentrations of volcanic rocks range from 30 ppm to 196 ppm. Because of the low concentration of sulfur, the whole rock sulfur isotope value ($\delta^{34}\text{S}_{\text{WR}}$) could be measured in only 4 samples. These samples display negative $\delta^{34}\text{S}_{\text{WR}}$ values between -12.5‰ and -7.0‰ (Fig. 3c), significantly lower than the presumed original magmatic values of $(-0.8\pm0.2)\%$ (Sakai et al., 1982). Initial Sr isotopic compositions of the volcanic rocks span a narrow range from 0.703312 to 0.703504 which are similar to the less altered volcanic rocks reported by Shin et al. (2009). These ($^{87}\text{Sr}/^{86}\text{Sr}$)_i values of volcanic rocks belong to the present mid-oceanic ridge basalt (Dickin, 2005).

DISCUSSION

Carbon and Oxygen Isotopes of Calcite

Volcanic rocks of the Barton Peninsula contain not only groundmass calcite but also calcite amygdaloids. The $\delta^{13}\text{C}_{\text{cal}}$ and $\delta^{18}\text{O}_{\text{cal}}$ values obtained on calcite of the Barton Peninsula are plotted in Fig. 4, which also shows the carbon and oxygen isotope variations in carbonates summarized by Deines (1989). Primary magmatic carbonates generally have $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values between -8‰ and -4‰ and between 6‰

Table 1 Isotopic compositions of O, H, C, S and Sr, contents of C, S and H₂O⁺ of investigated rocks with SiO₂ contents

Sample No.	$\delta^{18}\text{O}_{\text{WR}} (\text{‰})$	$\delta\text{D}_{\text{WR}} (\text{‰})$	$\delta^{34}\text{S}_{\text{WR}} (\text{‰})$	$\delta^{13}\text{C}_{\text{cal}} (\text{‰})$	$\delta^{18}\text{O}_{\text{cal}} (\text{‰})$	Rb (ppm)	Sr (ppm)	$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{m}}$	Error (ppm)
1	5.8	-72	ND	-4.2	2.6	1	486	0.703 417	11
2	-0.3	-72	-9.9	-	-	1	580	0.703 507	15
3	-0.4	-71	-7	-	-	2	555	0.703 485	11
4	1.3	-72	ND	-	-	16	536	0.703 535	12
5	3.9	-68	ND	-3.2	5.1	1	554	0.703 314	11
6	1.3	-66	-12.5	-	-	12	588	0.703 471	10
7	4.3	-71	ND	-4.1	4.3	8	612	0.703 360	12
8	7.2	-70	-7.6	-	-	29	535	0.703 461	11
9	1.7	-72	ND	-7.5	0.4	29	675	0.703 569	19
10	-1.1	-74	ND	-	-	26	584	0.703 445	10

Sample No.	$^{87}\text{Rb}/^{86}\text{Sr}$	$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{i}}^{1)}$	S (ppm)	C (ppm)	H ₂ O ⁺ (wt.%)	SiO ₂ (wt.%)
1	0.003 9	0.703 414	30	12 512	2.27	49.00
2	0.005 5	0.703 504	196	486	1.27	50.51
3	0.009 9	0.703 480	100	553	1.44	54.20
4	0.089 5	0.703 492	87	628	1.52	52.88
5	0.004	0.703 312	30	5 253	2.74	53.67
6	0.056 4	0.703 444	194	1 463	1.58	53.40
7	0.039 2	0.703 331	48	5 421	1.70	54.25
8	0.157 3	0.703 385	177	571	0.67	55.37
9	0.125 7	0.703 476	28	7 031	1.97	55.06
10	0.127 4	0.703 351	66	3 722	2.35	58.60

1) Calculated initial Sr isotopic ratios using 52 Ma, the age of basaltic andesite (Kim et al., 2000). ND: $\delta^{34}\text{S}_{\text{WR}}$ could not be measured due to the low concentration of sulfur. -: $\delta^{13}\text{C}_{\text{cal}}$ and $\delta^{18}\text{O}_{\text{cal}}$ could not be measured due to the small quantity of calcite. SiO₂: the data are reported by Yeo et al. (2004).

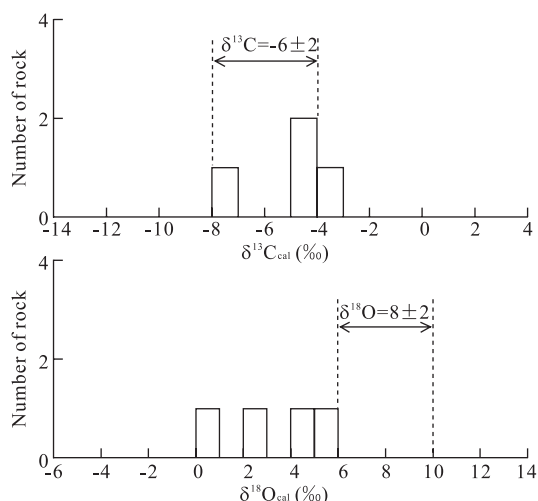


Figure 2. Histograms comparing the distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of calcite in the Barton Peninsula with primary magmatic values proposed by Taylor et al. (1967).

and 10‰, respectively (Taylor et al., 1967). The $\delta^{13}\text{C}_{\text{cal}}$ values of -7.5‰ to -3.2‰ are similar to magmatic carbon, but the $\delta^{18}\text{O}_{\text{cal}}$ values of 0.4‰ to 5.1‰ are depleted in ¹⁸O relative to magmatic carbon. High-temperature oxygen isotope exchange with depleted ¹⁸O meteoric water will tend to lower the $\delta^{18}\text{O}$ values of calcite (Deines, 1989). The $\delta^{13}\text{C}_{\text{cal}}$ values are similar to those of normal magmatic values, but the $\delta^{18}\text{O}_{\text{cal}}$ values are distinctly lower than primary magmatic values. Because meteoric water contains more oxygen compared to carbon, there can be a bigger shift for $\delta^{18}\text{O}$ values rather than $\delta^{13}\text{C}$ to more negative values. Thus, it can be stated that the isotopic compositions of calcite have been strongly controlled by meteoric water in this area. The homogeneous $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ depletions of calcite in the Barton Peninsula relative to magmatic carbonates suggest that depleted

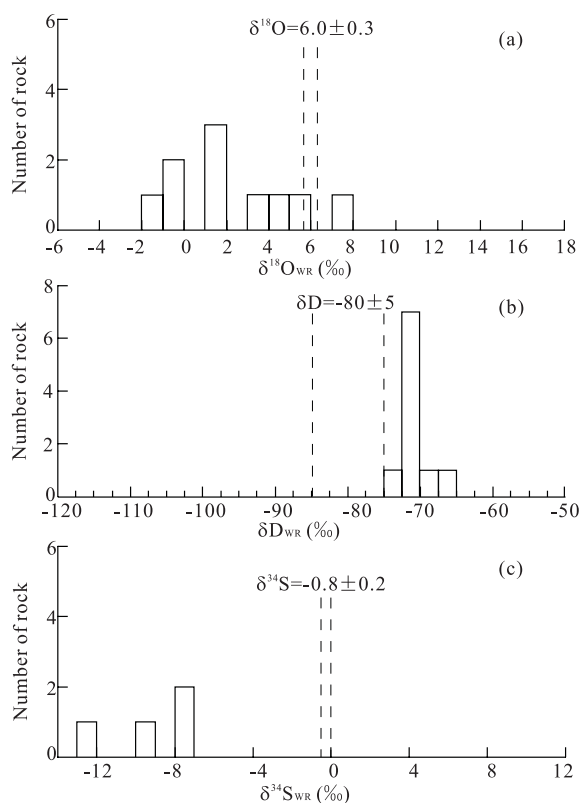


Figure 3. Histograms comparing (a) the distribution of $\delta^{18}\text{O}_{\text{WR}}$ values with the average data of island-arc basalts (Harmon and Hoefs, 1995); (b) the distribution of $\delta\text{D}_{\text{WR}}$ values with the average data of fresh basalt (Kyser and O'Neil, 1984); and (c) the distribution of $\delta^{34}\text{S}_{\text{WR}}$ values with the average data of magmatic values (Sakai et al., 1982).

^{18}O fluid circulation and high temperature alteration of volcanic rocks resulted in oxygen isotope exchange. So et al. (1995) had reported two $\delta^{13}\text{C}_{\text{cal}}$ and $\delta^{18}\text{O}_{\text{cal}}$ values of -5.0‰ to -4.2‰ and 9.9‰ to 10.9‰ from void-filling and vein calcite of the Barton Peninsula and had calculated $\delta^{18}\text{O}$ values of water in equilibrium with calcite at temperatures of $150\text{--}250\text{ °C}$ range from -2.1‰ to 3.7‰ . The calculated $\delta^{18}\text{O}_{\text{water}}$ values are consistent with a meteoric water source.

Oxygen and Strontium Isotopes

The $\delta^{18}\text{O}$ values of volcanics in the Barton Peninsula are comparable to the basalts altered at high temperatures recovered from the ocean floor or ophiolites (Gao et al., 2006; Teagle et al., 1998). They are also comparable to island arc basalts affected by hydrothermal alteration or magmatic assimilation of hydrothermally altered rocks (Bindeman et al., 2004;

Vroon et al., 2001). Because the plagioclase in mafic rock is very sensitive to fluid activity, the oxygen in plagioclase exchanges readily with fluid (Stakes and Vanko, 1986). At high temperature exchange with low- $\delta^{18}\text{O}$ fluid ($\sim 0\text{‰}$), a magmatic plagioclase ($\sim 6.0\text{‰}$) will show a decrease in its $\delta^{18}\text{O}$ value. At lower temperatures, the exchange will result in an increase (Agrinier et al., 1995). The extent of the $\delta^{18}\text{O}$ change also increases with the fluid/rock ratio. Agrinier et al. (1995) reported that the high value of $\delta^{18}\text{O}$ of mafic rock could have been produced by fluid ($\delta^{18}\text{O} = 0\text{‰}$) only at temperatures lower than 250 °C , while the low value of $\delta^{18}\text{O}$ of mafic rock requires hydrothermal interaction at temperatures higher than 300 °C .

Many recent studies have reported that hydrothermally altered basalt, which is rich in chlorite and/or actinolite, has relatively low $\delta^{18}\text{O}$ values (Teagle et al., 1998; Agrinier et al., 1995; Kawahata et al., 1987). Chlorite and actinolite are common secondary minerals in the Barton Peninsula and they were formed under moderate to high temperatures from ~ 250 to 300 °C (Kim et al., 2002). The $\delta^{18}\text{O}$ values of volcanic rocks in the Barton Peninsula range widely from -1.1‰ to 7.2‰ , probably reflecting the variation in the contents of secondary minerals, as well as in the temperature of alteration. The low $\delta^{18}\text{O}$ value of volcanic rocks from the Barton Peninsula is consistent with oxygen isotopic exchange with low $\delta^{18}\text{O}$ fluid at relatively high temperature presumed to be about 300 °C based on the data of Kim et al. (2002) and Agrinier et al. (1995).

Petrographic observations indicate that the primary plagioclase has been converted to secondary plagioclase, epidote, chlorite and calcite. The primary plagioclase ranges in composition from andesine to bytownite and the anorthite contents of secondary plagioclase are $\text{An}_5\text{--An}_{24}$ (Kim et al., 2002). Because plagioclase contains the bulk of the igneous strontium, and is more susceptible to alteration, we have evaluated oxygen-isotope values in combination with Sr isotopes. The values of $^{87}\text{Sr}/^{86}\text{Sr}$ of volcanics in the Barton Peninsula range from $0.703\ 314$ to $0.703\ 504$, which are similar to those determined in the Fildes Peninsula, King George Island (Machado et al., 2005). Shin et al. (2009) reported that the Sr isotope

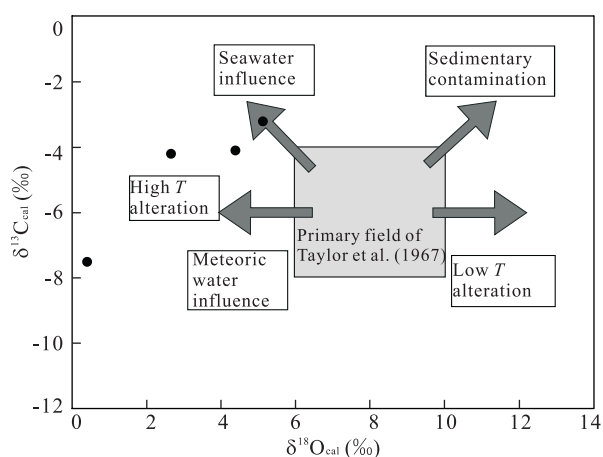


Figure 4. The plot of $\delta^{13}\text{C}_{\text{cal}}-\delta^{18}\text{O}_{\text{cal}}$ and schematic presentation of the main processes responsible for changes in the isotopic compositions (Deines, 1989). High-temperature oxygen isotope exchange with meteoric water or seawater that are depleted in ^{18}O relative to magmatic water will tend to lower the original $\delta^{18}\text{O}$ values of the carbonate.

compositions increased a little from fresh to altered volcanic rock samples. Although there are no available $^{87}\text{Sr}/^{86}\text{Sr}$ data on thermal fluids in the Barton Peninsula, it suggests that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of meteoric-hydrothermal fluids are generally higher than those of fresh basalts. The data of the bulk rock $^{87}\text{Sr}/^{86}\text{Sr}$ to 0.703 3–0.703 5 do not show a clear trend of pervasive interaction between fresh basalt and average hydrothermal fluid end-member. However, the $\delta^{18}\text{O}_{\text{WR}}-^{87}\text{Sr}/^{86}\text{Sr}$ diagram indicates that ^{18}O -depleted values and slightly fluctuated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of volcanic rocks in the Barton Peninsula result from high temperature alteration (Fig. 5).

Hydrogen Isotopes

Whole-rock δD values of the Barton Peninsula range from -74‰ to -66‰, and water contents range from 0.67 wt.% to 2.74 wt.%. The primary δD values of most tholeiite and alkali basalts are near $(-80\pm 5)\%$ and water contents vary from 0.15 wt.%–0.35 wt.% for tholeiites and up to 1.1 wt.% for alkali basalts (Kyser and O’Neil, 1984). The $\delta\text{D}_{\text{WR}}$ values are slightly higher and water contents are substantially higher than those of fresh basalt. The volcanic rocks of the Barton Peninsula commonly contain secondary minerals such as actinolite, chlorite and epidote. Because chlorite contains 13%–15% water, whereas

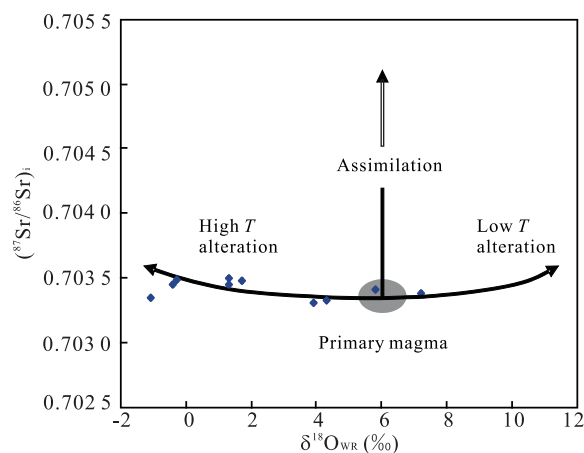


Figure 5. Correlation of $\delta^{18}\text{O}_{\text{WR}}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ showing the isotopic effects associated with hydrothermal alteration. The data of the Barton Peninsula are characterized by low $\delta^{18}\text{O}_{\text{WR}}$ which results from high temperature alteration.

actinolite and epidote contain only 2%–3%, the $\delta\text{D}_{\text{WR}}$ and water content are mainly determined by the D/H ratio of chlorite (Kawahata et al., 1987). Kyser and O’Neil (1984) reported the effects of several processes that may affect the original δD values and water contents of basalts. The effects of each process are shown in Fig. 6 as a series of curves that were calculated for a lava having a primary δD value of -80‰ and a water content of 0.2 wt.% using appropriate fractionation factors. As shown in Fig. 6, the slightly higher $\delta\text{D}_{\text{WR}}$ values and substantially higher H_2O wt.% than those of fresh basalt may be suggestive of the high temperature alteration of volcanic rocks in the Barton Peninsula.

Sulfur Isotopes

Low sulfur concentration

The low concentration of sulfur is typical of subaerial lava flows, but the causes of low sulfur concentration are controversial. Some studies indicate that island arc lavas are characterized by low S content (<100 ppm; Hamlyn et al., 1985; Ueda and Sakai, 1984) and that back arc lavas typically contain several hundred ppm less than MORB lavas of similar composition (Hochstaedter et al., 1990). These low S concentrations have been interpreted by some to reflect a low-S source for island arc and back arc magmas (Hamlyn and Keays, 1986; Ueda and Sakai, 1984). However, Nilsson and Peach (1993) pointed out that

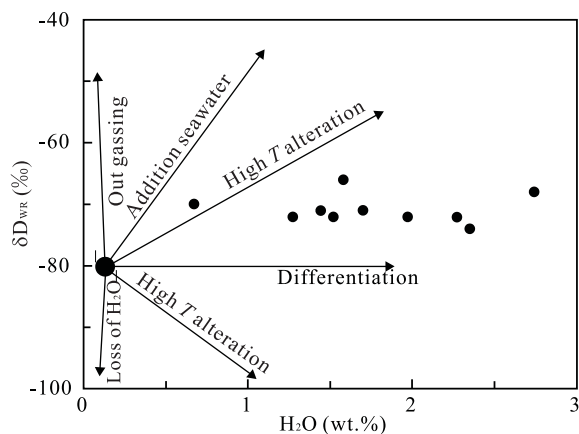


Figure 6. The plot of δD_{WR-H_2O} and calculated curves showing the effects of several processes that affected the original δD values and water contents of basalts (Kyser and O'Neil, 1984). The data may be suggestive of the high temperature alteration of volcanic rocks in the Barton Peninsula.

the low S concentrations in island arc and back arc lavas do not necessarily reflect a low S source but rather result from higher f_{O_2} in the convergent margin environment. At higher f_{O_2} condition, magmatic degassing may be effective at stripping S from the melt. This low concentration of sulfur is typical of subaerial lava flows that lose varying proportions of sulfur by outgassing of SO_2 . Outgassing of SO_2 can bring about low concentrations of sulfur and depletion of ^{34}S . Submarine basalt has 700 ± 100 ppm total S and $\delta^{34}S$ of $(0.7 \pm 0.1)\%$, whereas subaerial basalt has 150 ± 50 ppm total S and $\delta^{34}S$ of $(-0.8 \pm 0.2)\%$ (Sakai et al., 1982). Total S content and $\delta^{34}S$ values of Quaternary volcanic rocks from the Japanese Island Arc are about 40 ppm and $(4.4 \pm 2.1)\%$.

Some correlations are observed between the contents of S, C and H_2O (Fig. 7). The water contents (H_2O wt.%) show positive correlations with total C and negative correlations with S. There is a negative correlation between total C and S. Considering the fact that altered rocks contain calcite and have high H_2O contents, the correlations shown in Fig. 7 suggest that the formation of calcite and breakdown of sulfide result from hydrothermal metamorphism. Metals and sulfide are not significantly re-mobilized by hydrothermal metamorphic fluids until temperatures exceed ~ 350 °C (Seewald and Seyfried, 1990).

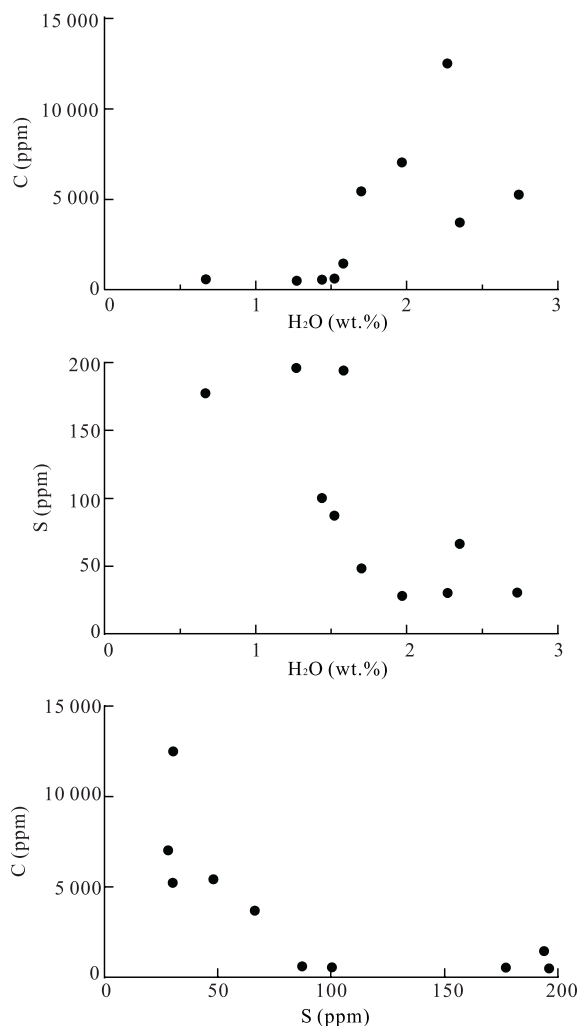


Figure 7. Water contents vs. total C and S correlations for volcanic rocks; the low S concentration and their negative correlation with the contents of water and C reflect formation of calcite and breakdown of sulfide during hydrothermal metamorphism.

Depleted sulfur isotopic composition

The $\delta^{34}S_{WR}$ values of the Barton Peninsula range from -12.5% to -7.0% , and are significantly lower than magmatic values of worldwide volcanic rocks. S isotope ratios have been reported from the volcanic rocks of convergent plate boundaries worldwide, coming from the Japanese island arc (Ueda and Sakai, 1984), the Indonesian arc system (DeHoog et al., 2001), and the Mariana islands (Alt et al., 1993). These studies have not identified depleted S isotope values such as those measured in the Barton Peninsula.

The highly depleted $\delta^{34}S$ values of the Barton

Peninsula can be related to fractionation accompanying oxidation of magmatic sulfide followed by partial reduction or incorporation of some bacteriogenic sulfide. There are two reports on sulfur isotope for ore deposits in the Barton Peninsula. The $\delta^{34}\text{S}$ values of pyrite in veins range from -20.1‰ to -14.6‰ and they are explained by the higher oxidation state of fluids (So et al., 1995). The $\delta^{34}\text{S}$ values of pyrite reported by Hwang and Lee (1998) that are disseminated in altered volcanic rocks range from -9.6‰ to -1.8‰ and have been explained by the high oxidation state of the precipitating fluids or incorporation of some sedimentary sulfides. Because the metamorphic event preceded sulfide mineralization and the metavolcanics have very low concentrations of sulfur, it is uncertain whether the $\delta^{34}\text{S}$ values of metavolcanics are genetically related to those of sulfides in mineralized rocks and veins. However, it is evident that the geothermal fluids of the Barton Peninsula were oxidizing and as Alt (1994) has suggested for volcanic rocks in the ocean crust, the negative $\delta^{34}\text{S}$ values (-26.1‰ to 4‰) and low sulfur concentration are consistent with isotopic fractionation during partial oxidation of igneous sulfides.

Bacteriogenic pyrite has an average $\delta^{34}\text{S}$ value between -32.2‰ (Nriagu et al., 1991) and -25‰ (Ohmoto and Goldhaber, 1997). Geochemical modeling, based on Sr-Nd isotope ratios on Tertiary volcanic rocks in King George Island, suggests that the primary calc-alkaline magmas were modified by the addition of small amounts of pelagic sediments contributed by subduction processes (Machado et al., 2005; Birkenmajer et al., 1991). Bacteriogenic sulfides may have been included with the pelagic sediment. For this reason its incorporation from the recycled pelagic sediments may account for the depleted $\delta^{34}\text{S}$ of volcanic rocks in the Barton Peninsula.

CONCLUSIONS

(1) The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of calcite in volcanic rocks range from -7.5‰ to -3.2‰ and 0.4‰ to 5.1‰, respectively. The homogeneous $\delta^{13}\text{C}$ and depleted $\delta^{18}\text{O}$ values relative to primary magmatic values reflect the effect of high temperature alteration of volcanic rocks on the Barton Peninsula.

(2) The $\delta^{18}\text{O}_{\text{WR}}$ of volcanic rocks range from

-1.1‰ to 7.2‰, and the majority of values are significantly low than those of primary magmatic values. The low $\delta^{18}\text{O}_{\text{WR}}$ values are also compatible with high temperature alteration involving a relatively low- $\delta^{18}\text{O}$ fluid.

(3) Initial Sr isotopic compositions of the volcanic rocks span a narrow range from 0.703 312 to 0.703 504 which belong to the present mid-oceanic ridge basalt. The values of $^{87}\text{Sr}/^{86}\text{Sr}$ of volcanic rocks in the Barton Peninsula are similar to those determined in the Fildes Peninsula, King George Island.

(4) The $\delta\text{D}_{\text{WR}}$ and H_2O contents of volcanic rocks range from -74‰ to -66‰ and 0.67 wt.% to 2.74 wt.%, respectively. The high $\delta\text{D}_{\text{WR}}$ and H_2O wt.% of volcanic rocks compared to values from fresh basalt are also suggestive of high temperature alteration.

(5) The $\delta^{34}\text{S}_{\text{WR}}$ of the volcanic rocks range from -12.5‰ to -7.0‰ and can be accounted for by isotopic fractionation related to oxidation and re-reduction or the incorporation of some bacteriogenic sulfide.

(6) The S contents are less than 196 ppm, and are negatively correlated with C and H_2O contents. These features reflect the formation of calcite and the breakdown of sulfides during high temperature alteration.

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