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Hydrogen, Oxygen and Sulfur Isotope Studies of Seafloor Hydrothermal System at the Desmos Caldera, Manus Back-arc Basin, Papua New Guinea: An Analogue of Terrestrial Acid Hot Crater-lake

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Abstract: The Onsen site is an active submarine hydrothermal system hosted by the Desmos caldera in the Eastern Manus Basin, Papua New Guinea. The hydrothermal fluid is very acidic (pH=1.5) and abundant native sulfur is deposited around the vent. The $\delta^{34}S$ values of native sulfur range from -6.5 to -9.3 ‰. $\delta^{34}S$ values of H_2S and SO_4 in the hydrothermal fluid are -4.3 to -9.9 ‰ and +18.6 to +20.0 ‰, respectively. These $\delta^{34}S$ values are significantly lower than those of the other hydrothermal systems so far reported. These low $\delta^{34}S$ values and the acidic nature of the vent fluids suggest that volcanic SO_2 gas plays an important role on the sulfur isotope systematic of the Onsen hydrothermal system. Relationship among the $\delta^{34}S$ values of S-bearing species can be successively explained by the model based on the disproportionation reaction starting from the volcanic SO_2 gas. The predicted $\delta^{34}S$ values of SO_2 agree with the measured whole rock $\delta^{34}S$ values. δD and $\delta^{18}O$ values of clay minerals separated from the altered rock samples also suggest the contribution of the magmatic fluid to the hydrothermal system. Present stable isotopic study strongly suggests that the Onsen hydrothermal site in the Desmos caldera is a magmatic submarine hydrothermal system.

Keywords: Manus Basin, seafloor hydrothermal system, hydrogen isotope, oxygen isotope, sulfur isotope, native sulfur

1. Introduction

Hydrothermal mineralization along the mid-oceanic ridge systems and back-arc basin spreading centers is one of the most actively researched subject in the Earth Science. Most of these hydrothermal deposits are either end-products of simple basalt-seawater interaction (e.g. TAG hydrothermal field, Hannington et al., 1988; East Pacific Rise, Graham et al., 1988) or felsic volcanic rocks-seawater interaction with significant magmatic fluid involvement (e.g. Pacmanus site, Manus back-arc basin, Yang et al., 1996; Binns et al., 1995; Hina Hina site, Lau back-arc basin, Herzig et al., 1998). Identifying the role and significance of magmatic fluid involvement in such mineralization is vital in understanding the sources of sulfur and metals in the formation of minerals deposits in submarine settings.

The chemistry of the vent fluid discharging at the Desmos caldera has been a target of many geochemical studies (Gamo et al., 1997; Ishibashi et al., 1998; Douville et al., 1999). The geology, mineralization and alteration at the Onsen site were discussed in detail by Gena et al. (1997, 1999, 2001). Gamo et al. (1997) suggested that incorporation of magmatic fluid involvement in the Onsen hydrothermal system, based on stable isotope analysis of hydrothermal fluid (δD_{H_2O} = -8.1 ‰ and $\delta^{34}S_{H_2S}$ = -5.6 ‰). Similarly, Miyabe et al. (2004) suggested magmatic contribution to the Mariana Arc hydrothermal system, based on stable isotope analysis of native sulfur and hydrothermal fluid ($\delta^{34}S_S$ = -6.0 ‰, $\delta^{34}S_{H_2S}$ = -6.0 to -10.0 ‰).

In this study, we intend to assess the source of sulfur and fluid involved in the acid-sulfate type of alteration in the Desmos caldera. A series of native sulfur, clay minerals and hydrothermal fluid were analyzed for the sulfur, oxygen and hydrogen isotope data. The new isotope data are used to refine the interpretation of the source of sulfur and fluid responsible for the mineralization in the Desmos caldera.

2. Regional Setting in Manus Basin

The Manus back-arc basin is bounded by calc-alkaline volcanic islands of Manus, New Ireland and New Britain to the north, north-east and south respectively (Fig. 1A). The Central Manus Basin is offset by the Dyaul and Willaumez transform faults to the east and west respectively (Fig. 1A), while the Eastern Manus Basin (EMB) is bounded to the east by Weitin transform fault and to the

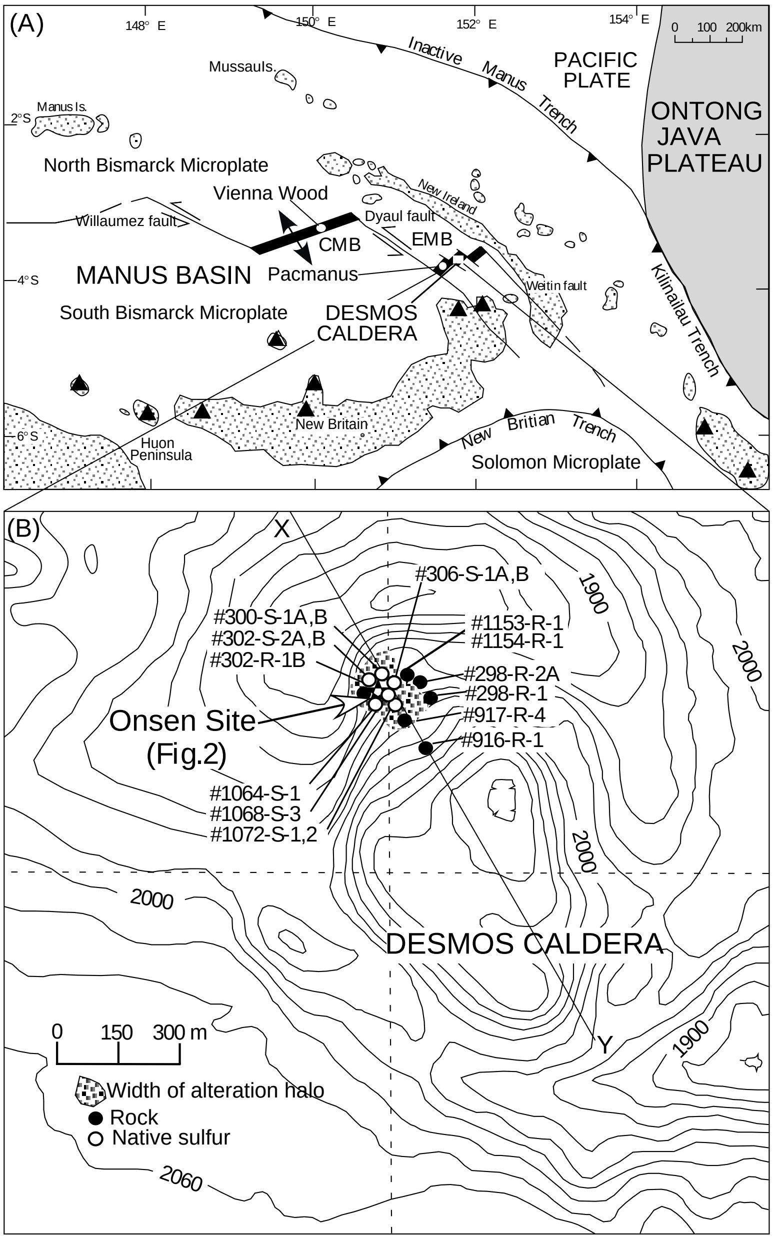

Fig. 1 (A): Tectonic setting of the Manus back-arc basin with location of Vienna Wood, Pacmanus and Desmos caldera. The Central Manus Basin (CMB) and Eastern Manus Basin (EMB) spreading centers (shaded in black) are off-set by Willaumez, Dyaul and Weitin transform faults. (B): An aerial view of Desmos caldera, slightly elongated in the north-northwest direction with a length of 2 km. The Onsen hydrothermal site is indicated with arrow. The black line X-Y transacts the center of the hydrothermal activity as shown on Figure 3. The solid and white dots represent sampling points of rock and native sulfur used in this study (contours in meters).

west by Dyaul transform fault. Associated with the Manus back-arc basin are the Vienna Wood and Pacmanus hydrothermal systems which have been documented by a lot of researchers (e.g. Both et al., 1986; Tufar, 1989; Scott and Binns, 1995; Binns et al., 1993; Gamo et al., 1993, 1997; Yang and Scott, 1996). The mineral assemblage and character of the ores from Vienna Wood is quite similar to volcanogenic massive sulfide deposits hosted by ancient ophiolite and presently forming seafloor hydrothermal deposits along mid-oceanic ridge system (Gena et al., 2002). The mineral assemblage and character of the ores from Pacmanus hydrothermal fields match closely with ancient Kuroko-type ore deposits (Gena et al., 2001; Scott and Binns, 1995; Binns et al., 1993).

3. Desmos Caldera

The Desmos caldera is part of the Eastern Manus Basin (Fig. 1A) and was discovered by the AQUARIUM expedition in 1990 (Gamo et al., 1993). The Desmos caldera is slightly elongated in the NNW direction with a dimension of 1.5 by 2.0 km and deep circular depression of about 150-250 meters (Fig. 1B). A total of 18 dives were made in the Desmos caldera over a four year period (1995, 1996, 1998, 1999) using Shinkai 6500 and Shinkai 2000 (Gena et al., 2001). The vigorous venting milky white smokers with low pH of 1.54 to 2.1 and temperatures of 88 to 120°C were discovered at the northwest terrace of the Desmos caldera during the 1995 Manus Flux cruise and called Onsen hydrothermal site (Fig. 1B). The small terrace at about 2000 meters BSL is located at the northwest slope, while the caldera floor is about 2100 meter below sea level (Fig. 1B). From the dive observations, the caldera floor composed predominantly of fresh pillow lava of basaltic andesite. The lithology changes abruptly from pillow lava to hyaloclastite deposits of basaltic andesite in the upper terrace (Gena et al., 2001). The distribution of the hyaloclastite is restricted to the periphery of the Onsen site (~300 meters in diameter). The fragments of basaltic andesite in the distal part of the Onsen site are weakly altered by low temperature shimmering water while fragments closer to the active vents are strongly altered and cemented together by native sulfur (Fig. 2A). The milky white hydrothermal fluids are discharged through the native sulfur mound (Fig. 2B).

A cross section through the Desmos caldera shows that

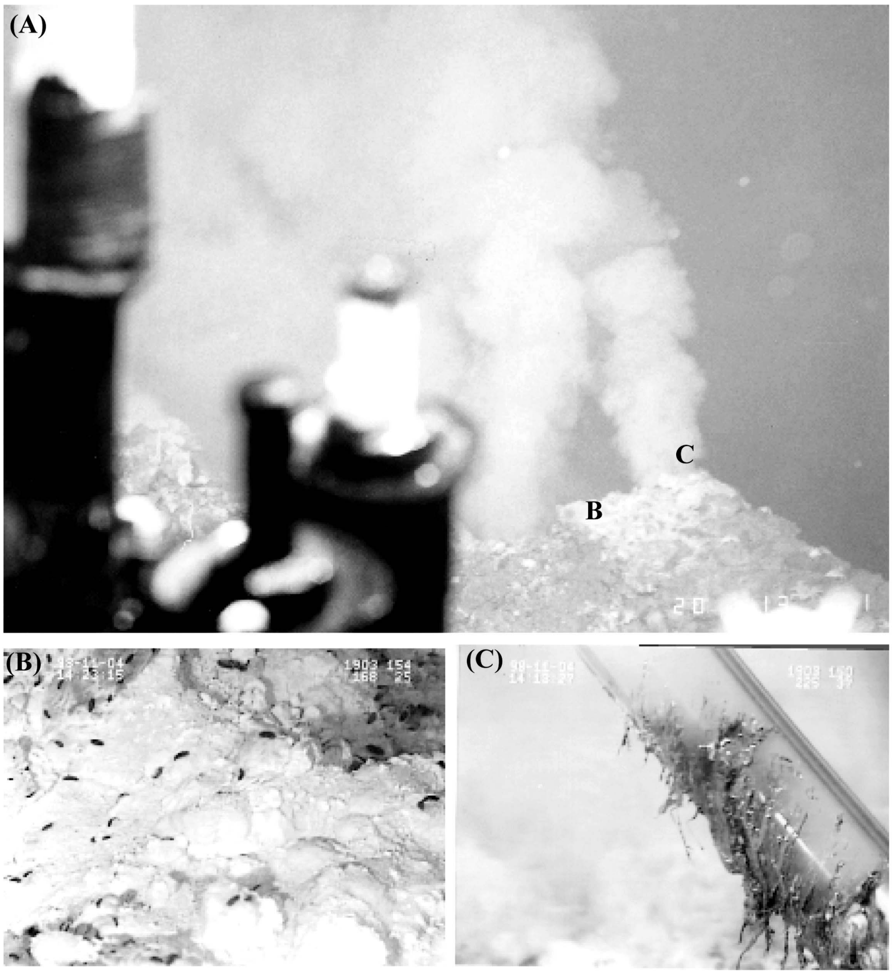

Fig. 2 (A) The Onsen site as observed from the submersible Shinkai 2000, discharging white hydrothermal fluids through the native sulfur mound. (B) The bulbous native sulfur mound at the Onsen site partly coated with bacterial mat and scaleworm. (C). Precipitation of native sulfur on the cylinder of the push corer held above the white smoker. The symbol B and C on Figure 2A correspond with the location of Figures 2B and 2C.

the northwestern side of the caldera is elevated by about 100 meters compared to the caldera floor and southeastern side of the caldera (Fig. 3). This may indicate that after subsidence of the Desmos caldera, resurgent volcanic activity is restricted to the northwestern margin of the caldera.

4. Sample Location and Description

The hydrothermal fluid and native sulfur samples were collected from the Onsen site while the highly altered basaltic andesite samples with white color were collected 60 meters southeast of the present hydrothermal activity and 30 meters east of the Onsen site (Fig. 1B).

The hydrothermal precipitates of blackish to yellowish native sulfur and hydrothermal fluids were collected around the vent and native sulfur mound (Fig. 2A) where low temperature venting fluids were observed in 1995 and 1999 (Gamo et al., 1997; Ishibashi et. al., 1998). Whether the native sulfur is derived from molten sulfur pools like those of the aerial crater lakes (Giggenback, 1974) is beyond the submarine visibility. However, the vigorously venting milky white fluids observed during the cruises (Mausflux 1995, BIOACCESS 1996, BIOACCESS 1998 and BIOACCESS 1999) strongly suggest presence of molten sulfur pool within the mound. This is evident by rapid precipitation of native sulfur on the push corer held above the white smokers (Fig. 2C).

5. Sample Preparation and Analysis

5.1. Altered basaltic andesite

The highly altered basaltic andesite samples were pulverized and clay minerals were separated by hydraulic elutriation. The separated mineral samples were examined by XRD analyses and found to be kaolinite with less than 10 % of mixed layered clay minerals (Tanada, unpubl. data). It is assumed that presence of minor amount of mixed layered clay mineral will not significantly affect the hydrogen and oxygen isotope analyses. Any interlayer water or absorbed water was removed under vacuum at 200°C. The constitutional water of the clay minerals was obtained by heating under vacuum condition at 1000°C (Godfrey, 1962). The hydrogen liberated during this process was converted to H_2O by reacting with CuO at 500°C. The obtained water was reduced to hydrogen gas by passing it through uranium maintained at 800°C. The oxygen of the dehydrated clay minerals was extracted using the bromine pentafluoride method and converted to CO_2 over hot graphite (Clayton and Mayeda, 1963). The hydrogen gas was measured for δD while carbon dioxide was measured for $\delta^{18}O$ at Akita University. All the isotope analysis for the samples is reported as per mil deviation with respect to the SMOW standard (Table 1).

Table 1 Oxygen, hydrogen and sulfur isotope values of minerals and hydrothermal fluids from Desmos caldera.

Sample Number *Rock*	*Mineral separated*		δD(‰)	$\delta^{18}O$ (‰)	δD_{H_2O}(‰)	$\delta^{18}O_{H_2O}$(‰)	Year Year
#298 -R-01	kaolinite		-28	4.4	-12.8	-1.2	1995
#917 -R-04	kaolinite		-22	5.2	-6.8	-0.4	1995
Precipitates	*Mineral separated*		$\delta^{34}S$(‰)	SO_4(‰) **added***			Year
#300 -S-01A	Native sulfur		-6.9	16.4			1995
#300 -S-01B	Native sulfur		-7.5	15.7			1995
#302 -S-02A	Native sulfur		-6.5	16.7			1995
#302-S-02B	Native sulfur		-7.7	15.5			1995
#306-S-01A	Native sulfur		-6.9	16.3			1995
#306-S-01B	Native sulfur		-8.3	14.9			1995
#1064-S-01	Native sulfur		-8.9	14.4			1998
#1068-S-03	Native sulfur		-8.5	14.7			1998
#1072-S-01	Native sulfur		-9.3	13.9			1998
#1072-S-02	Native sulfur		-9.3	13.9			1998
Sample Number	H_2S (m*M*)	SO_4 (m*M*)	$\delta^{34}S_{H_2S}$(‰)	$\delta^{34}S_{SO_4}$(‰)			Year
#302-F-1	5.3	30.1	-5.5	20.0			1995
#302-F-2	8.1	32.2	-5.7	19.9			1995
#1072-F-4	1.5	42.0	-7.6	19.5			1998
#1072-F-5	1.0	39.7	-7.7	19.7			1998
#1072-F-6	2.8	51.6	-5.5	18.5			1998
#1073-F-5	1.4	41.8	-7.4	19.4			1998
#1073-F-6	0.9	39.7	-7.8	19.8			1998

Note: * Sulfate added through disproportionation reaction (reaction 1)

5.2. Native Sulfur, H_2S and SO_4 in hydrothermal fluid

Representative native sulfur and H_2S and SO_4^{2-} in the hydrothermal fluid samples were used for sulfur isotope analysis at Institute for the Study of Earth's Interior (ISEI), Okayama University using the analytical techniques of Yanagisawa and Sakai (1983). The results of the native sulfur, H_2S and SO_4^{2-} are reported as $\delta^{34}S$ per mil (‰) with respect to the Canyon Diablo Troilite (CDT) (Table 1).

6. Results and Discussions

The results obtained for native sulfur, clay minerals and hydrothermal fluids are summarized in Table 1 and are plotted in Figures 4.

6.1. δD and $\delta^{18}O$ of kaolinite and source of fluid

The δD and $\delta^{18}O$ values of the two kaolinite samples are shown in Table 1 and are plotted on Figure 4. The δD and $\delta^{18}O$ values of the fluid which was in equilibrium with kaolinite at 270°C are estimated using the equations of Gilg and Sheppard (1996) and Savin and Lee (1988), respectively. They are also tabulated on Table 1 and plotted on Figure 3. The temperature used to calculate the fluid values were directly based on the mean trapping temperature of the fluid inclusions in quartz (Gena et al., 2001). The temperature (270°C) is well within the maximum stability limit of kaolinite-quartz formation (273± 10°C; Hemley et al., 1980). Although the number of samples is limited, the fluids associated with the formation of kaolinite have a narrow range (δD_{H_2O} = -6.8 to -12.8 ‰ and $\delta^{18}O_{H_2O}$ = -0.4 to -1.2 ‰) along a trend that suggests a mixing of predominantly seawater and some magmatic fluid (Fig. 4). The δD of water calculated in this study is consistent with the δD value of fluid (-8.1 ‰) reported by Gamo et al. (1997). If simple mixing between seawater and magmatic fluid is assumed, then the kaolinite precipitated from seawater slightly mixed with magmatic fluids.

6.2. $\delta^{34}S$ values of native sulfur, H_2S and SO_4

The $\delta^{34}S$ values of eleven native sulfur samples and seven hydrothermal fluids were analyzed to deduce the source of the sulfur (Table 1). The $\delta^{34}S$ values of native sulfur (-6.5 to -9.3 ‰) and H_2S (-4.3 to -9.9 ‰) are much lighter than $\delta^{34}S$ values of aqueous sulfides and sulfide minerals reported on the active seafloor hydrothermal systems so far reported (-5.7 to +7.3 ‰; Gamo et al., 1997; de Ronde, 1995; Shank et al., 1995). The $\delta^{34}S$ values of the SO_4^{-2} are also lower by about 1.0 to 2.5 ‰ compared to the $\delta^{34}S$ values of ambient seawater sulfate (21 ‰). Furthermore, SO_4^{-2} concentrations of the collected hydrothermal fluid samples are higher than that of ambient seawater sulfate (Table 1). It can also be recognized that the $\delta^{34}S$ values of native sulfur and H_2S_{fluid} collected in 1998 are about 2 to 3 ‰ lighter than the native sulfur and H_2S_{fluid} collected in 1995 (Table 1). The differences may be due to a time variation of the hydrothermal activity.

6.3. Process responsible for low $\delta^{34}S$ values of S-compounds

The isotopically light sulfur compounds observed in the

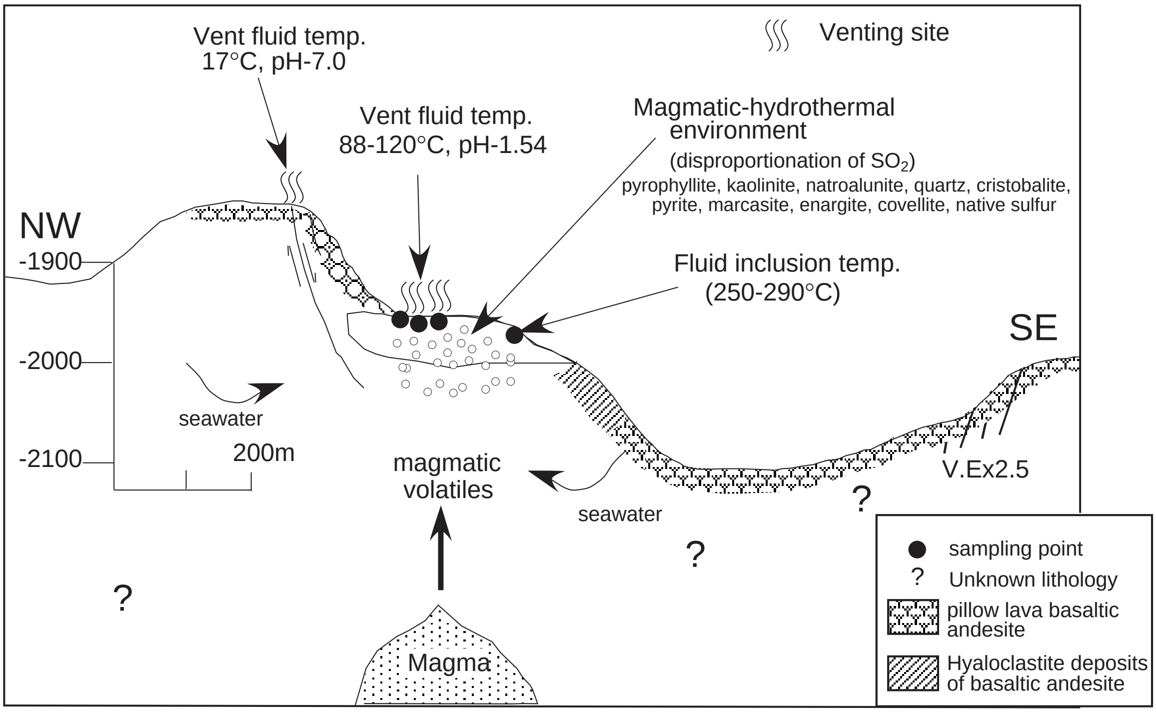

Fig. 3 The schematic cross section along the line X-Y on Figure 1B of the Desmos caldera with surface geology, hydrothermal activity, possible magmatic-hydrothermal environment and the acid-sulfate type of alteration is shown. The possible involvement of magmatic volatiles and seawater is indicated.

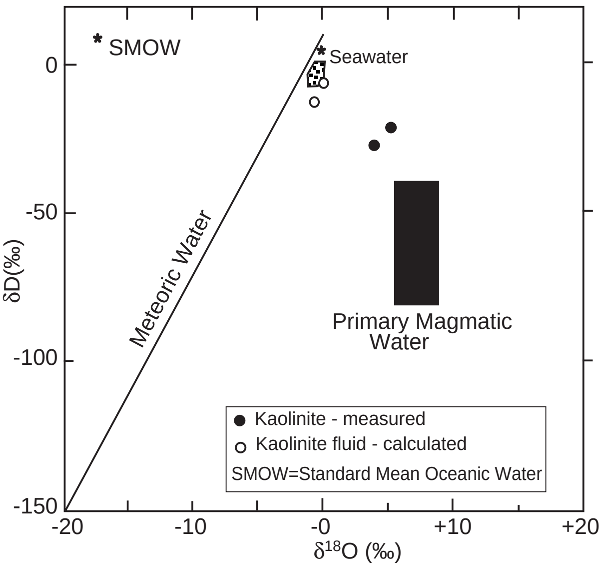

Fig. 4 Diagram of δD vs. $\delta^{18}O$ for clay minerals (kaolinite) and their parent fluid. The δD_{H_2O} and $\delta^{18}O_{H_2O}$ values were calculated using a temperature of 270°C and kaolinite-water fractionation equations of Gilg and Sheppard (1996, hydrogen) and Savin and Lee (1988, oxygen). For reference, the fields of primary magmatic water (Taylor, 1974), seawater and line of meteoric water (Epstein et al., 1965) are also plotted. The elongated trend of the clay mineral and water implies mixing of seawater and magmatic water which is responsible for the alteration.

samples from the Desmos caldera may be produced through several possible mechanisms including addition of isotopically light sulfur compounds of biogenic origin, isotopic exchange reaction between reduced and oxidized sulfur species or contribution of sulfur directly from a magmatic volatile phase (Herzig et al., 1998).

Remobilization of biogenic sulfur in sediment was thought to be the main source of isotopically light sulfur in the sedimented seafloor hydrothermal system (Shanks et al., 1995). The typical example of bacteriogenic sulfur involvement was reported for the hydrothermal precipitates from the Guaymas Basin (Peter and Shanks, 1992). However, the absence of sediments in the Desmos caldera precludes a similar contribution of isotopically light sulfur of biogenic origin in the sediment environment.

Mixing of H_2S-rich vent fluids with SO_4-rich seawater at 200 to 300°C can result in simultaneous reduction of SO_4 and oxidation of H_2S (Ohmoto and Rye, 1979). This process may yields isotopically light sulfate and heavy sulfides, depending on the temperature of the sulfur isotope exchange reaction. However, sulfur isotope exchange reaction cannot change the concentration of sulfide and sulfate in the solution. The end-member hydrothermal solution of the Desmos caldera has SO_4^{2-} concentration higher than seawater (28 m*M*; Gamo et al., 1997) and very low $\delta^{34}S_{H_2S}$, suggesting that sulfur isotope exchange reaction between aqueous H_2S and SO_4^{2-} is not responsible for the $\delta^{34}S$ values of aqueous sulfate and sulfur (Table 1).

Sulfur released from the silicate magma is mainly in the form of SO_2 or H_2S gases. The sulfur gases are dominated by SO_2 at magmatic temperatures (Sakai et al., 1984). The sulfur or sulfide derived from the disproportionation reaction will have $\delta^{34}S$ values less than that of original SO_2, while the sulfate will have $\delta^{34}S$ values greater than the original SO_2 (Ohmoto and Lasaga, 1982). Therefore, the injection of magmatic SO_2 followed by disproportionation reaction could produce SO_4^{2-} with light $\delta^{34}S$ than seawater sulfate depending on the $\delta^{34}S$ of SO_2 gas. The very low pH (1.54), high concentration of H_2S (3.5 to 9.7 m*M*, n=5) and low δD_{H_2O} (-8.1 ‰, n=2) in the vent fluid also suggest magmatic fluid involvement (Gamo et al., 1997).

6.4. Dispropotionation of magmatic SO_2 in Desmos caldera

The sulfur isotope data analyzed in this study (Table 1) can be used as a mean to discriminate the sulfur isotope fractionation pathways. Since there is abundant native sulfur at the Onsen site, the disproportionation reaction of SO_2 gas in the Desmos caldera would be expressed by the following reaction.

$$3SO_2 + 2H_2O \rightarrow S + 2H_2SO_4 \qquad (1)$$

The $\delta^{34}S$ values of native sulfur and sulfate range from -6.5 to -9.3 ‰ (Table 1) and +18.5 to +20 ‰ respectively. The $\delta^{34}S$ value of sulfate in the sample, which is a mixture of seawater sulfate and end-member of the hydrothermal fluid, is lower than seawater values (21 ‰), suggesting that sulfate with low $\delta^{34}S$ values produced during SO_2 disproportionation reaction has been added. During the SO_2 disproportionation reaction (reaction 1), a large kinetic isotopic fractionation would take place between sulfate and elemental sulfur, followed by slow approach to equilibrium (Kusakabe et al., 2000). The homogenization temperature of the fluid inclusions (250–290°C) is much higher than the end-member of the present hydrothermal activity (80–120°C). Therefore, we assumed the temperature of the disproportionation reaction took place at 290°C. By assuming that the reaction (1) proceeded stoichiometrically under sulfur isotope equilibrium, the $\delta^{34}S_{SO_4}$ values added to the hydrothermal fluid were calculated to be +15.2 ‰ using the method of Kusakabe et al. (2000) and an average $\delta^{34}S$ value of native sulfur (-8.0 ‰, Table 1). The average $\delta^{34}S$ value of native sulfur (-8.0 ‰) was used in the preceding calculations although there is significant variation in the $\delta^{34}S$ values of native sulfur collected between 1995 and 1998. The calculated $\delta^{34}S$ values of sulfate added through disproportionation reaction are much lighter than seawater sulfate (Table 1). The low $\delta^{34}S$ values of sulfate measured for vent fluid samples (18.5 to 20.0 ‰, Table 1) are the result of mixing between the sulfate produced by reactions 1 and the seawater sulfate. The original $\delta^{34}S$ values of the magmatic SO_2 gas involved in the disproportional reaction (reaction 1) was estimated to be +7.5 ‰ based on the mass balance calculation of reaction 1.

One fresh basaltic andesite sample from the Desmos caldera was analyzed for the concentration and isotope ratio of sulfur using the method of Ueda and Sakai (1983). The total sulfur content of 162 ppm (S^{2-} = 32 ppm, SO_4^{2-} = 130 ppm) and $\delta^{34}S_{\Sigma S}$ value of +7.5 ‰ were obtained. The total sulfur content is much lower than the average submarine basalts (700 ± 100 ppm; Sakai et al., 1982), which may be due to degassing of sulfur species from the magma during eruption. Agreement of the calculated $\delta^{34}S$ values of the magmatic gases (+7.5 ‰) and analyzed basaltic andesite (+7.5 ‰) support the model that the underlying basaltic andesite magma contributes magmatic SO_2 to the Onsen hydrothermal systems.

6.5. Analogue of terrestrial acid hot crater lake

The hot hydrothermal fluid discharging in the Desmos caldera has very low pH (1.5 to 2.1) and high concentration of SO_4 and H_2S compared to ambient seawater (Table 1). Abundant native sulfur and molten sulfur are common features at the Onsen hydrothermal site (Fig. 2). The alteration and mineralization in the Desmos caldera is of the acid sulfate type (Gena et al., 2001).

Most of the terrestrial hot crater lakes have extremely low pH (e.g. 0.4, Kawah Ijen volcano, Indonesia; Delmelle and Bernard, 1994). In addition, the abundant sulfur spherules and molten sulfur are common in the terrestrial acid hot crater lakes like Yugama (Kusatsu-Shirane volcano, Central Japan), Kawah Ijen volcano (Indonesia), Poas (Costa Rica), Khloridnoe, Bannoe and Maly Semiachick volcanoes (Kamchatka) (Takano et al., 1994; Kusakabe et al., 2000). Furthermore, high $\delta^{34}S_{SO_4}$ values and large difference in $\delta^{34}S$ values between sulfate and native sulfur in terrestrial acid hot crater lakes suggest that SO_2 disproportionation reaction in a magmatic hydrothermal system is the dominant mechanism (Rye et al., 1992).

The geochemical signatures observed in the Demos caldera are consistent with the terrestrial acid hot crater lakes which suggest that the Onsen hydrothermal site is a submarine analogue of the terrestrial acid hot crater lake.

7. Conclusion

The Onsen site located in the Desmos caldera present a unique opportunity to examine acid-sulfate type of alteration and mineralization related to an active hydrothermal system on the seafloor. From this study we have made the following conclusions:

(1) The native sulfur and aqueous SO_4 and H_2S from

the Desmos caldera have extremely low $\delta^{34}S$ values.

(2) These low $\delta^{34}S$ values of aqueous sulfate and native sulfur are produced by disproportionation reaction of magmatic SO_2 gas.

(3) The calculated $\delta^{34}S$ value of SO_2 by mass balance calculation agrees with the measured $\delta^{34}S$ value of the whole rock. It supports our present model that the underlying basaltic andesite magma is directly responsible for contribution magmatic SO_2 to the Onsen hydrothermal systems.

(4) Both the $\delta^{18}O$ and δD values of kaolinite and the calculated $\delta^{18}O_{H_2O}$ and δD_{H_2O} values of the kaolinite-forming fluid suggest a mixing of magmatic fluid and seawater in the Desmos caldera.

From the oxygen, hydrogen and sulfur isotope studies we concluded that the magmatic volatiles have contributed a lot of sulfur and fluids to the Onsen hydrothermal system, Desmos caldera.

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