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Sulfur isotopic composition of hydrothermal precipitates from the Lau back-arc: implications for magmatic contributions to seafloor hydrothermal systems

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Abstract The sulfur isotopic composition of sulfides and barite from hydrothermal deposits at the Valu Fa Ridge back-arc spreading center in the southern Lau Basin has been investigated. Sulfide samples from the White Church area at the northern Valu Fa Ridge have $\delta^{34}\text{S}$ values averaging $+3.8\text{‰}$ ($n = 10$) for bulk sphalerite-chalcopyrite mineralization and $+4.8\text{‰}$ for pyrite ($n = 10$). Barite associated with the massive sulfides exhibits an average of $+20.7\text{‰}$ ($n = 10$). Massive sulfides from the active Vai Lili hydrothermal field at the central Valu Fa Ridge have much higher $\delta^{34}\text{S}$ ratios averaging $+8.0\text{‰}$ for bulk sphalerite-chalcopyrite mineralization ($n = 5$), $+9.3\text{‰}$ for pyrite samples ($n = 5$), and $+8.0\text{‰}$ and $+10.9\text{‰}$ for a chalcopyrite and a sphalerite separate, respectively. The isotopic composition of barite from the Vai Lili field is similar to that of barite from the White Church area and averages $+21.0\text{‰}$ ($n = 8$). Sulfide and barite samples from the Hine Hina area at the southern Valu Fa Ridge have $\delta^{34}\text{S}$ values that are considerably lighter than those observed for samples from the other areas and average -4.9‰ for pyrite ($n = 9$), -4.0 and -5.7‰ for two samples of sphalerite-chalcopyrite intergrowth, and -3.4‰ for a single chalcopyrite separate. The total spread in the isotopic composition of sulfides from Vai Lili and Hine Hina is more than 20‰ over a distance of less than 30 km. The $\delta^{34}\text{S}$ values of sulfides at Hine Hina are the lowest values so far reported for volcanic-hosted poly-

metallic massive sulfides from the modern seafloor. Barite from the Hine Hina field also has unusually light sulfur with $\delta^{34}\text{S}$ values of $+16.1$ to $+16.7\text{‰}$ ($n = 5$). Isotopic compositions of the sulfides at Hine Hina indicate a dramatic decrease in $\delta^{34}\text{S}$ from ordinary magmatic values and, in the absence of biogenic sulfur and/or boiling, imply a unique ^{34}S -depleted source of probable magmatic origin. Sulfide-barite mineralization in the Hine Hina area is associated with a distinctive alteration assemblage consisting of cristobalite, pyrophyllite, kaolinite, opal-CT, talc, pyrite, native sulfur, and alunite. Similar styles of alteration are typically known from high-sulfidation epithermal systems on land. Alunite-bearing, advanced argillic alteration in the Hine Hina field confirms the role of acidic, volatile-rich fluids, and a $\delta^{34}\text{S}$ value of $+10.4\text{‰}$ for the sulfur in the alunite is consistent with established kinetic isotope effects which accompany the disproportionation of magmatic SO_2 into H_2S and H_2SO_4 . The Hine Hina field occurs near the propagating tip of the Valu Fa back-arc spreading center (i.e., dominated by dike injections and seafloor eruptions) and therefore may have experienced the largest contribution of magmatic volatiles of the three fields. The sulfur isotopic ratios of the hydrothermal precipitates and the presence of a distinctive epithermal-like argillic alteration in the Hine Hina field suggest a direct contribution of magmatic vapor to the hydrothermal system and support the concept that magmatic volatiles may be an important component of some volcanogenic massive sulfide-forming hydrothermal systems.

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Introduction

Sulfides forming at modern sediment-free mid-ocean ridges exhibit a range of $\delta^{34}\text{S}$ values from -0.8 to $+6.3\text{‰}$ with an average value of $+3.2\text{‰}$ ($n = 461$; Hekinian et al. 1980; Arnold and Sheppard 1981; Styr et al. 1981; Skirrow and Coleman 1982; Kerridge et al. 1983; Shanks et al. 1984; Zierenberg et al. 1984; Shanks

and Seyfried 1987; Bluth and Ohmoto 1988; Hannington and Scott 1988; McConachy 1988; Woodruff and Shanks 1988; Kase et al. 1990; Marchig et al. 1990; Duckworth et al. 1995; Knott et al. 1995; Stuart et al. 1995). The isotopic composition of the sulfides indicates contributions of sulfur from two sources, namely mid-ocean ridge basalt (MORB, $\delta^{34}\text{S} \pm 0\text{‰}$; Sakai et al. 1984) and seawater ($\delta^{34}\text{S} + 20.9\text{‰}$; Rees et al. 1978). Arnold and Sheppard (1981) observed that the isotopic composition of sulfides from the East Pacific Rise at 21°N ($+2.1\text{‰}$) can be explained by non-equilibrium mixing of about 10% sulfur from reduced seawater sulfate with about 90% sulfur of basaltic origin. The variation in the isotopic composition of the sulfides is explained by varying proportions of reduced seawater sulfate and basaltic sulfur leached from the underlying volcanics.

Experimental data and theoretical models for seafloor hydrothermal systems indicate that the circulation of seawater through the upper oceanic crust results in the formation of anhydrite at temperatures of about $150\text{--}200^\circ\text{C}$ (Shanks et al. 1981; Janecky and Shanks 1988; Bowers 1989). Because the concentration of Ca in seawater is only 30% of the concentration of sulfate, only part of the seawater sulfate precipitates as anhydrite. Leaching of additional Ca from the basaltic wall rock increases the amount of anhydrite precipitation, but about 0.62 mmol/kg of excess sulfate remains in the hydrothermal seawater (Bischoff and Dickson 1975). At temperatures of about 250°C , the remaining sulfate is reduced to sulfide as a consequence of the oxidation of ferrous Fe in pyroxene or olivine or through conversion of igneous pyrrhotite to pyrite in the basalt. The reduction of seawater sulfate at high temperatures ($>250^\circ\text{C}$ – 400°C) and low water/rock ratios is rapid and quantitative and does not lead to isotopic fractionation, i.e., the initial value around $+21\text{‰}$ remains unchanged (Shanks et al. 1981; Ohmoto and Lasaga 1982; Shanks and Seyfried 1987; Alt 1994). Mixing of this isotopically heavy sulfur with sulfur of basaltic origin is one way of explaining the isotopic variations commonly found in seafloor massive sulfides. Heavier sulfur in the sulfides indicates a larger component of reduced seawater sulfate in the hydrothermal fluids, and $\delta^{34}\text{S}$ values of about $+6\text{‰}$ would indicate a seawater/basalt sulfur ratio of about 30:70. Anhydrite and barite associated with the sulfides typically have the isotopic composition of contemporaneous seawater ($+21\text{‰}$).

Bowers (1989) noted that hydrothermal end member fluids discharging from the basaltic basement are strongly dominated by a basaltic $\delta^{34}\text{S}$ signature, with only a very minor contribution from seawater sulfate reduced to sulfide in the recharge zone. Under these circumstances, large variations in the $\delta^{34}\text{S}$ of the sulfides forming at the seafloor may be due to sulfate reduction during mixing in the chimney environment. Janecky and Shanks (1988) showed that mixing of hydrothermal fluids with seawater, either close to the seafloor or in the walls of sulfide chimneys and edifices, can account for

$\delta^{34}\text{S}$ of up to $+4.5\text{‰}$. Small variations of $\delta^{34}\text{S}$ in seafloor massive sulfides may thus also be explained by variations in the permeability of sulfide structures as a controlling factor for the degree of fluid/seawater mixing. $\delta^{34}\text{S}$ greater than $+4.5\text{‰}$ require additional fluid/rock interaction in the feeder zone beneath the vent sites.

Gradients in the isotopic composition of sulfides within individual chimneys are also common (e.g., lighter sulfur in the center and heavier sulfur at the margin or vice versa). These variations may be explained by fluid-seawater mixing in the walls of the chimneys, by temporal variations in the isotopic composition of H_2S in the hydrothermal fluids due to changing water/rock reactions at depth during the evolution of a hydrothermal system, or by replacement of early sulfate by sulfides within the chimney (see Bluth and Ohmoto 1988; Woodruff and Shanks 1988). Small-scale variations in sulfur isotopic ratios may also be explained by reactions between hydrothermal fluids and pre-existing sulfides or sulfates (Janecky and Shanks 1988).

In contrast to mid-ocean ridge type massive sulfides, sulfide deposits forming at some immature back-arc spreading centers such as the Okinawa Trough are characterized by significantly higher sulfur isotopic ratios, ranging from $+4.3$ and $+10.7\text{‰}$ (Halbach et al. 1989). These deposits are commonly associated with calc-alkaline volcanic rocks (e.g., andesites, rhyolites). The $\delta^{34}\text{S}$ ratios of island-arc andesites and rhyolites range between $+5$ and $+7\text{‰}$ (avg. $+4$ to 5‰ ; Ueda and Sakai 1984; Woodhead et al. 1987) compared to $+0.1 \pm 0.5\text{‰}$ for MORB (Sakai et al. 1984). The ^{34}S -enrichment observed in island-arc volcanics is thought to be related to subduction of hydrated oceanic crust and sediments containing seawater sulfate (Woodhead et al. 1987; Alt et al. 1993). Pb isotope data by Fouquet and Marcoux (1995) have shown the likely involvement of oceanic crust and sediments in the genesis of lavas in the southernmost Lau back-arc. Back-arc basin basalts from the Mariana Arc have $\delta^{34}\text{S}$ values of $1.1 \pm 0.5\text{‰}$, which overlap those for the arc and MORB. These rocks, however, are products of a mature back-arc rift (Alt et al. 1993). Felsic volcanic rocks produced during the earlier stages of back-arc development strongly reflect the influence of the subducting slab on the melting region (Hawkins and Melchior 1985) and may have $\delta^{34}\text{S}$ values similar to island-arc volcanics (i.e., avg. $+4$ to 5‰). Consequently, hydrothermal fluids circulating through felsic back-arc volcanic rocks may acquire sulfur isotopic ratios higher than in endmember fluids at mid-ocean ridges, owing to the presence of heavy crustal sulfur.

In this work we report on sulfur isotope ratios for sulfides and barite from hydrothermal vents in the Lau back-arc basin. The $\delta^{34}\text{S}$ values for sulfides show a spread of more than 20‰ ($+16.2$ to -7.7‰ $\delta^{34}\text{S}$) over a distance of less than 30 km . Samples from several sites in the Lau Basin indicate important non-equilibrium variation in $\delta^{34}\text{S}$ that cannot be explained by simple mixing of sulfur from two isotopically distinct sulfur sources

with the composition of seawater sulfate and crustal sulfur. The anomalous isotopic composition of the hydrothermal precipitates, together with the presence of an acid-sulfate alteration mineral assemblage, may indicate direct magmatic contributions of volcanic SO_2 to the hydrothermal system.

Geologic setting

The Lau Basin is a marginal back-arc region behind the Tonga-Kermadec subduction zone, about 1700 km north-northeast of New Zealand (Fig. 1a). Hydrothermal activity was discovered with the French submersible *Nautilus* in 1989 along the Valu Fa Ridge, the active back-arc spreading center of the southern Lau Basin (Fouquet et al. 1993). The ridge extends for at least 120 km and consists of three *en echelon*, north-northeast-striking segments: the northern, central, and southern Valu Fa Ridge (Fig. 1b). Each segment is about 40–50 km long and is separated by small (< 5 km) non-transform offsets (Collier and Sinha 1990). The active, southward propagating segment approaches to within 20–40 km of the active Tofua volcanic arc. Recent volcanic activity along the ridge includes a highly differentiated suite of volcanics consisting of Fe-Ti basalts, andesites and dacite (Jenner et al. 1987; Frenzel et al. 1990; Sunkel 1990). The degree of fractionation increases towards the south and approaches rhyolitic composition at the propagating tip of the southernmost ridge segment (Fouquet et al. 1993) where the Pb isotopic composition in the sulfides indicate a source of Pb very close to that of the island arc (Fouquet and Marcoux 1995).

Hydrothermal deposits were located on all three segments of the Valu Fa Ridge (Fouquet et al. 1991, 1993; Fig. 1b). At the northern segment, inactive sphalerite-barite chimneys and diffuse low-temperature (25 °C) hydrothermal activity were observed at a water depth of about 1950 m ("White Church area", Fig. 2a). On the central Valu Fa Ridge, active high-temperature black smokers (320–342 °C) and lower temperature with smokers (250–320 °C) occur on top of a massive sulfide mound at about 1700 m water

depth ("Vai Lili" vent field, Fig. 2b). On the southern part of the ridge, large areas (several hundred m^2) are dominated by diffuse, low-temperature (< 40 °C) venting at depths between 1850 and 1900 m ("Hine Hina" vent field, Fig. 2c). Inactive barite-sphalerite chimneys also occur locally.

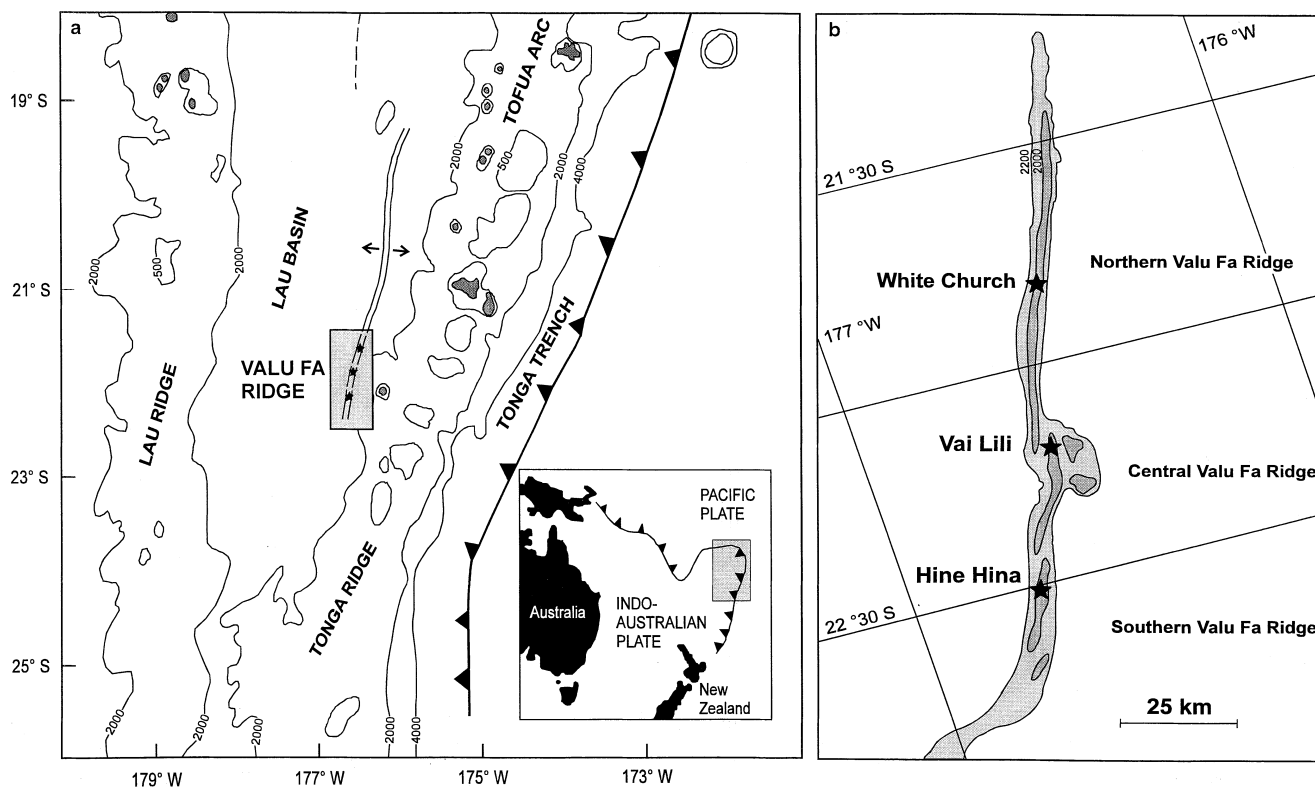
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Structural mapping at White Church, Vai Lili, and Hine Hina has revealed a dramatic difference in the extent of faulting (i.e., tectonic extension) and recent volcanism in the different areas, with tectonic extension dominant in the White Church area and magmatic activity dominant at Hine Hina further to the south (Fouquet et al. 1993).

White Church area

Mineralization in the White Church area is confined to fault zones at the top and along the flanks of the ridge (Wiedicke and Kudrass 1990). The area of inactive sphalerite-barite chimneys (several meters high and 1–2 m in diameter) and mounds is approximately 200 × 300 m and occurs at water depths between 1946 and 1966 m (Fig. 2a). Hundreds of small, inactive Mn chimneys occur along a fault scarp to the south of the White Church area. Diffuse low-temperature hydrothermal venting is also controlled by faults and restricted to the ridge crest along the southern part of the rift

Fig. 1 a Location of the Valu Fa back-arc ridge between the remnant Lau Ridge and the active Tonga arc in the southern Lau Basin. Stars indicate the position of hydrothermal deposits. **b** Sites of hydrothermal deposits at the three segments of the Valu Fa Ridge: White Church area, Northern Valu Fa Ridge; Vai Lili area, Central Valu Fa Ridge; Hine Hina area, Southern Valu Fa Ridge. The Southern Valu Fa Ridge is the actively southward propagating tip of the ridge



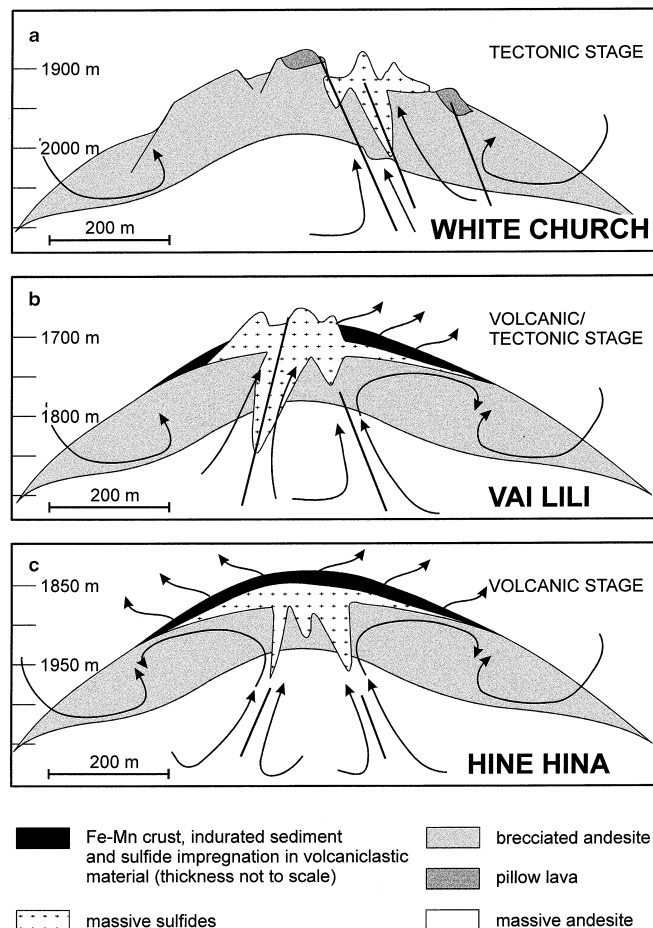


Fig. 2a–c Schematic vertical cross section through the White Church, Vai Lili, and Hine Hina hydrothermal fields at the Valu Fa Ridge indicating the various stages of volcanic versus tectonic development (modified after Fouquet et al. 1993). *Arrows* indicate fluid circulation paths

segment (Herzig et al. 1993). The presence of sulfide-cemented volcanic breccia indicates higher temperature seafloor precipitation within the fault zones. The White Church area is in a tectonic stage of development and hydrothermal activity is largely controlled by tectonic extension (Fouquet et al. 1993).

Vai Lili field

The Vai Lili vent field covers an area of 100×400 m at water depths of 1680–1740 m (Fig. 2b) where the substrate is made up of volcanoclastic material. The field consists of at least 10 discrete clusters of active black and white smokers (up to 15 m high) underlain by a massive sulfide mound measuring 50×200 m and 15 m in height. The mound consists of massive sphalerite-barite precipitates at the top and chalcopyrite-rich sulfides at the base. Mineralization is controlled by a major normal fault running subparallel to the ridge, and portions of a stockwork zone have been exposed by block rotation (Herzig et al. 1993), indicating an advanced stage of tectonic activity (Fouquet et al. 1993).

Hine Hina field

In the Hine Hina area (Fig. 3), the top of the ridge (1850 m) consists of approximately 50 m of autobrecciated volcanic rocks and volcanoclastic sediments which are underlain by massive lava

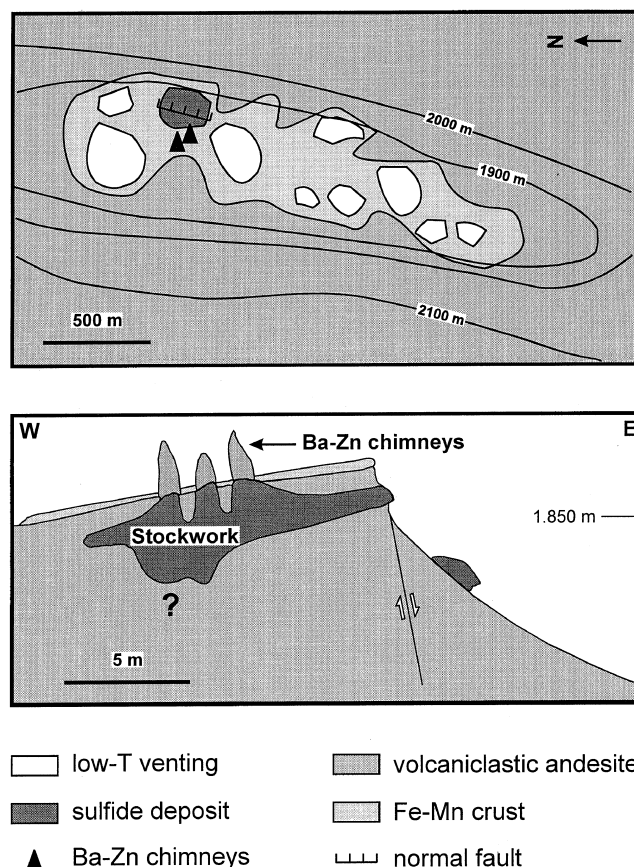


Fig. 3 Schematic diagrams illustrating the geologic setting of the Hine Hina hydrothermal field (*top*) and a vertical cross section through the Hine Hina hydrothermal deposit (modified after Fouquet et al. 1993)

flows (Fouquet et al. 1993). Widespread low-temperature Mn-Fe oxide crusts (up to 10 cm thick, Fig. 4c, d) and hydrothermally indurated sediment, locally associated with small cauliflower-shaped Mn oxide mounds (Fig. 4g), cover the altered remnants of eroded white andesite domes (Fig. 4e, f). The white color is due to the strong alteration of the andesitic material. The alteration assemblage in the earthy white andesite material consists of cristobalite, pyrophyllite, kaolinite, opal-CT, talc, pyrite, native sulfur, and alunite (Herzig et al. 1990; Von Stackelberg et al. 1990; Herzig et al. 1993). Native sulfur locally cements less altered andesite fragments and hyaloclastites or occurs as vesicle filling in strongly bleached but still consolidated white andesite (Fig. 4a, b). The strongly altered volcanic material also contains disseminated sulfide mineralization in the form of fresh shiny pyrite crystals. The disseminated pyrite was exposed by the recent break-up of Mn-Fe crusts that capped the white andesite domes. Fragments of the Fe-Mn crusts, 1–2 m in size, are now sliding off the mound (Fig. 4d). Locally, massive Cu-Fe sulfides occur as a horizontal layer beneath the Mn-Fe crusts and on top of indurated sediment and altered andesite (Fig. 3) suggesting sulfide precipitation beneath the sealing Mn-Fe crusts. In some areas small Ba-Zn chimneys also occur along faults that have focused hydrothermal upflow (Fig. 4h). In contrast to the White Church and Vai Lili hydrothermal fields, the Hine Hina field appears to have developed in an area of dominantly magmatic extension and recent volcanic activity (Fig. 2).

Samples and methods

Samples for this study were collected in 1989 during the French-German diving campaign *NAUTILAU* using the French submersible

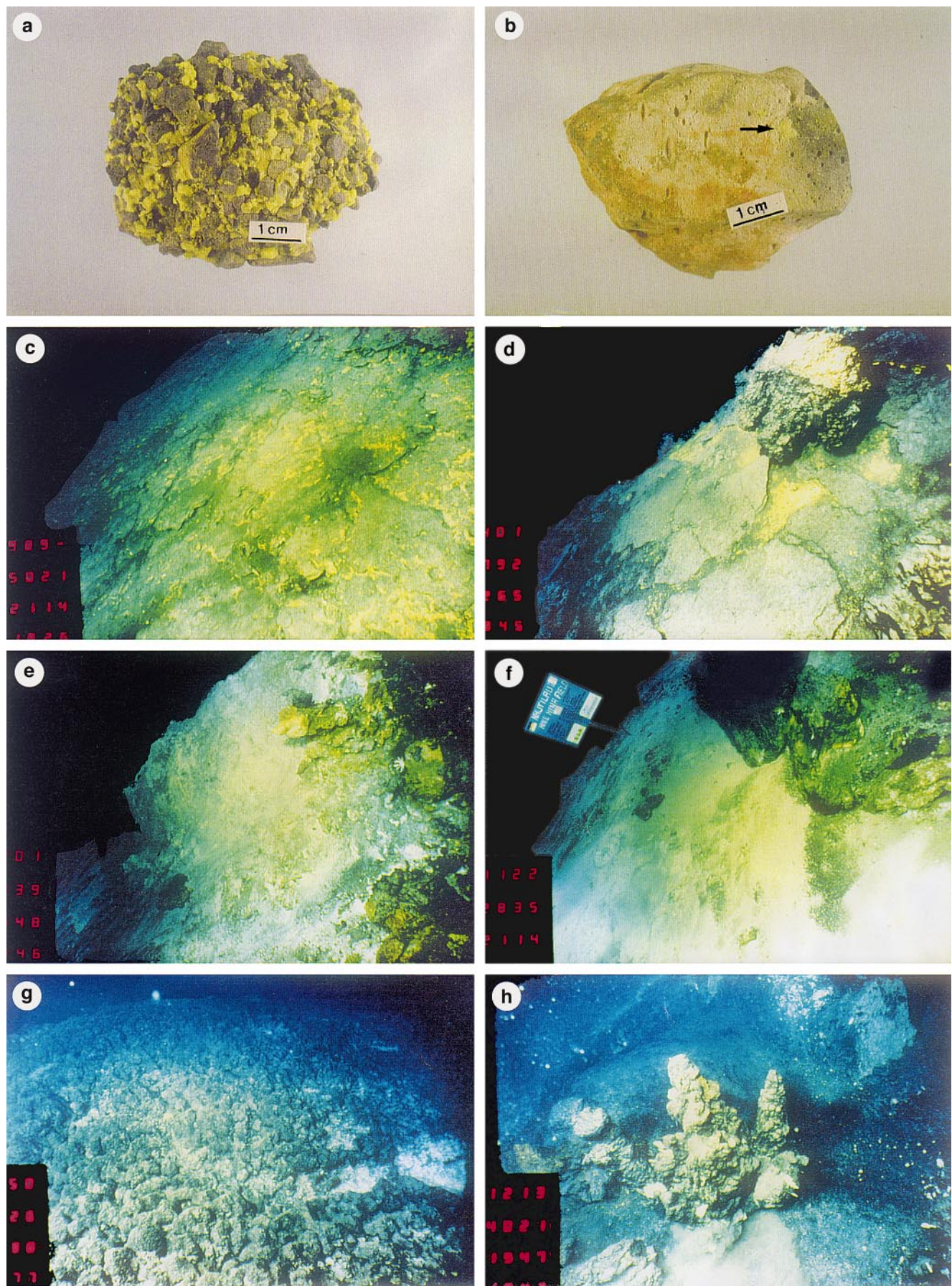


Fig. 4a–h Photographs of hand specimens and seafloor images from the Hine Hina hydrothermal field (Southern Valu Fa Ridge). **a** Native sulfur cementing altered andesite fragments; **b** native sulfur (*arrow*) occurring as vesicle filling in strongly hydrothermally bleached and altered andesite; **c** low-temperature Mn-Fe crusts (up to 10 cm thick) covering altered white andesite domes; **d** broken Mn-Fe crusts sliding off the mound exposing altered white andesite. Inactive barite-sphalerite structure at the *upper right* of photograph measures about 1 m in diameter. **e** Exposed part of highly altered white andesite dome which originally was covered by Mn-Fe crusts (horizontal scale about 8 m). **f** Strongly altered and bleached white volcanic material containing fresh shiny pyrite sand. *Sign* in the back has a size of about 1 × 1.5 m and indicates the location of the Hine Hina hydrothermal field as discovered with *Nautila* during the French-German *NAUTILAU* project. **g** Cauliflower-shaped Mn oxide mounds in the Hine Hina area (horizontal scale about 10 m). **h** Inactive barite-sphalerite chimneys (1–2 m high) from which samples for this study were collected



Nautila and during surface cruises with the German research vessel *Sonne* (SO-48: 1987; SO-67: 1990). A total of 31 sulfide and barite samples and associated alunite from the diving campaign with *Nautila* as well as one sulfide sample and three samples of native sulfur from the *Sonne* cruises were selected for analysis (Table 1). These samples are representative for hydrothermal products oc-

curing at the northern, central and southern Valu Fa Ridge (White Church, Vai Lili and Hine Hina hydrothermal fields). Sulfides and sulfate were separated by a combination of heavy liquids and chemical methods; sulfides were leached from barite-rich samples with hot HCl and HNO₃. During this procedure, some sulfur is precipitated out as native sulfur, which is dissolved with chloroform. Alunite was extracted from one sample of altered andesite following the method described by Wasserman et al. (1992). After chemical separation and extraction, isotopic ratios in the sulfur were determined for sphalerite + chalcocopyrite, pyrite, native sulfur, barite, and alunite. Analyses were performed at the stable isotope facilities of Freiberg University of Mining and Technology, Germany, and at the University of Ottawa, Canada. Analyses are reported as standard δ notation relative to Canyon Diablo Troilite (CDT). The error of reproducibility is better than $\pm 0.2\text{‰}$ (1s) based on multiple analyses of standards.

Results

Sulfur isotope ratios obtained for sulfides, barite, and native sulfur from the northern (White Church area), central (Vai Lili area) and southern Valu Fa Ridge (Hine Hina area) are reported in Table 1. Figure 5 summarizes the results for sulfides and barite. These data indicate

Table 1 Sulfur isotopic data ($\delta^{34}\text{S}_{\text{CDT}}\text{‰}$) for sulfides, barite, and native sulfur from White Church, Vai Lili, and Hine Hina hydrothermal areas at the Valu Fa back-arc ridge (SW Pacific)

	Sphalerite + Chalcocopyrite	Pyrite	Native sulfur	Barite
White Church				
06-01-01-01	4.5	4.8		21.2
06-01-01-02	4.6	5.3		18.8
06-01-02-01	3.6	4.6		20.6
06-01-03-01		3.1		21.2
07-06-02-01	3.7	2.2		20.6
07-06-02-02	4.2	4.0		20.9
08-07-01	4.2	5.9		20.9
10-04-02	4.0	4.2		20.9
10-07-01	2.8	6.8		19.5
10-07-02	2.7	6.6		21.9
68 KD 2	2.2 (+ pyrite)			
Vai Lili				
18-04-01	8.4	9.3		20.9
18-04-02	7.2	10.9		21.3
18-05-Ac				21.7
18-05-Bd				20.4
18-05-Be				20.5
18-05-01	7.8	10.2		21.1
18-05-02	9.3	16.2		20.4
20-04	8.0 (chalcocopyrite)			
22-03	10.9 (sphalerite)	8.2		
22-05-01	7.6	8.0		21.8
Hine Hina				
12-01		-5.7		
16-01				16.7
16-02	-4.0	-7.3		
16-02	-3.4 (chalcocopyrite)	-4.8		16.3
16-02		-2.8		
16-03		-3.9		16.6
16-04-01		-6.8		
16-04-02		-7.7		
16-05-01		-4.2		16.1
16-05-02		-4.2		
16-06	-5.7			16.4
130GA			-4.8	
131GA			-2.4	
244GA			-3.0	

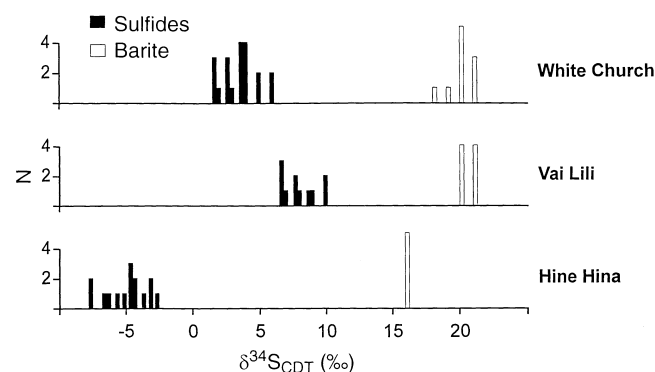


Fig. 5 Plot of sulfur isotopic ratios for sulfides and barite from White Church, Vai Lili, and Hine Hina deposits of the Valu Fa Ridge

significant differences in the isotopic composition of sulfides and barite collected from the three segments of the Valu Fa Ridge.

$\delta^{34}\text{S}$ in samples from the northern Valu Fa Ridge (White Church area) vary between $+2.7$ and $+4.6\text{‰}$ (avg. $+3.8\text{‰}$, $n = 9$) for bulk sphalerite-chalcopryrite mineralization, a single value of $+2.2\text{‰}$ for a sphalerite-chalcopryrite-pyrite intergrowth, and $+2.2$ and $+6.8\text{‰}$ (avg. $+4.7\text{‰}$, $n = 10$) for pyrite. Barite associated with the massive sulfides exhibits a range of $\delta^{34}\text{S}$ values from $+18.8$ to $+21.9\text{‰}$ with an average of $+20.7\text{‰}$ ($n = 10$).

Massive sulfides from the active Vai Lili hydrothermal field have much higher sulfur isotope ratios, between $+7.1$ and $+9.3$ (avg. $+8.0\text{‰}$, $n = 5$) for bulk sphalerite-chalcopryrite mineralization. Chalcopryrite and sphalerite separates have $\delta^{34}\text{S}$ values of $+8.0\text{‰}$ and $+10.9\text{‰}$, respectively. The $\delta^{34}\text{S}$ of six pyrite samples analyzed from the Vai Lili chimneys are also between $+8.0\text{‰}$ and $+10.9\text{‰}$ (avg. $+9.3\text{‰}$, $n = 5$) with one sample outlier at $+16.2\text{‰}$. Fractionation between the sulfide minerals and H_2S in the hydrothermal fluids is small at temperatures $> 150^\circ\text{C}$ (Ohmoto and Lasaga 1982), so that the $\delta^{34}\text{S}$ of the sulfides are considered to be close to that of the reduced sulfur in the hydrothermal fluids. The isotopic composition of barite from the Vai Lili field is essentially the same as that of barite from the White Church area and ranges from $+20.4$ to $+21.8\text{‰}$ (avg. $+21.0\text{‰}$, $n = 8$). The sulfide-sulfate pairs give unreasonable temperatures and hence exhibit isotopic disequilibrium, based on known temperature-dependent fractionation factors, typical of most seafloor hydrothermal systems (Ohmoto 1986).

Sulfide and barite chimney samples from the Hine Hina area (see Fig. 4h) have $\delta^{34}\text{S}$ which are considerably lighter than those of samples from the White Church and Vai Lili areas (Fig. 5) and are also distinct from other seafloor massive sulfide deposits (Fig. 6). The isotopic composition of pyrite varies between -2.8 and -7.7‰ with an average of -5.3‰ ($n = 9$). Two samples of sphalerite-chalcopryrite intergrowths have $\delta^{34}\text{S}$ of -4.0 and -5.7‰ , respectively. A single chalcopryrite separate had a $\delta^{34}\text{S}$ of -3.4‰ . Barite separates from sulfide-barite

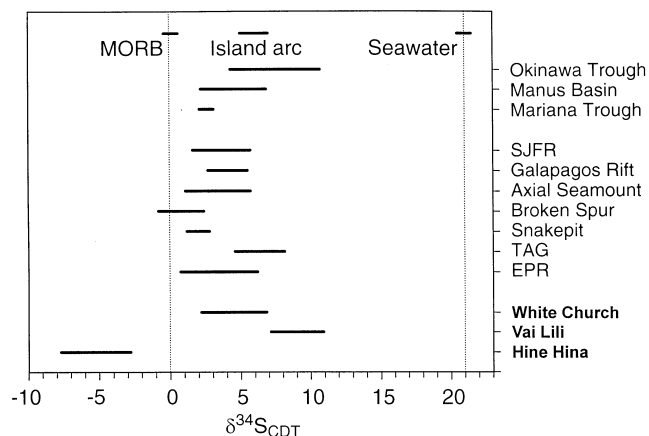


Fig. 6 Compilation of sulfur isotopic data ($\text{‰ } \delta^{34}\text{S}$) for back-arc and mid-ocean ridge sulfides with ranges for sulfides from White Church, Vai Lili, and Hine Hina hydrothermal areas. References: *MORB*, Sakai et al. (1984); *island-arc*, Ueda and Sakai (1984); *seawater*, Rees et al. (1978); *Okinawa Trough*, Halbach et al. (1989); *Manus Basin*, Lein et al. (1993); *Mariana Trough*, Kusakabe et al. (1990); *Southern Juan de Fuca Ridge (SJFR)*, Shanks and Seyfried (1987); *Galapagos Rift*, Knott et al. (1995); *Axial Seamount*, Hannington and Scott (1988); *Broken Spur*, Duckworth et al. (1995); *Snakepit*, Kase et al. (1990); *TAG*, Herzig et al. (1998); *East Pacific Rise (EPR)*, McConachy (1988), Bluth and Ohmoto (1988), Stuart et al. (1995), Hekinian et al. (1980), Arnold and Sheppard (1981), Styr et al. (1981), Kerridge et al. (1983), Zierenberg et al. (1984), Woodruff and Shanks (1988), Marchig et al. (1990)

precipitates collected in the Hine Hina area are also characterized by unusually light sulfur, with $\delta^{34}\text{S}$ of $+16.1$ to $+16.7\text{‰}$ for five samples analyzed. As in other deposits, the large difference in the isotopic compositions of the sulfides and the barite indicates that the reduced and oxidized sulfur species did not equilibrate isotopically and that the H_2S and SO_4 behaved independently.

Barite from other seafloor deposits with $\delta^{34}\text{S}$ less than that of seawater probably formed as a mixture of seawater sulfate, and sulfate produced by the oxidation of light H_2S in the vent fluids. Hannington and Scott (1988) noted light sulfur in barite (19.2‰ , $n = 8$) from hydrothermal chimneys at Axial Seamount (Juan de Fuca Ridge), and also interpreted this to reflect the incorporation of isotopically light sulfur from the oxidation of H_2S in the hydrothermal fluids. Mixing of H_2S -rich vent fluids with SO_4 -rich seawater at $200\text{--}300^\circ\text{C}$ can result in the simultaneous reduction of SO_4 and oxidation of H_2S (Ohmoto and Rye 1979), leading to anomalously light barite and heavy sulfides. However, the sulfides at Hine Hina are light, not heavy, suggesting that reduction of seawater SO_4 was not involved in the precipitation of the sulfides. The 4 to 5‰ decrease in the $\delta^{34}\text{S}$ composition of barite at Hine Hina, in comparison to the White Church and Vai Lili fields, is consistent with the much lighter reduced sulfur in the hydrothermal fluids indicated by the isotopically light sulfides (e.g., -5‰ at Hine Hina versus $+9\text{‰}$ $\delta^{34}\text{S}$ at Vai Lili). This sulfide was apparently oxidized to S^{32} -enriched SO_4 and mixed with heavy seawater SO_4 to produce the light barite.

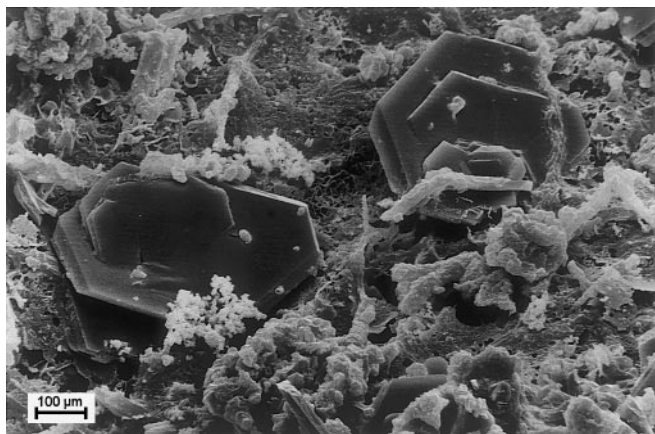


Fig. 7 SEM photograph of alunite from the Hine Hina field typically forming platy crystals which is the characteristic habit of alunite formed from hydrothermal solutions with a large magmatic vapor component (see Arribas et al. 1995)

Three separates of native sulfur from the andesite breccias and hyaloclastite deposits surrounding the Hine Hina field have $\delta^{34}\text{S}$ values of -2.4 , -3.0 , and -4.8‰ (Table 1). The native sulfur is isotopically identical to the sulfides collected from chimneys at the center of the field and suggests a common sulfur source. The abundance of native sulfur in the altered andesites at Hine Hina (Fig. 4a, b) indicates a large excess of dissolved sulfur which may reflect an enrichment in volatiles as a result of the condensation of a vapor phase arising from boiled fluids or a degassing magma.

The most intensely altered white andesite in the Hine Hina field contains alunite as well as native sulfur. The alunite is intergrown with pyrite in cristobalite-rich rocks containing kaolinite and pyrophyllite (lining cavities). The alunite occurs mainly in open spaces and is notably platy or tabular (Fig. 7), a habit typical of alunite in magmatic-hydrothermal systems (Arribas et al. 1995). It has the composition of natroalunite (mostly Na-rich, with minor K) and is intergrown with another alunite-group mineral, woodhouseite (Ca- and P-bearing). The sulfur in alunite separated from a sample of altered andesite has a $\delta^{34}\text{S}$ value of $+10.4\text{‰}$. Coexisting pyrite in the same sample has an isotopic compositions of -5.3‰ .

Possible sources of sulfur and the significance for magmatic contributions to submarine hydrothermal systems

The $\delta^{34}\text{S}$ ratios of sulfides in most volcanic-dominated hydrothermal systems on the mid-ocean ridges and back-arc spreading centers fall within a narrow range of values close to that of magmatic sulfur (0 and $+4$ to 5‰ $\delta^{34}\text{S}$), and are almost always greater than 0‰ (e.g., as at White Church and Vai Lili: Fig. 6). The isotopic signature of the Hine Hina sulfides requires a highly fractionated source of light sulfur which cannot be

accounted for by simple non-equilibrium mixing between seawater SO_4 and H_2S leached from a volcanic basement. Isotopically light sulfur, similar to that observed in the sulfides from the Hine Hina field, may be produced in several ways, including biogenic reduction of seawater SO_4 , fractionation of sulfur between reduced and oxidized species as a result of large shifts in the oxidation state of the fluids (e.g., by boiling), or by the evolution of light sulfur directly from a magmatic volatile phase.

In a closed system, it is theoretically possible to shift the $\delta^{34}\text{S}$ of aqueous H_2S to lower values, simply by the progressive deposition of sulfides or sulfates relatively enriched in ^{34}S . However, in modern seafloor hydrothermal systems it is unlikely that such closed-system effects are important.

The remobilization of biogenic sulfur in marine sediments is generally thought to be the most important source of isotopically light sulfur in seafloor hydrothermal systems (e.g., Goldhaber and Kaplan 1974; Shanks et al. 1995, Zierenberg 1994). Until this study, sulfides from sediment-covered spreading centers in the Guaymas Basin were the only documented examples of hydrothermal precipitates on the modern ocean floor with negative $\delta^{34}\text{S}$ values. The thick sequence of turbiditic sediments in the Guaymas Basin are notably organic and sulfide-rich, and bacteriogenic sulfur in the vent fluids has produced sulfides with $\delta^{34}\text{S}$ values as low as -3.7‰ (e.g., Peter and Shanks 1992; Seewald et al. 1994). Barite from the same deposits also exhibits a wide range of $\delta^{34}\text{S}$ values, from $+29\text{‰}$ to as low as $+4\text{‰}$. The absence of sediments in the neovolcanic zone of the Valu Fa Ridge, however, precludes a similar contribution of isotopically light sulfur of biogenic origin.

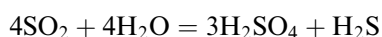
There is no doubt that bacteria play an important role in seafloor hydrothermal systems and that bacteria can influence the sulfur isotopic systematics in the hydrothermal precipitates. However, the level of bacterial activity at Hine Hina is no different than that observed in other vent fields (White Church, Vai Lili). Thus, the anomalous sulfur isotopic signatures in the Hine Hina precipitates compared to White Church and Vai Lili is unlikely to be a consequence of bacterial activity.

Boiling of hydrothermal fluids and separation of a volatile phase can cause radical variations in the isotopic composition of sulfides deposited by the boiling fluids and at the same time produce a gas-rich phase capable of producing acid-sulfate alteration (see later). McKibben and Eldridge (1990) observed that rapid shifts from positive to negative $\delta^{34}\text{S}$ values in the vapor-dominated zones of boiling epithermal systems are likely related to the preferential oxidation of H_2^{34}S , induced by the loss of $\text{H}_2(\text{g})$ during boiling. However, the magnitude of these shifts appears highly variable at the grain scale, leading to considerable isotopic heterogeneity in the samples. In the Lau Basin, boiling has not been observed and is unlikely to have played a role in the isotopic history of vent fluids, owing to the water depths at the vent sites (1680 to 1966 m). The maximum measured

temperatures at the seafloor (342 °C, Vai Lili field) are below the boiling temperatures for seawater at these pressures. Thus, significant boiling which is required to have an impact on the sulfur isotope fractionation can be ruled out.

Abundant evidence exists to indicate inputs of magmatic volatiles, including sulfur, to submarine hydrothermal systems (e.g., de Ronde 1995; Kadko et al. 1995; Alt 1995), and in the absence of biogenic sulfur, this is the most likely source of light sulfur in the Hine Hina field. Exsolution of magmatic volatiles at depth may contribute substantially to the dissolved CO₂, CH₄, and SO₂ in subseafloor hydrothermal fluids (e.g., Alt et al. 1989). Furthermore, substantial losses of sulfur during crystallization of lavas on the seafloor suggests that degassing during volcanic eruptions may also be significant (e.g., Moore and Fabbi 1971). Recently, Sedwick et al. (1992) described direct magmatic inputs of volcanic sulfur in low-temperature hydrothermal vents at a mid-plate seamount (Loihi volcano, Hawaii), and McMurtry et al. (1993) has described important contributions of volcanic sulfur in vents at a submarine arc setting in the Marianas.

Sulfur released from silicate melts is mostly SO₂ and H₂S, the relative importance of which is controlled by the reaction: SO₂(g) + H₂(g) = H₂S(g) + O₂(g). At magmatic temperatures, the sulfur gases are dominated by SO₂ (Sakai et al. 1984; Wallace and Carmichael 1992). In the deep parts of a hydrothermal system, volcanic SO₂ will be reduced to H₂S and sulfides forming from these fluids would have δ³⁴S values close to 0‰ (i.e., approximating magmatic values in a MORB-dominated setting). Thus mixing between magmatic SO₂ and an evolved hydrothermal fluid at high temperatures will have little or no effect on the isotopic composition of the sulfur in the fluid, as the δ³⁴S of the H₂S already leached from the volcanics is close to that of the magmatic SO₂. However, if the volcanic gases cool below 300–400 °C, the SO₂ will disproportionate rapidly according to the reaction:



The disproportionation of SO₂ into reduced and oxidized species is accompanied by a kinetic isotope effect which causes the sulfide to become enriched in ³²S and the sulfate to become enriched in ³⁴S (Ohmoto and Rye 1979; Ohmoto and Lasaga 1982). The δ³⁴S of the sulfides deposited from the fluid will be <0‰ and the δ³⁴S of sulfate minerals derived from the same fluid will be >0‰ (although substantially lower than seawater sulfate). In the near surface, oxidizing environment, the H₂SO₄ dissociates further to produce acids which leach the rocks. This may lead to the formation of characteristic acid-sulfate alteration assemblages.

The occurrence of alunite and pyrite in the samples from Hine Hina is similar to that of acid-sulfate assemblages formed from hydrothermal solutions with a large magmatic vapor component (e.g., Heald et al.

1987; Stoffregen 1987; Rye et al. 1992; Hedenquist and Lowenstern 1994; Arribas 1995). The high concentrations of P in the alunite may also reflect a magmatic component, as suggested for some subaerial epithermal systems (Aoki 1991). It is unlikely that evolved seawater could have produced the extremely acid conditions necessary to form alunite, without the presence of additional acids such as H₂SO₄ derived from volcanic SO₂. Alunite-bearing assemblages are indicative of extremely acid, high-sulfidation conditions, and alunite stability is generally limited to pH < 3 (e.g., Hemley et al. 1980; Stoffregen 1987). In subaerial acid-sulfate systems it is generally acknowledged that the source of the acidity is magmatic sulfur (e.g., Giggenbach 1987), and these systems typically form in the root zones of volcanic domes where fluids are charged with condensed magmatic volatiles (e.g., Heald et al. 1987). At high temperatures, alunite forms from the hypogene production of H₂SO₄ from the volcanic SO₂, although in the near-surface environment, alunite may also form during acid leaching caused by the oxidation of H₂S. The latter is common in subaerial geothermal systems, especially in steam-heated environments above active boiling zones. H₂S, which becomes concentrated in the condensed volatile phase above the boiling zone, is oxidized to H₂SO₄ and thereby contributes to the acidity of the near-surface groundwaters. At Hine Hina, we have ruled out the possibility of boiling, so the acid-sulfate conditions could not have been produced by condensed gases arising from a boiling vent.

The sulfur isotope data provide a means of discriminating between these processes. The generation of acid directly from volcanic gases produces isotopically light sulfide and heavy sulfate through the disproportionation of the volcanic SO₂. As a result, hypogene sulfates such as alunite will be notably heavy, while associated sulfide minerals may have δ³⁴S values significantly lower than the starting composition. The large difference between the δ³⁴S of alunite and that of coexisting pyrite in the Hine Hina field, coupled with the highly acidic conditions required to stabilize the alunite, strongly suggests the involvement of magmatic SO₂ (e.g., Rye et al. 1992). In contrast simple oxidation of H₂S should not result in significant isotopic differences between the coexisting sulfides and sulfates. Alunite formed by near-surface oxidation or weathering of pre-existing sulfides (i.e., supergene alunite) will have essentially the same isotopic composition as the sulfides since the fractionation of sulfur caused by these processes is negligible (Ohmoto and Rye 1979).

At Hine Hina, the sulfur in alunite is 15‰ heavier than the sulfide in coexisting pyrite, consistent with disproportionation of volcanic SO₂, and not near-surface oxidation of H₂S, as the most likely mechanism for acid generation. Assuming a δ³⁴S value of close to +4‰ for the original volcanic SO₂ (see Ueda and Sakai 1984), an isotopic mass balance between the sulfides (e.g., -5‰ in pyrite) and coexisting sulfates (e.g., +10‰ in alunite) at Hine Hina suggests a molar H₂S/SO₄ ratio of about

1 in the acid fluids. The hypogene origin of alunite is supported by the presence of cogenetic pyrophyllite, which is stable relative to kaolinite only at high temperatures (e.g., in excess of 250–300 °C: Hemley et al. 1980; Stoffregen 1987). This association is consistent with vent temperatures observed elsewhere on the Valu Fa Ridge and confirms that the acid conditions necessary to form the alunite were unlikely to have evolved solely by the oxidation of H₂S during late-stage mixing and cooling of the vent fluids.

At Hine Hina, the most abundant native sulfur is found within a zone, about 100 m wide, surrounding the barite-sulfide chimneys, but does not coincide with the zone of active low-temperature venting and base metal mineralization. The native sulfur may represent excess H₂S transported to the margins of the upflow zone or more likely the remnants of volcanic sulfur associated with the extrusion of the andesite dome. The presence of alunite together with the native sulfur strongly supports the derivation of both sulfide and sulfate sulfur from magmatic SO₂. The sulfide in the nearby chimneys may have been derived partly from leaching of pre-existing native sulfur in the volcanics during a period of more focused, high-temperature venting at the site of the chimneys. Isotopic fractionation during this near-surface leaching should be small and the composition of the sulfides deposited at the seafloor would closely mimic that of the remobilized volcanic sulfur.

Concluding remarks

The differences in the mineralogy, geochemistry, and isotopic composition of the sulfides between the White Church and Vai Lili areas and the Hine Hina field most likely reflect the progressive increase in volcanic activity along the ridge from north to south. There is no indication that the volcanic rocks at Hine Hina are more evolved or are more likely to have produced a volatile phase than the rocks at Vai Lili, but the different styles of hydrothermal mineralization and alteration are thought to be closely related to differences in the local volcanic and tectonic evolution of the spreading center (e.g., Fig. 2; Fouquet et al. 1993). Von Stackelberg (1990) and Wiedicke and Kudrass (1990) noted that the northern segments of the Valu Fa Ridge are presently undergoing tectonic extension while the southern, propagating tip of the ridge system is the most volcanically active. The local evolution of the spreading center has had an important impact on the style of hydrothermal discharge at the three sites (Fouquet et al. 1993). Present-day volcanic activity is mostly developed at the southward propagating tip of the Valu Fa Ridge (Hine Hina area). A magma chamber was seismically imaged at 3.2 ± 0.2 km depth beneath the Central Valu Fa Ridge (Collier and Shina 1992) and may be even shallower further south.

Subduction along the Tonga Trench is oblique to the Valu Fa Ridge such that the Hine Hina field is closest to

the subducting Pacific Ocean plate. The increase in the Pb isotopic composition from the White Church to the Hine Hina field (Fouquet and Marcoux 1995) reflects a small increase in the contribution of Pb from subducted Pacific Ocean sediments. However, the increase in sedimentary Pb is not reflected in the S isotopes and contrasts with sediment-covered ridge hydrothermal systems.

The more prolific volcanic activity at the Hine Hina field is consistent with an increase in the contribution of magmatic volatiles to the hydrothermal system (see Yang and Scott 1996). Recent eruptions of massive andesite domes on this segment of the spreading center were likely responsible for the release of volcanic SO₂. At Hine Hina a thick crust of Mn-oxides may serve to insulate the underlying volcanics, partly trapping the rising magmatic vapors. Intense fracturing and the high permeability of the volcanic substrate during the later tectonic stage, as at Vai Lili, may contribute to extensive mixing between seawater and the rising high-temperature fluids, so that contributions from a magmatic source and associated isotopic effects may be masked. The evolving nature of volcanic and tectonic activity at the southward-propagating tip of the Valu Fa Ridge also suggests that the magmatic signature in the sulfides at Hine Hina may eventually be overprinted as hydrothermal circulation during a later tectonic stage becomes more rock-dominated.

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References

- Alt JC (1994) A sulfur isotopic profile through the Troodos ophiolite, Cyprus: primary composition and the effects of seawater hydrothermal alteration. *Geochim Cosmochim Acta* 58: 1825–1840
- Alt JC (1995) Sulfur isotopic profile through the oceanic crust: sulfur mobility and seawater-crustal sulfur exchange during hydrothermal alteration. *Geology* 23: 585–588
- Alt JC, Anderson TF, Bonell L (1989) The geochemistry of sulfur in a 1.3 km section of hydrothermally altered oceanic crust, DSDP Hole 504B. *Geochim Cosmochim Acta* 53: 1011–1023
- Alt JC, Shanks WC III, Jackson MC (1993) Cycling of sulfur in subduction zones: The geochemistry of sulfur in the Mariana

- Island Arc and back-arc trough. *Earth Planet Sci Lett* 119: 477–494
- Aoki M (1991) Mineralogical features and genesis of alunite solid solution in high temperature magmatic-hydrothermal systems. *Geol Surv Japan Rep* 277: 35–37
- Arnold M, Sheppard SMF (1981) East Pacific Rise at latitude 21°N: Isotopic composition and origin of the hydrothermal sulphur. *Earth Planet Sci Lett* 56: 148–156
- Arribas A Jr (1995) Characteristics of high-sulfidation epithermal deposits, and their relation to magmatic fluid. In: Thompson JFH (ed) *Magma, fluids and ore deposits*. Mineral Association of Canada Short Course Notes 23: 419–454
- Arribas A Jr, Cunningham CG, Rytuba JJ, Rye RO, Kelly WC, Podwysocki MH, McKee EH, Tosdale RM (1995) Geology, geochronology, fluid inclusions, and isotope geochemistry of the Rodalquilar gold alunite deposit, Spain. *Econ Geol* 90: 795–822
- Bischoff JL, Dickson FW (1975) Seawater-basalt interaction at 200 °C and 500 bars: implications for origin of seawater heavy metal deposits and regulation of seawater chemistry. *Earth Planet Sci Lett* 25: 385–397
- Bluth GJ, Ohmoto H (1988) Sulfide-sulfate chimneys on the East Pacific Rise, 11° and 13°N latitude. Part II: sulfur isotopes. *Can Mineral* 26: 505–515
- Bowers TS (1989) Stable isotope signatures of water-rock interaction in mid-ocean ridge hydrothermal systems: sulfur, oxygen, and hydrogen. *J Geophys Res* 94: 5775–5786
- Collier JS, Sinha MC (1992) Seismic mapping of a magma chamber beneath the Valu Fa Ridge, Lau Basin. *J Geophys Res* 97: 14031–14053
- Collier JS, Sinha MC (1990) Seismic images of a magma chamber beneath the Lau Basin back-arc spreading centre. *Nature* 346: 646–648
- de Ronde CEJ (1995) Fluid chemistry and isotopic characteristics of seafloor hydrothermal systems and associated VMS deposits: potential for magmatic contributions. In: Thompson JFH (ed) *Magma, fluids, and ore deposits*. Mineral Association of Canada Short Course Notes 23: 479–509
- Duckworth RC, Knott R, Fallick AE, Rickard D, Murton BJ, van Dover C (1995) Mineralogy and sulphur isotope geochemistry of the Broken Spur sulphides, 29°N, Mid-Atlantic Ridge. In: Parson LM, Walker CL, Dixon DR (eds) *Hydrothermal vents and processes*. *Geol Soc Spec Publ* 87: 175–189
- Fouquet Y, Marcoux E (1995) Lead isotope systematics in Pacific hydrothermal sulfide deposits. *J Geophys Res* 100: 6025–6040
- Fouquet Y, von Stackelberg U, Charlou JL, Donval JL, Erzinger J, Foucher JP, Herzig PM, Mühe R, Soakai S, Wiedicke M, Whitechurch H (1991) Hydrothermal activity and metallogenesis in the Lau back-arc basin. *Nature* 349: 778–781
- Fouquet Y, von Stackelberg U, Charlou JL, Erzinger J, Herzig PM, Mühe R, Wiedicke M (1993) Metallogenesis in back-arc environments: the Lau Basin example. *Econ Geol* 88: 2154–2181
- Frenzel G, Mühe R, Stoffers P (1990) Petrology of the volcanic rocks from the Lau Basin, Southwest Pacific. *Geol Jahrb* 92: 395–479
- Giggenbach WF (1987) Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand. *Appl Geochem* 2: 143–161
- Goldhaber MB, Kaplan IR (1974) The sulfur cycle. In: Goldberg ED (ed) *The sea*, vol 5., John Wiley and Sons, New York, pp 569–655
- Halbach P, Nakamura K, Wahsner M, Lange J, Sakai H, Käselitz L, Hansen R-D, Yamano M, Post J, Prause B, Seifert R, Michaelis W, Teichmann F, Kinoshita M, Märtens A, Ishibashi J, Czerwinski S, Blum N (1989) Probable modern analogue of Kuroko-type massive sulphide deposits in the Okinawa Trough back-arc basin. *Nature* 338: 496–499
- Hannington MD, Scott SD (1988) Mineralogy and geochemistry of an hydrothermal silica-sulfide-sulfate spire in the caldera of Axial-Seamount, Juan de Fuca Ridge. *Can Mineral* 26: 603–625
- Hawkins JW, Melchior JT (1985) Petrology of Mariana Trough and Lau Basin basalts. *J Geophys Res* 90: 11431–11468
- Heald P, Foley NK, Hayba DO (1988) Comparative anatomy of volcanic-hosted epithermal deposits: acid-sulfate and adularia-sulfate types. *Econ Geol* 82: 1–26
- Hedenquist JW, Lowenstern JB (1994) The role of magmas in the formation of hydrothermal ore deposits. *Nature* 370: 519–527
- Hekinian R, Fevrier M, Bischoff JL, Picot P, Shanks WC III (1980) Sulfide deposits from the East Pacific Rise near 21°N. *Science* 207: 1433–1444
- Hemley JJ, Montoya JW, Marinenko JW, Luce RW (1980) Equilibria in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and some general implications for alteration/mineralization processes. *Econ Geol* 75: 210–228
- Herzig PM, von Stackelberg U, Petersen S (1990) Hydrothermal mineralization from the Valu Fa Ridge, Lau back-arc basin (SW Pacific). *Mar Mining* 9: 271–301
- Herzig PM, Hannington MD, Fouquet Y, von Stackelberg U, Petersen S (1993) Gold-rich polymetallic sulfides from the Lau back-arc and implications for the geochemistry of gold in seafloor hydrothermal systems in the Southwest Pacific. *Econ Geol* 88: 2182–2209
- Herzig PM, Petersen S, Hannington MD (1998) Geochemistry and sulfur isotopic composition of the TAG hydrothermal mound, Mid-Atlantic Ridge, 26°N. In: Herzig PM, Humphris SE, Miller J (eds) *Proc Ocean Drilling Program*, 158 (in press)
- Janecky DR, Shanks WC III (1988) Computational modelling of chemical and isotopic reaction processes in seafloor hydrothermal systems: chimneys, massive sulfides, and subjacent alteration zones. *Can Mineral* 26: 805–825
- Jenner GA, Cawood PA, Rautenschlein M, White WM (1987) Composition of back-arc volcanics, Valu Fa Ridge, Lau Basin: evidence for a slab-derived component in their mantle source. *J Vol Geoth Res* 32: 209–222
- Kadko D, Baross J, Alt J (1995) The magnitude and global implications of hydrothermal flux. In: Humphris SE, Zierenberg RA, Mullineaux LS, Thompson RE (eds) *Seafloor hydrothermal systems: physical, chemical, biological, and geological interactions*. *Geophys Monogr* 91: 446–466
- Kase K, Yamamoto M, Shibata T (1990) Copper-rich sulfide deposits near 23°N, Mid-Atlantic Ridge: chemical composition, mineral chemistry, and sulfur isotopes. In: Detrick R, Honnorez J, Bryan WB, Juteau T et al. (eds) *Proc Ocean Drilling Program, Scientific Results*, College Station, TX, 106/109, pp 163–172
- Kerridge JF, Haymon RM, Kastner M (1983) Sulfur isotope systematics at the 21°N site, East Pacific Rise. *Earth Planet Sci Lett* 66: 91–100
- Knott R, Fallick AE, Rickard D, Baecker H (1995) Mineralogy and sulphur isotope characteristics of a massive sulphide boulder, Galapagos Rift, 85°55'W. In: Parson LM, Walker CL, Dixon DR (eds) *Hydrothermal vents and processes*. *Geol Soc Spec Pub* 87: 207–222
- Kusakabe M, Mayeda S, Nakamura E (1990) S, O and Sr isotope systematics of active vent materials from the Mariana backarc basin spreading axis at 18°N. *Earth Planet Sci Lett* 100: 275–282
- Lein AY, Ul'yanova NV, Grinenko VA, Bibikova YV, Lisitsyn AP (1993) Mineralogical and geochemical features of the Manus Basin hydrothermal sulfide ores, Bismarck Sea. *Geochem Int* 30: 57–71
- Marchig V, Puchelt H, Rösch H, Blum N (1990) Massive sulfides from ultra-fast spreading ridge, East Pacific Rise at 18–21°S: a geochemical stock report. *Mar Mining* 9: 459–493
- McConachy TF (1988) Hydrothermal plumes and related deposits over spreading ridges in the northeast Pacific Ocean: the East Pacific Rise near 11°N and 21°N, Explorer Ridge, and the J. Tuzo Wilson Seamounts. Unpubl PhD Thesis, University of Toronto, 403 p
- McKibben MA, Eldridge CS (1990) Radical sulfur isotope zonation of pyrite accompanying boiling and epithermal gold de-

- position: a shrimp study of the Valles Caldera, New Mexico. *Econ Geol* 85: 1917–1925
- McMurtry GM, Sedwick PN, Fryer P, VonderHaar DL, Yeh H-W (1993) Unusual geochemistry of hydrothermal vents on submarine arc volcanoes: Kasuga Seamounts, Northern Mariana arc. *Earth Planet Sci Lett* 114: 517–528
- Moore JG, Fabbri BP (1971) An estimate of juvenile sulfur content of basalt. *Contrib Mineral Petrol* 33: 118–127
- Ohmoto H (1986) Stable isotope geochemistry of ore deposits. In: Valley JW, Taylor HP, O'Neil JR (eds) *Stable isotopes in high temperature geological processes*. *Rev Min* 16, Mineralogical Society of America, pp 491–560
- Ohmoto H, Lasaga AC (1982) Kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems. *Geochim Cosmochim Acta* 46: 1727–1745
- Ohmoto H, Rye RO (1979) Isotopes of sulfur and carbon. In: Barnes HL (ed) *Geochemistry of hydrothermal ore deposits*. 2nd edn. J. Wiley and Sons, New York, pp 509–567
- Peter JM, Shanks WC III (1992) Sulfur, carbon, and oxygen isotope variations in submarine hydrothermal deposits of Guaymas Basin, Gulf of California, USA. *Geochim Cosmochim Acta* 56: 2025–2040
- Rees CE, Jenkins WJ, Monster J (1978) The sulfur isotopic composition of ocean water sulfate. *Geochim Cosmochim Acta* 42: 377–381
- Rye RO, Bethke PM, Wassermann MD (1992) The stable isotope geochemistry of acid sulfate alteration. *Econ Geol* 87: 225–238
- Sakai H, des Marais DJ, Ueda A, Moore JG (1984) Concentrations and isotope ratios of carbon, nitrogen and sulfur in ocean-floor basalts. *Geochim Cosmochim Acta* 48: 2433–2441
- Sedwick PN, McMurtry GM, MacDougall JD (1992) Chemistry of hydrothermal solutions from Pele's Vents, Loihi Seamount, Hawaii. *Geochim Cosmochim Acta* 56: 3643–3667
- Seewald JS, Seyfried WE, Shanks WC (1994) Variation in the chemical and stable isotope composition of carbon and sulfur species during organic-rich sediment alteration: an experiment and theoretical study of hydrothermal activity at Guaymas Basin, Gulf of California. *Geochim Cosmochim Acta* 58: 5065–5082
- Shanks WC III, Seyfried WE Jr (1987) Stable isotope studies of vent fluids and chimney minerals, southern Juan de Fuca Ridge. Sodium metasomatism and seawater sulfate reduction. *J Geophys Res* 92: 11387–11399
- Shanks WC III, Bischoff JL, Rosenbauer RJ (1981) Seawater sulfate reduction and sulfur isotope fractionation in basaltic systems: interaction of seawater with fayalite and magnetite at 200–350 °C. *Geochim Cosmochim Acta* 45: 1977–1995
- Shanks WC III, Koski RA, Woodruff LG (1984) Mineralogy and stable isotope systematics of sulfide deposits from the Juan de Fuca Ridge (Abst.). *EOS, Am Geophys Union Trans* 65: 1113
- Shanks WC III, Böhlke JK, Seal RR II (1995) Stable isotopes in mid-ocean ridge hydrothermal systems: interactions between fluids, minerals, and organisms. In: Humphris SE, Zierenberg RA, Mullineaux LS, Thompson RE (eds) *Seafloor hydrothermal systems: physical, chemical, biological, and geological interactions*. *Geophys Monogr* 91: 194–221
- Skirrow R, Coleman ML (1982) Origin of sulfur and geothermometry of hydrothermal sulfides from the Galapagos Rift, 86°N. *Nature* 299: 142–144
- Stoffregen R (1987) Genesis of acid sulfate alteration and Au-Cu-Ag mineralization of Summitville, Colorado. *Econ Geol* 82: 1575–1591
- Stuart FM, Harrop PJ, Knott R, Fallick AE, Turner G, Fouquet Y, Rickard D (1995) Noble gas isotopes in 25000 years of hydrothermal fluids from 13°N on the East Pacific Rise. In: Parson LM, Walker CL, Dixon DR (eds) *Hydrothermal vents and processes*. *Geol Soc Spec Publ* 87: 133–143
- Styrt MM, Brackmann AJ, Holland HD, Clark BC, Pisutha-Arnond V, Eldridge CS, Ohmoto H (1981) The mineralogy and the isotopic composition of sulfur in hydrothermal sulfide/sulfate deposits on the East Pacific Rise, 21°N latitude. *Earth Planet Sci Lett* 53: 382–390
- Sunkel G (1990) Origin of petrological and geochemical variations of Lau Basin lavas (SW Pacific). *Mar Mining* 9: 205–234
- Ueda A, Sakai H (1984) Sulfur isotope study of Quaternary volcanic rocks from the Japanese Island Arc. *Geochim Cosmochim Acta* 48: 1837–1848
- von Stackelberg U (1990) R.V. Sonne cruise SO48: summary of results testing a model of mineralization. *Mar Mining* 9: 135–144
- von Stackelberg U, Marchig V, Müller P, Weiser T (1990) Hydrothermal mineralization in the Lau and North Fiji Basins. *Geol Jahrb D* 92: 547–613
- Wallace P, Carmichael ISE (1992) Sulfur in basaltic magmas. *Geochim Cosmochim Acta* 56: 1863–1847
- Wasserman MD, Rye RO, Bethke PM, Arribas A Jr (1992) Methods for separation and total stable isotope analysis of alunite. *US Geol Surv Open File Rep* 92–9
- Wiedicke M, Kudrass H-R (1990) Morphology and tectonic development of the Valu Fa Ridge, Lau Basin (Southwest Pacific): results from a deep-towed side-scan sonar survey. *Mar Mining* 9: 145–156
- Woodhead JD, Harmon RS, Fraser DG (1987) O, S, Sr and Pb isotope variations in volcanic rocks from the Northern Mariana Islands: implications for crustal recycling in intra-oceanic arcs. *Earth Planet Sci Lett* 83: 39–52
- Woodruff LG, Shanks WC III (1988) Sulfur isotope study of chimney minerals and hydrothermal fluids from 21°N, East Pacific Rise: hydrothermal sulfur sources and disequilibrium sulfate reduction. *J Geophys Res* 93: 4562–4572
- Yang K, Scott SD (1996) Possible contribution of a metal-rich magmatic fluid to a sea-floor hydrothermal system. *Nature* 383: 420–423
- Zierenberg RA (1994) Data report: sulfur content of sediments and sulfur isotope values of sulfide and sulfate minerals from Middle Valley. In: Mottl MJ, Davies EE, Fisher AT et al. (eds) *Proc Ocean Drilling Program, Scientific Results*, College Station, TX, 139: 739–748
- Zierenberg RA, Shanks WC III, Bischoff JL (1984) Massive sulfide deposits at 21°, East Pacific Rise: chemical composition, stable isotopes, and phase equilibria. *Geol Soc Am Bull* 95: 922–929

Note added in proof After submission of this paper, Gamo et al. (1997) have provided more evidence in support of our conclusions. The data by Gamo et al. based on analyses of dissolved gases in vent fluids from the *DESMOS* caldera in the Manus back-arc basin, Papua New Guinea, exactly duplicate our findings. Similar to us, Gamo et al. have interpreted their data as a result of the incorporation of a magmatic fluid to a seafloor hydrothermal system.

Gamo T, Okamura K, Urabe T, Auzende J-M, Ishibashi J, Shitashima K, Chiba H (1997) Acid and sulfate-rich hydrothermal fluids from the Manus back-arc basin, Papua New Guinea. *Geology*, 25: 139–142