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SULFIDE–SULFATE CHIMNEYS ON THE EAST PACIFIC RISE, 11° AND 13°N LATITUDES. PART II: SULFUR ISOTOPES

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ABSTRACT

Sulfide minerals from eleven separate hydrothermal vents, and vent-fluid H_2S from five vents along the East Pacific Rise at 11° and 13°N latitudes were analyzed for sulfur isotopic compositions. On average, $\delta^{34}S$ (sulfide) values (4.1 ±0.6‰) are among the heaviest found for ridge-crest hot-spring systems. The $\delta^{34}S$ (sulfide) values of chimneys at 11° and 13°N are similar, although those at 13°N define a slightly wider range. Analyses of lateral samples of chimneys show a central depletion of $\delta^{34}S$ in chimney walls at 13°N, and a small decrease from the interior to exterior at 11°N. Chimneys analyzed along their length show decreasing isotopic ratios upward. Measurements of coexisting sulfides suggest isotopic disequilibrium, but the $\delta^{34}S$ values of sulfides sampled from the inner walls of the chimneys are within ±0.5‰ of discharging vent-fluid H_2S. These observations, in light of the chimney-growth model in Part I, suggest that: (i) the hydrothermal systems at vent sites from 13°N and those at 11°N are each tied to a single magma chamber at depth; (ii) the $\delta^{34}S(H_2S)$ of the discharging fluids changed gradually from +1.7 in the early stage to +5.0‰ in the later stage of hydrothermal activity; (iii) the change is attributed to the increased contribution of H_2S derived from reduction of seawater sulfate compared to the H_2S from leaching of basalt at deeper parts of the plumbing system; and (iv) the variations in the $\delta^{34}S$ of vent-fluid H_2S and of sulfides within chimney walls were probably caused by rapid chemical reactions of dissolution, reprecipitation, and replacement between hydrothermal fluids and earlier sulfide minerals in the chimney, rather than by kinetic isotope effects during precipitation of sulfides or by generation of H_2S by sulfate reduction within the chimney structure.

Keywords: sulfur isotopes, chimneys, sulfides, vent fluids, hydrothermal systems, East Pacific Rise.

SOMMAIRE

Nous avons analysé les compositions isotopiques des sulfures prélevés de onze évents hydrothermaux distincts, ainsi que le H_2S dans la phase fluide émise de cinq évents le long de la ride Est-Pacifique, entre les parallèles 11° et 13°N. En général, les valeurs $\delta^{34}S$ des sulfures (4.1 ±0.6‰) figurent parmi les plus élevées des systèmes géothermiques des rides océaniques. Les valeurs $\delta^{34}S$ pour les sulfures des cheminées sont semblables à 11° et à 13°N, mais celles des systèmes à 13°N montrent une plus grande variation. Les analyses des échantillons pris le long d'une traverse latérale à travers la paroi d'une cheminée révèlent une réduction en $\delta^{34}S$ vers le centre à 13°N, et une légère réduction de l'intérieur vers l'extérieur à 11°N. Le long d'une cheminée, le rapport isotopique diminue vers le haut. Les mesures effectuées sur les sulfures coexistants indiquent un déséquilibre isotopique; les valeurs $\delta^{34}S$ des sulfures prélevés le long de la paroi interne d'une cheminée concordent, à 0.5‰ près, avec la composante H_2S du fluide de l'évent. Considérées à la lumière de notre modèle pour l'évolution d'une cheminée, proposé dans l'article précédent, nos observations indiquent que (i) les systèmes géothermiques aux sites à 13°N (ou à 11°N), sont reliés à une seule chambre magmatique en profondeur. (ii) La valeur $\delta^{34}S$ du fluide hydrothermal déchargé change graduellement de +1.7, à un stade précoce, à +5.0‰ vers la fin de l'évolution hydrothermale d'un système. (iii) Ce changement résulterait d'une augmentation de la contribution du H_2S par réduction de sulfate de l'eau de mer, et d'une diminution du H_2S dérivé par lessivage de basaltes à plus grandes profondeurs. (iv) La variation dans le rapport $\delta^{34}S$ du H_2S des fluides, aussi bien que des sulfures des parois des cheminées, serait due aux réactions chimiques rapides, déterminant la dissolution, la reprécipitation, et le remplacement impliquant des fluides hydrothermaux et des sulfures précoces dans la cheminée, plutôt qu'aux effets cinétiques isotopiques pendant la précipitation des sulfures ou la formation de H_2S par réduction de sulfate dans l'édifice d'une cheminée.

(Traduit par la Rédaction)

Mots-clés: isotopes de soufre, cheminées, sulfures, sulfates, fluides des évents, zonation, ride Est-Pacifique.

INTRODUCTION

This paper reports the results of sulfur isotope investigations of H_2S in vent fluids and sulfide minerals from the chimneys at 11° and 13°N, East Pacific Rise (EPR), which have been described in detail in Part I (Graham *et al.* 1988). The specific aims of our investigation in Part II were to: (1) establish the isotopic relationship between hydrothermal fluids and chimney sulfides (*i.e.*, the extent of equilibrium, magnitude of fractionation factors); (2) investigate changes in the sulfur isotope composition of sulfides and hydrothermal fluids during chimney growth; and (3) put constraints on the sources of sulfide–sulfur and the hydrology of these hydrothermal systems.

SAMPLING AND ANALYTICAL TECHNIQUES

The configuration of a typical vent at 11° and 13°N, composed of a main and several auxiliary chimneys, is schematically illustrated in Figure 1. Discharging fluids were sampled from the main and auxiliary vents by means of titanium-syringe water-bottles, manipulated by the pilot of the submersible ALVIN. Hydrothermal fluids and corresponding chimneys (typically the upper ~50 cm of the struc-

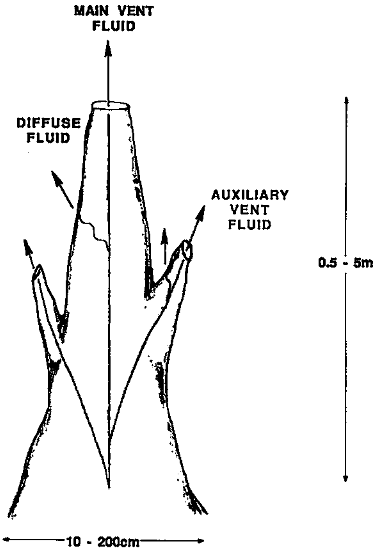

FIG. 1. Schematic configuration of a sulfide–sulfate chimney at 11°–13°N, EPR. Fluid flow is of three main types: main vent discharge, auxiliary vent discharge, and diffuse flow through the chimney walls.

TABLE 1. H_2S CONCENTRATION AND SULFUR ISOTOPIC COMPOSITIONS OF VENT FLUIDS AT 11° AND 13°N, EPR

Vent	Dive	Temp (°C)	H_2S (mmol/kg)	Bottle #	$\delta^{34}S(H_2S)$	Chimney Type
1	1366		2.9			main
6	1372	354	8.2	6	4.7	main
8	1373	380	4.5	5	3.2	auxiliary
				6	3.5	main
				7	2.3	auxiliary
9	1379		4.4	2	4.9	main
				6	4.7	main
10	1377	347	8.0	2	4.6	main
11-A	1380		12.2	2	4.1	main
				9	4.9	main
11-B				5	4.8	auxiliary
				6	5.2	main

Footnote: Fluid temperatures and H_2S concentrations are from Bowers *et al.* (1988). Two different chimneys ("A" and "B") were sampled for vent-fluids at vent site #11; however, only the mound was sampled for sulfides.

ture) were collected within minutes of each other. Samples from inactive vents and mounds at the bases of the chimneys were also collected. Details of the fluid sampling procedure are described in Von Damm (1983) and Von Damm *et al.* (1985). Fluid chemistry for the six active chimneys sampled from 11° and 13°N, including the three chimneys described in Graham *et al.* (1988), is reported in Bowers *et al.* (1988).

The temperatures of the discharging fluids (Table 1) were obtained with a thermocouple probe. Normal temperature readings for the vent fluids are considered to be accurate within ±5°C, based on repetitive measurements. Problems were encountered if the probe was not placed correctly in the vent. Vent fluids appeared to ride up the probe and heat the thermocouple casing, resulting in occasional suspect readings, such as the 380°C temperature obtained for vent 8 (A.C. Campbell, pers. comm. 1986). Although this temperature was reported by Bowers *et al.* (1988), they did not consider it to be a reliable number. The probe failed completely after dive 1377 and no further temperatures were recorded.

Samples for sulfur isotope analysis were drawn from the titanium sample bottles shipboard, and were treated with a solution of $0.1M$ cadmium acetate to precipitate H_2S as CdS. During sampling, these solutions were flushed with nitrogen gas to remove any oxygen. Although the sulfide precipitates (CdS) were exposed to air for a short time, cadmium sulfide is relatively resistant to oxidation when precipitated from solution (Gavelin *et al.* 1960). In the laboratory at The Pennsylvania State University, the CdS precipitates were filtered, and boiled with an excess quantity of $0.1M$ $AgNO_3$ to convert them to Ag_2S.

Selected sections of chimney samples were set in epoxy blocks and polished for microscopic analysis. A section 1 mm thick was sliced off for petrographic study (Graham *et al.* 1988), and the remainder was used for isotopic, atomic absorption, or X-ray diffraction analysis. Bulk-rock samples of the chimneys and specific portions of polished sections were extracted with a dental drill, using a carbide steel bit.

Specific sulfide phases were separated and purified by chemical means. Samples were ground to a powder and reacted under a stream of de-oxygenated argon gas with $3N$ HCl at 60°C for 2–3 hours. The HCl was used to dissolve sphalerite, wurtzite and pyrrhotite, producing H_2S gas (pyrrhotite was never recovered in sufficient quantities to analyze for $\delta^{34}S$). This gas was passed through an H_2O trap to recapture HCl, then through a trap of 0.1 N $AgNO_3$ to recover H_2S as Ag_2S. Any anhydrite present was dissolved as aqueous sulfate in HCl. Pyrite, chalcopyrite, and other copper–iron sulfides which are non-reactive to HCl were collected by filtration.

Residual sulfides and the Ag_2S precipitates were thoroughly mixed with copper oxide, and reacted *in vacuo* at 1050°C. The evolved SO_2 gas was purified by passage through a series of cold traps to remove H_2O, CO_2 and non-condensable gases. The SO_2 gas samples were analyzed for $^{34}S/^{32}S$ ratios on a Nuclide Corporation, 6-60-RMS, dual collector mass spectrometer. Results are reported as $\delta^{34}S$ per mil (‰) values with respect to Cañon Diablo troilite. Our

TABLE 2. SULFUR ISOTOPIC COMPOSITION OF SULFIDE MINERALS AT 11° AND 13°N, EPR

						$\delta^{34}S$ (‰)		
Vent	Dive	Sample #	Location	Zones	Mineralogy	$CuFeS_2$	FeS_2	ZnS
1	1366	1-a	L	5	ISS ≥ cpy » mc, py	4.3		
		1-b	C	2+3	wtz/spl + py » ISS, cpy		1.7	3.1
		1-c	E	3	py ≈ mc » cpy + wtz/spl		3.6	3.3
		1-d	E	3	py ≈ mc		3.3	
2	1369	1-a	C	3	py » cpy		3.7	
		1-b	E	2	py » cpy + wtz/spl		4.2	4.1
		2-a	E	2			3.9	4.0
3	1370	1-a	I	8	ZnS-rich band			4.2
		1-b	C	7	colloform mc » py band		4.1	
		1-c1	C	6	massive py > mc band		2.8	
		1-c2	C	6	" "		2.7	
		1-d	E	5	cpy ≈ ISS » py band	4.3		
4	1375	1-a	E	3	py » cpy		3.0	
5	1371	1-a	C	3	py + wtz/spl		2.8	3.0
6	1371	1-a	L	5	cpy	5.0		
		1-b	I	5	cpy » py	4.2		
		1-c	C	4	py » cpy » mc, bor, cov		4.7	
		2-a	L	5	cpy	4.5		
		2-b	I	5	cpy	4.3		
		3-a	E	3	cpy » py	4.7		
6	1372	1-a	L	5	cpy	4.2		
		1-b	I	5	cpy » py	4.2		
		1-c	E	5 (+3)	cpy » py	4.5		
		2-a	I	5	cpy » py	4.4		
		2-b	E	5 (+3)	cpy » py	4.2		
7	1373	1-a	I	3	py » cpy, wtz/spl	2.9	2.5	
8	1373	1-a	I	5+4	cpy ≥ py » bor	3.7		
		2-a	I	3,4,5	py ≥ cpy » bor		4.0	
		3-a	I	5+4	cpy ≥ py » bor	4.2		
		4-a	I	5+4	cpy ≥ py » bor	4.8		
9	1379	1-a	I	5	iss > cpy > py	4.3		
		1-b	E	3	py » cpy		3.7	
		2-a	L	5	cpy ≈ iss ≥ py	4.5		
		2-b	I	5,3,2	cpy > iss ≈ py	4.2		
		2-c	I	5+3	cpy ≈ iss ≥ py » mc	4.3		
		2-d	I	5+3	cpy > iss ≈ py » mc	4.1		
		3-a	L	5+3	cpy ≈ py ≥ iss	4.9		
		3-b	C	3	py » cpy	4.4		
		4-a	E	3+2	spl/wtz			3.8
10	1377	1-a	I	5	cpy	4.4		
		1-b	C	4	cpy > py > bor » cov	4.3		
		2-a	L	5	cpy	4.2		
		2-b	I	5	cpy + py	4.7		
		3-a	L	5	cpy	4.2		
		3-b	I	5	cpy	4.3		
		4-a	I	5	cpy	4.2		
		5-a	E	3	spl/wtz			4.1
11	1380	1-a	E	3+2	py + wtz		3.7	4.2
		2-a	E	3+2	py » cpy + wtz/spl		4.0	4.0

(1) The numbers (1-5) refer to those of chip or cross section samples from the same chimney; the letters (a-d) to different portions of the same chips or cross section.
(2) The letter refers to the sample location in cross-section: L = the inner wall lining of the conduit, I = the massive sulfide layer, C = the zone of transition from massive sulfides to the anhydrite-rich exterior, and E = the exterior of the chimney.
(3) Zone classifications are from Part I (Graham *et al.* 1988).
(4) The mineralogy describes only the portion of the sample analyzed for sulfur isotopes. The symbols denote relative respective quantities: a » b = more than 90% for a and less than 10% for b; a > b = 75-90% a, 25-10% b; a ≥ b = 60-75% a, 40-35% b. cpy = chalcopyrite, py = pyrite, mc = marcasite, spl = sphalerite, wtz = wurtzite, bor = bornite, cov = covellite and iss = intermediate solid solution.

TABLE 2'. DESCRIPTIONS OF TABLE 2 SULFIDES

Vent	Sample Descriptions
1	The tip of a conduit; in cross section, the sample is 2 cm in width, with a 2-3 mm opening. Sample 1-a from the massive sulfide band at the core, 1-b from the porous central zone, 1-c from the exterior, including sulfides lining a fossil worm tube, and 1-d from only sulfides lining worm tubes.
2	Two loose fragments of a clogged (extinct) chimney of ~8 cm outer diameter. Sample 1a from sulfides near the center of the conduit, and samples 1b and 2a from the exterior.
3	Extinct chimney (see Vent D description in Graham *et al.* 1988). The sulfides were drilled from four distinct, concentric bands about the opening (samples a-d from interior to exterior).
4	A fossil worm tube lining of an extinct vent fragment.
5	A worm tube-encrusted, extinct vent fragment.
6	A fragment (~2-3 cm thickness) of an active chimney sampled on dive 1371. Samples 1 and 2 drilled from polished sections of complete cross sections through the vent. Sample 3 from the exterior of the chimney sample.
6	A larger fragment of the same chimney as above, recovered on dive 1372. The conduit is roughly oblong (5 x 10 cm inner diameter and 8 x 15 cm outer diameter). Samples 1 and 2 drilled from polished sections of the cm-thick massive sulfide inner layer and a small portion of the anhydrite-rich outer zone. Samples 1-c and 2-b taken 2-3 cm from the exterior of the conduit.
7	A porous, friable chimney fragment from a low T (108°C) vent.
8	See chimney A description in Graham *et al.* (1988). The samples are drilled from the narrow, 1-2 mm wide sulfide layer. Sample 1 from the top of the chimney, 2 and 3 from the center, and 4 from its base.
9	See chimney C description in Graham *et al.* (1988). Sample 1 from an auxiliary conduit 30 cm above the base of the chimney. Sample 2 from the base of the vent containing a number of distinct bands of sulfides, separated by zones of high porosity. Samples 2a-d taken respectively from the interior to the exterior of the sulfide layer. Sample 3 from the base of the chimney sample, at the boundary between an active and extinct channelway. Sample 4 from the exterior, 30 cm above the base.
10	See chimney B description in Graham *et al.* (1988). The fluids were discharging through two connected channelways. Samples 1, 2 and 3 from opposite ends of the two channelways. Sample 4 from the massive sulfide layer at the connection between the two channelways, and sample 5 from the anhydrite-rich exterior of the chimney.
11	Two fragments from the basal mound of two active chimneys, 11A and 11B, coated by iron-oxides and fossil worm tubes. Sample 1 sulfides separated by hand picking cubic pyrite and hexagonal wurtzite. Sample 2 obtained by chemical extraction as described in the text.

analytical uncertainty, based on replicate measurements of standard samples, is typically within ±0.15‰ (1.5σ).

RESULTS

Our analyses include 11 H_2S samples of vent fluid from five vent sites, and 57 sulfide mineral separates from one to four mineralogical zones present in each of 10 chimneys (vents) and 1 basal mound. The $\delta^{34}S$ values and descriptions of these samples are presented in Tables 1 and 2, respectively. In the following sections, the sulfur isotopic characteristics of samples from 11°-13°N are summarized (Figs. 2, 3), and compared with those from other ocean-ridge systems reported by previous investigators (Fig. 4).

Hydrothermal fluids

The $\delta^{34}S$ values of H_2S in 11 vent-fluid samples from five active chimneys range from +2.3 to 5.2‰, with a mean and 1.5σ of 4.3 ±1.3‰ (Table 1, Fig. 2). Four of the five chimneys have isotopically similar fluids (between +4.1 and 5.2‰), but the three samples from vent 8 are one to two per mil lighter. Comparison of H_2S concentration and $\delta^{34}S(H_2S)$ of the fluids shows no obvious correlation.

In two cases where fluids were sampled both from main and auxiliary conduits, H_2S from the latter is isotopically lighter, by 0.3 and 1.2‰ at vent 8, and

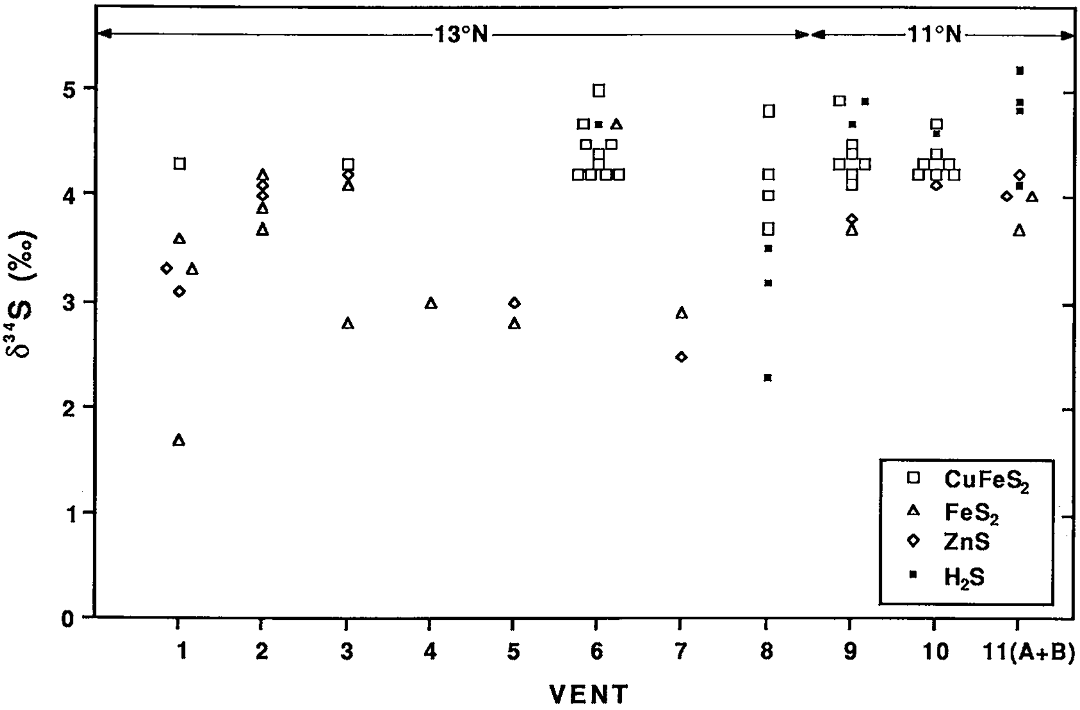

FIG. 2. $\delta^{34}S$ values of sulfide minerals and H_2S samples from 11° and 13°N, EPR. Note that the majority of $\delta^{34}S$ values lie within a range of +3 to 5‰.

by 0.4‰ at vent 11-B. At vent 9, fluids were sampled before and after the top of the chimney was broken off by the ALVIN pilot. A decrease in the $\delta^{34}S$ values of 0.2‰ was measured in the samples of vent-fluids H_2S after the breakage, but these values are not statistically distinct.

As shown in Figure 4, the $\delta^{34}S(H_2S)$ values at 11°–13°N are similar, but generally heavier than those at 21°N (+1.3 to 5.5‰; Kerridge *et al.* 1983, Woodruff & Shanks 1988), and less variable and generally lighter than those at Juan de Fuca (+4.0 to 7.4‰; Hannington *et al.* 1986, Shanks & Seyfried 1987).

Sulfide minerals

The $\delta^{34}S$ values of sulfide minerals from 10 vent sites and one mound, together with the $\delta^{34}S(H_2S)$ of vent fluids, are compared in Figure 2. Variations in the $\delta^{34}S$ values within individual chimneys (where more than one sulfide zone was analyzed) are compared in Figures 3a–h. The mineralogical zones, as defined in Part I (Graham *et al.* 1988), are characterized by specific mineral assemblages: outermost zone 1 (anhydrite with minor marcasite, pyrite and wurtzite), zone 2 (marcasite + wurtzite with minor pyrite), zone 3 (mostly pyrite with minor marcasite, sphalerite and wurtzite), zone 4 (bornite and other sulfur-rich Cu–Fe sulfides with minor pyrite and chalcopyrite), zone 5 (nearly monomineralic chalcopyrite), zone 6 (pyrite with minor marcasite and sphalerite), zone 7 (marcasite with minor wurtzite), and zone 8 (wurtzite with minor pyrite). Zones 1 through 5 are observed in nearly all active chimneys from 11° and 13°N, although the extent of development and preservation of each mineralogical zone varies. Zones 6 through 8 are observed only in one extinct and clogged chimney (vent 6 in this study; chimney D in Part I) as fillings inside the chalcopyrite-rich zone 5. The important features in Table 2, and Figures 2, 3 and 4 are summarized below.

Range of $\delta^{34}S$ at 11° and 13°N. The total range of $\delta^{34}S$ values for the 57 sulfide-mineral separates is from +1.7 to 5.0‰, with a mean and 1.5σ of 4.1 ±0.6‰. There is little difference in the average $\delta^{34}S$ values among chimneys at 13°N (3.8 ±1.1‰) and those at 11°N (4.2 ±0.4‰), although individual chimneys at 13°N tend to show more variation (up to ~3‰).

The average $\delta^{34}S$ value of +4.1‰ for sulfide minerals at 11° and 13°N EPR is the highest among hot-spring systems at unsedimented ridge crests (Fig. 4). At 21°N, the average $\delta^{34}S$ value of sulfides is +2.5‰ (Hékinian *et al.* 1980, Arnold & Sheppard

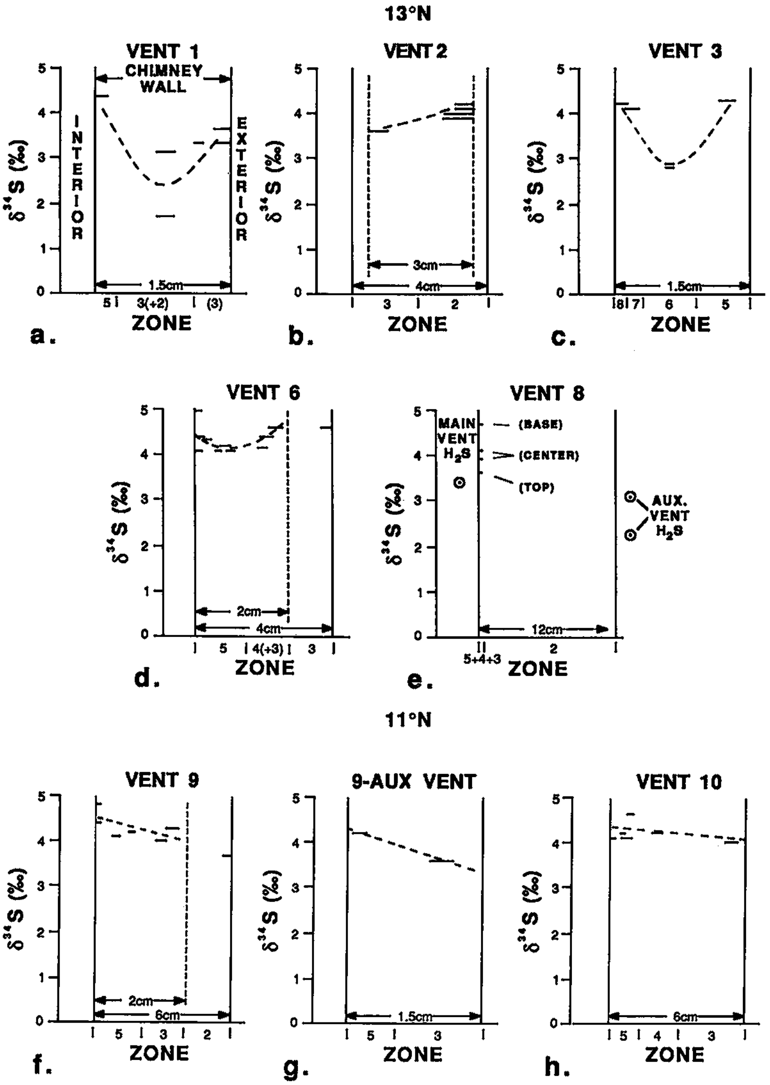

FIG. 3. $\delta^{34}S$ values of sulfide minerals and H_2S samples from 13° and 11°N EPR, plotted with respect to the physical location in a cross-sectional view of the chimney wall (line width = sampling resolution), and the mineralogical zones from Part I (Graham *et al.* 1988). The approximate scales for each chimney cross-section are located at the base of the diagrams. Dashed lines are inferred (best fit) isotopic trends through the chimney wall.

1981, Styrt *et al.* 1981, Kerridge *et al.* 1983, Zierenberg *et al.* 1984, Woodruff & Shanks 1988); on the southern Juan de Fuca Ridge, the average is +3.2‰ (Shanks & Seyfried 1987).

Active versus extinct vents. There is little difference in the $\delta^{34}S$ values of sulfides from the active and inactive chimneys: +4.1 ±0.9‰ for 38 sulfide separates from five black smokers (#1, 6, 8, 9, 10); +3.6 ±0.9‰ for 13 sulfide separates from four extinct chimneys (#2, 3, 4, 5), and +2.5 and 2.9‰ for 2 sulfide separates from a low-temperature (108°C) vent (#7).

There is little observed difference between active and exinct chimneys at 21°N: the average $\delta^{34}S$ value is +2.7 ±1.4‰ for 83 analyses of active vents, and +2.1 ±0.8‰ for 29 analyses of extinct vents (Hékinian *et al.* 1980, Arnold & Sheppard 1981, Kerridge *et al.* 1983, Zierenberg *et al.* 1984, Woodruff & Shanks 1988).

Isotopic relations of coexisting sulfides. Sulfur iso-

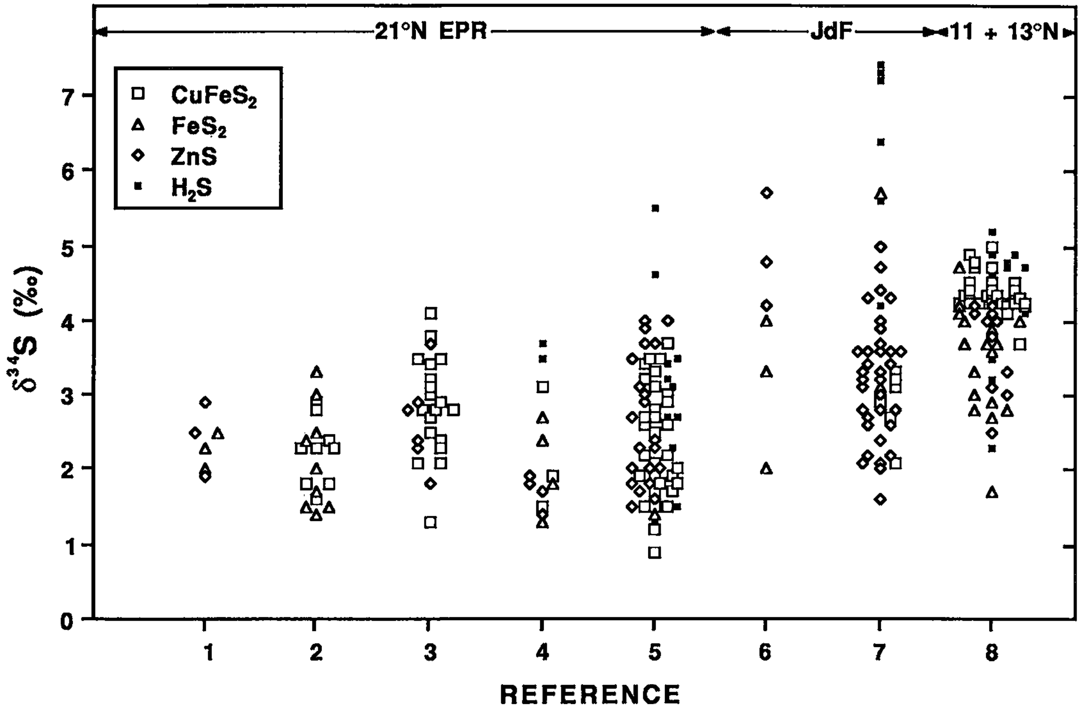

FIG. 4. Comparison of $\delta^{34}S$ values of sulfide minerals and H_2S samples from seafloor hot-spring sites, at 21°N, EPR (1–5), central and southern Juan de Fuca Ridge (6 and 7, respectively), and 11° and 13°N, EPR (8). References are: 1 Hékinian *et al.* (1980); 2 Arnold & Sheppard (1981); 3 Styrt *et al.* (1981); 4 Kerridge *et al.* (1983); 5 Woodruff & Shanks (1988); 6 high, low and mean FeS_2 and ZnS values reported by Hannington *et al.* (1986); 7 Shanks & Seyfried (1987); 8 this study.

topic disequilibrium is common among "coexisting" sulfides at 11° and 13°N. If the sulfide minerals had attained equilibrium at $T = 100$–400°C, the differences in the $\delta^{34}S$ values (Δ) should be: $\Delta_{py\text{-}ZnS}$ = 2.2–0.7‰ and $\Delta_{py\text{-}cp}$ = 3.2–1.0‰ (Ohmoto & Rye 1979). However, the observed $\Delta_{py\text{-}ZnS}$ values of eight coexisting pyrite–wurtzite/sphalerite pairs and the $\Delta_{py\text{-}cp}$ value of one pyrite–chalcopyrite all fall outside of the above ranges.

The isotopic relationships of 21°N chimneys yield similar results: not one of nine measured pyrite–ZnS pairs falls within the range of equilibrium temperatures, and of four pyrite–chalcopyrite pairs, only one falls within the range (yielding a temperature of 340 ±40°C). At Juan de Fuca, one pyrite–sphalerite pair yields 106 ±55°C, and four chalcopyrite–sphalerite pairs fall outside the range of equilibrium formation.

Mineralogy versus $\delta^{34}S$. Chalcopyrite exhibits the highest $\delta^{34}S$ values and the narrowest range among the sulfide minerals: +3.7–5.0‰ (4.4 ±0.4‰) for 30 samples. In contrast, the FeS_2 phases (mostly pyrite and minor marcasite) yield the lowest $\delta^{34}S$ values and the widest range: +1.7–4.7‰ (3.4 ±1.1‰) for 17 samples. The ZnS phases (sphalerite + wurtzite) show intermediate characteristics: +2.5–4.2‰ (3.7 ±0.9‰) for 10 samples.

At 21°N, the two most thorough isotopic studies of sulfide mineralogy found similar relationships only between average $\delta^{34}S$ values of chalcopyrite and pyrite. Zierenberg *et al.* (1984) measured the following: for four chalcopyrite separates, an average of 4.3 ±0.3‰ (range from +4.0 to 4.5‰); for eight wurtzite separates 3.3 ±1.3‰ (+1.9 to 4.1‰), and for 3 pyrite separates 1.8 ±0.3‰ (+1.5 to 2.2‰). Woodruff & Shanks (1988) found: for 29 chalcopyrite separates 2.4 ±1.0‰ (+0.9 to 3.7‰); for 21 of sphalerite 2.7 ±1.3‰ (+1.5 to 4.0‰), and for 3 of pyrite 1.6 ±0.2‰ (+1.4 to 1.7‰).

At the southern Juan de Fuca Ridge, Shanks & Seyfried (1987) found much different $\delta^{34}S$ relationships than those at either 11°–13°N or 21°N: six chalcopyrite separates average 2.9 ±0.7‰ (+2.1 to 3.3‰); 34 of sphalerite average 3.2 ±0.2‰ (+1.6 to 5.0‰), and two of pyrite measure +3.1 and 5.7‰.

Lateral zoning of $\delta^{34}S$ *within chimneys.* Most of the chalcopyrite samples come from zones 4 and 5, and most FeS_2 and ZnS from zones 2 and 3; therefore, the existence of differences in $\delta^{34}S$ among the sulfide phases mentioned above is reflected as a general trend of increasing $\delta^{34}S$ values from the outer zones (2–3) to the inner zones (4–5). This trend is also observed between the FeS_2 phases of zones 2–3 (+1.7–4.2‰ for 12 samples) and those of zones 4–5 (+4.0 and 4.7‰ for 2 samples), and between the chalcopyrite of zone 3 (+2.5‰ for 1 sample) and that of zones 4–5 (+3.7–5.0‰ for 29 samples). In vents 1, 2 and 6 of 13°N, the outermost parts of the chimneys (zone 2 or 3) have higher $\delta^{34}S$ values than the inner parts of zones 3 and 2 (by 0.5 to 2‰; Figs. 3a,b,d). A similar $\delta^{34}S$ pattern of higher values for samples near the external and internal walls, and lower values for those at the interior of a chimney is observed in extinct vent 3 from 13°N (Fig. 3c). Chimneys from 11°N demonstrate either small, relatively systematic decreases or no change in $\delta^{34}S$ values from the interior to the exterior, without a central isotopic depletion (Figs. 3f–h).

The lateral zoning of $\delta^{34}S$ found in 11°–13°N chimneys differs from that found in other ocean-ridge systems. Styrt *et al.* (1981) and Woodruff & Shanks (1988) observed a general trend of increasing $\delta^{34}S$ values from the interior to the exterior of chimneys at 21°N EPR, although some opposite trends were also observed. Hannington *et al.* (1986) found that $\delta^{34}S$ values of sulfides increased on average by more than one per mil towards the exterior of a sulfide spire (40 cm diameter) on the central Juan de Fuca Ridge. Shanks & Seyfried (1987) reported "random variations" through cross-sections of two separate, mineralogically homogeneous ("Type B") chimney samples from the southern Juan de Fuca Ridge. However, they also analyzed one mineralogically zoned ("Type A") chimney, and noted that exterior sulfides are generally isotopically heavier than interior sulfides.

Vertical zoning of $\delta^{34}S$ within chimneys. In vent 8, which is comprised of a thin (1–2 mm) sulfide layer (zones 3–5) and a thick (~12 cm) outer portion (zone 2), the sulfides in zones 3–5 (mostly chalcopyrite) exhibit a continuous decrease of 1.1‰ from the base to the top of a ~60 cm-long chimney (Fig. 3e). In vent 9, six sulfides from the main chimney conduit have an average $\delta^{34}S$ value about 0.5‰ heavier than three sulfides 30 cm above the base (two from an auxiliary conduit and one from the exterior of the main conduit).

Apparently, our study includes the only lengthwise isotopic analysis of a mineralogically zoned chimney. Shanks & Seyfried (1987) measured $\delta^{34}S$ values vertically along the core of a texturally and mineralogically homogeneous ("Type B") chimney at Juan de Fuca. They found no isotopic trends along a 35-cm transect.

$\delta^{34}S$ relationship between vent-fluid H_2S and sulfide minerals. The $\delta^{34}S$ values of vent-fluid H_2S are typically larger by 0.2–0.5‰ than sulfide minerals from the innermost zone of a chimney (vents 6, 7, 9 and 10). However, at vents 8 and 9, sulfides from the inner wall are isotopically heavier by 0.2 to ~1.5‰ than corresponding H_2S samples.

In all of the hydrothermal discharge sites, $\delta^{34}S$ values of vent-fluid H_2S are usually equal to or higher than corresponding chimney sulfides: the average fractionation value is 0.4‰ at 11° and 13°N, 0.6‰ at 21°N, and 3.2‰ on the southern Juan de Fuca Ridge. Kerridge *et al.* (1983) reported $\delta^{34}S$ values of +3.5 and 3.7‰ for two samples of vent fluid at 21°N. These values were nearly two per mil heavier than chimney sulfide minerals from the same vent sites. In a more extensive study at 21°N, Woodruff & Shanks (1988) found that vent-fluid H_2S from the most recent (1985) dives at 21°N ranged in isotopic composition from +1.3 to 5.5‰. These values were either similar to, or slightly heavier than, sulfides from the inner walls of the chimney. Shanks & Seyfried (1987) found that vent-fluid H_2S on the southern Juan de Fuca Ridge ranged from +4.0 to 7.4‰; this represented an enrichment in $\delta^{34}S$ of up to 4‰ relative to sulfides in the associated chimneys.

DISCUSSION

Previous models of isotopic variations in chimneys

Several different mechanisms have been proposed to explain variations in the $\delta^{34}S$ values of H_2S and sulfide minerals associated with mid-ocean-ridge hydrothermal systems, including: kinetic isotope effects between H_2S and sulfide minerals; sulfate reduction within the mounds and chimney structures; and temporal changes in the $\delta^{34}S$ of discharging fluids caused by changes in the temperature and geometry of the hydrothermal plumbing system.

Kinetic isotope effects. Kerridge *et al.* (1983) suggested that the two per mil difference measured between two vent-fluid samples and chimney sulfide minerals at 21°N could be explained by a kinetic isotope fractionation factor of $\alpha = 1.00183$ between H_2S and sulfide minerals. However, this kinetic isotopic fractionation factor is unrealistically large; the maximum kinetic isotopic fractionation factor between H_2S and sulfide minerals observed in the laboratory is ~1.0005 (H. Ohmoto, unpub. data). The observed fractionation factors between H_2S and sulfides on the innermost layer of most chimneys at 11°–13°N are between 0.9985 and 1.0005. If the kinetic isotopic fractionation factor was greater than one, and preferential removal of isotopically lighter sulfur from discharging fluids occurred during fluid passage through the chimney conduit, $\delta^{34}S$ values of chimney sulfides would necessarily become progressively heavier towards the top, the opposite of what is observed in vents 8 and 9. Therefore, it is unlikely that kinetic isotopic effects played an important role in the variation of $\delta^{34}S$ values of discharging fluids and chimney sulfides.

Local sulfate reduction. Shanks & Seyfried (1987) and Woodruff & Shanks (1988) suggested that the pristine hydrothermal fluids at 21°N and the southern Juan de Fuca Ridge had a uniform $\delta^{34}S$ (H_2S) value of +1 to 2‰, and that the variably heavier $\delta^{34}S$ values of chimney sulfides (up to +5.7‰) and vent-fluid H_2S (up to +7.4‰) were caused by variable degrees of incorporation of isotopically heavy seawater sulfate (anhydrite and pore fluids) in the chimney wall and in the mounds. These authors further suggested a mechanism of sulfate reduction by Fe^{2+} in the hydrothermal fluids.

If seawater sulfate fixed as anhydrite [$\delta^{34}S(SO_4) \approx +20‰$] or present as pore fluids in chimney walls was reduced to H_2S by interaction with hydrothermal fluids and incorporated into sulfide minerals, the $\delta^{34}S$ values of sulfide minerals would be expected to become progressively higher upward and outward in the chimney wall. Although such a $\delta^{34}S$ pattern has been observed in some chimneys at 21°N, opposite trends have also been noted at 21°N (Woodruff & Shanks 1988) and in most of the chimneys at 11°–13°N. The time required for fluids to travel through chimneys is probably on the order of seconds (Macdonald *et al.* 1980), or may be slightly larger if variations in fluid-discharge rates occur (Turner & Campbell 1987). Under laboratory conditions of T = 350°C and pH's of 2.3 and 5.3, H_2S is produced by Fe^0 reduction of sulfate at an average rate of only $\sim 10^{-6}$ moles/hour in a $10^{-2}M$ sulfate solution (Drean 1978). Therefore, it seems improbable that a significant quantity of H_2S can be generated by reduction of seawater sulfate within the chimney wall. Local sulfate reduction is probably not a major factor in the variation of $\delta^{34}S$ values of discharging fluids and chimney sulfides at 11°–13°N.

Temporal $\delta^{34}S$ (H_2S) variation. Variation in the $\delta^{34}S$ values of chimney sulfides has been interpreted by Styrt *et al.* (1981) and Bluth & Ohmoto (1986) as temporal variation in the $\delta^{34}S$ values of H_2S in the exiting fluids, because at temperatures ≥250°C, the equilibrium fractionation between H_2S and sulfides is minor. Fluid variations were explained in terms of the changes in the relative proportion of H_2S from two sources: reduced sulfur leached from basalt ($\delta^{34}S \approx 0‰$), and reduction of seawater sulfate ($\delta^{34}S \approx +20‰$) by ferrous iron in the basalts in deeper parts of the hydrothermal system, due to changes in the thermal and hydrological regimes.

Further study has revealed problems with this interpretation. The overall trend in the $\delta^{34}S$ values from the exterior to the interior wall is similar in most chimneys from 11°–13°N, but the pattern of $\delta^{34}S$ variation across chimney walls is not exactly identical among the individual chimneys, and a $\delta^{34}S$ variation of more than 2‰ is not uncommon within a scale of millimeters across a chimney wall. Vertical $\delta^{34}S$ zoning of up to 1.1‰ also occurs in sulfides along the inner wall of vents 8 and 9. According to the models of Styrt *et al.* (1981) and Bluth & Ohmoto (1986), these observations need to be interpreted by (i) extremely rapid changes in the nature (T and geometry) of plumbing systems, because the chimney growth rates appear to be quite high; and (ii) by plumbing systems for individual vents that are not entirely connected, even among those located only a few hundred meters apart. Although actual rates are difficult to determine, two observations suggest very rapid growth. In 1982, Hékinian *et al.* (1983) excavated an active chimney at 13°N EPR, and returned 5 days later to find a new structure had grown to a height of 40 cm. In 1985, the first author visited 21°N, and witnessed the discovery of a previously uncharted active chimney in a vent field which had been explored twice earlier (in 1979 and 1981), suggesting that a mature chimney may develop within several years.

Proposed model of isotopic variation in chimneys

To explain the isotopic characteristics of sulfides in the chimneys, and of H_2S in the discharging fluids, our proposed model involves: (1) a gradual, nearly unidirectional change in $\delta^{34}S$ (H_2S) of the hydrothermal fluids with time, to either more positive values (*e.g.*, 11°–13°N EPR), or less positive values (*e.g.*, 21°N EPR, southern Juan de Fuca Ridge), depending on the nature of the large-scale plumbing system; and (2) rapid dissolution/reprecipitation/replacement reactions between H_2S and earlier sulfides in the chimney walls, which cause local isotopic variations in the chimneys.

Our mineralogical study of chimneys from 11°–13°N (Part I by Graham *et al.* 1988) suggests that the chimney growth takes place primarily by: development of zone 1 by precipitation of anhydrite, FeS_2 and ZnS on the exterior wall of a chimney due to rapid mixing of hydrothermal fluids and cold seawater; continuous dissolution of the sulfides and sulfates, particularly along the inner wall, by later hydrothermal fluids; successive metasomatic transformation of zone 1 minerals to zone 2 (anhydrite-poor, ZnS- and FeS_2-rich), zone 3 (pyrite-rich), zone 5 (chalcopyrite-rich), and to zone 4 (bornite-rich) due to reactions with hydrothermal fluids that diffused through the chimney wall. According to this model, sulfides in all zones within chimney walls inherit chemical and isotopic characteristics of all stages of hydrothermal activity, but the proportion of the later fluid characteristics to the earlier fluid characteristics increases from the exterior to interior wall. That is, the $\delta^{34}S$ of sulfides on the inner wall (*e.g.*, zone 5) is more representative of the $\delta^{34}S(H_2S)$

of the most recent fluid, whereas those inside of the chimney wall (*e.g.*, zones 2–3) partly reflect the $\delta^{34}S(H_2S)$ of earlier fluids. The observed general trend of increasing $\delta^{34}S$ values of sulfides from zones 2–3 to zone 5, and the isotopic relationship between sulfides of zone 5 to H_2S of main-vent fluids, therefore, suggest a general trend of change in the $\delta^{34}S(H_2S)$ of the discharging fluids from <3‰ in the early stage to ~5‰ in the later stage.

Our model explaining the $\delta^{34}S$ variation of chimney sulfides and vent-fluid H_2S at 11°–13°N is schematically illustrated in Figure 5. We estimate that the $\delta^{34}S(H_2S)$ of the earliest discharging fluid is +1.7‰, represented by the lowest $\delta^{34}S(py)$ in zones 2–3 of vent 1, and that of the latest fluid is +5.0‰, which is represented by main vent-fluids at vent sites 6, 9, 10, and 11 (uncertainties of ±1‰ in the estimated values are not critical in the following discussion). The change from 1.7 to 5.0‰ in $\delta^{34}S(H_2S)$ was probably gradual. During the early stage of hydrothermal activity, the hydrothermal fluids produce ZnS and FeS_2 of ~1.7‰ in zones 1–2 of the chimney. During the later stage, reactions between hydrothermal fluids with $\delta^{34}S(H_2S) = 5.0$ and earlier sulfides produce $\delta^{34}S$(sulfide) values between 1.7 and 5.0‰, with the inner-wall sulfides (chalcopyrite of zone 5) trending closer to +5.0‰ because of the larger contribution of new hydrothermal H_2S relative to old sulfide sulfur. Because the transformation of zones 1 through 5 occurs with preferential dissolution by hydrothermal fluids and replacement by chalcopyrite of ZnS relative to FeS_2 (see Part I by Graham *et al.* 1988), some pyrite in zone 3 tends to retain the sulfur isotopic characteristics of the earlier zone-2 pyrite. This process explains the variability of $\delta^{34}S(py)$ compared to that of the other sulfides, and also the central minima in $\delta^{34}S$ patterns observed in some chimneys at 13°N.

According to our model in Figure 5, rapid chemical reactions between hydrothermal fluids and earlier chimney sulfides may cause the $\delta^{34}S(H_2S)$ of recent vent fluids at 11°–13°N to lie between +5.0 and 1.7‰. This depends on the degrees of reaction between vent fluids and earlier chimney sulfides, which are controlled to some extent by the conduit opening and thickness of the chimney wall. Indeed, the $\delta^{34}S(H_2S)$ values of auxiliary vent fluids are found to be lower than that of main vent-fluids (Table 1). In vent 8, the channel opening is very small (~1 mm). Hydrothermal fluids travelling through such small openings would have reacted more with the earlier sulfide minerals, which could explain why the $\delta^{34}S(H_2S)$ of even the main vent-fluid is as low as 3.5‰. A continuous decrease in the $\delta^{34}S(H_2S)$ from ~5 to 3.5‰ as fluids travelled upward in vent 8 explains the upward decrease in the $\delta^{34}S$ values from 4.8 to 3.8‰ for the sulfide minerals on the conduit wall.

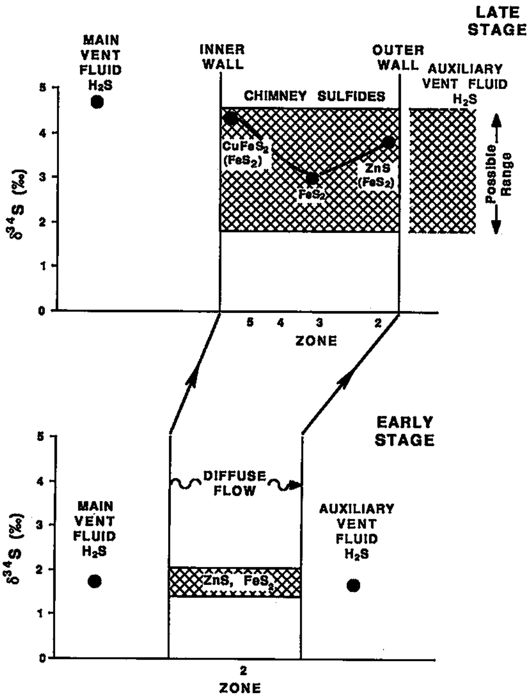

FIG. 5. Two-stage diagram of a chimney cross-section, describing the model of sulfur isotopic evolution of fluids and chimneys at 11° and 13°N, EPR. In the early stage, vent-fluid H_2S of $\delta^{34}S = +1.7$‰ produced sulfide minerals of ~1.7‰, with no difference in the $\delta^{34}S(H_2S)$ values between the main and auxiliary vent fluids. In the later stage, the $\delta^{34}S(H_2S)$ of the main vent fluid was +4.7‰. Reactions between this H_2S with the earlier sulfide minerals in the chimney wall produced the sulfide minerals and auxiliary vent-fluid H_2S with $\delta^{34}S$ values between 1.7 and 4.7‰. The bold line indicates the isotopic trend found in some 13°N chimneys.

Application to other seafloor hot-spring locations. With one exception, it is difficult to compare the details of our work with most other published isotopic studies. Woodruff & Shanks (1988) included photos detailing their sampling locations for two chimneys at 21°N; these data are plotted in Figure 6. The isotopic trends over a 2-cm cross-section are clearly the reverse of what we have observed in this study. Our model suggests that the $\delta^{34}S$ values of the discharging vent-fluid H_2S at 21°N decreased from >6‰ in the early stage to ~1‰ in the later stage. Acquisition of some sulfur from dissolution of earlier (and isotopically heavier) sulfides would explain why the $\delta^{34}S(H_2S)$ values tend to be much (up to 2.3‰) higher than the $\delta^{34}S$ values of sulfides on the inner chimney wall at 21°N. This would also explain the heavy (~6‰) values of the exterior bornite-rich layer as replacement of earlier, isotopically heavy chalcopyrite.

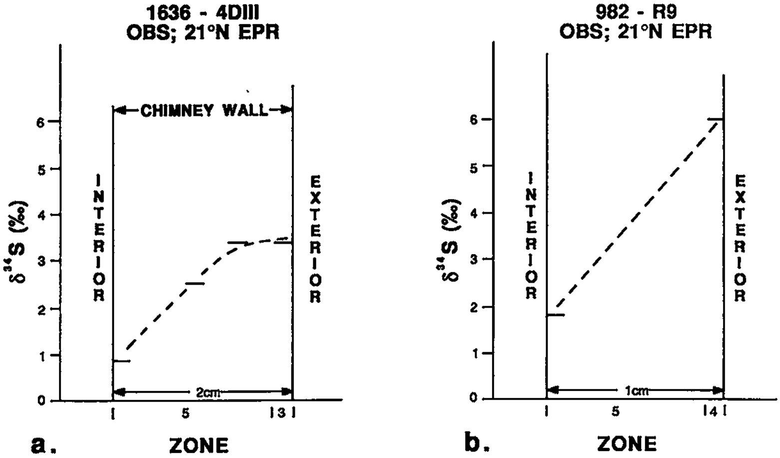

FIG. 6. Lateral trends of $\delta^{34}S$ values of sulfide minerals in chimney walls at the Ocean Bottom Siesmograph (OBS) vent site, 21°N, EPR (from Woodruff & Shanks 1988). The assignments of sulfides to the mineralogical zones (3, 4, and 5) are based on their sample descriptions.

Sources of hydrothermal H_2S. Similarities in the $\delta^{34}S(H_2S)$ history of discharging fluids at various sites of 11° and 13°N suggest that the sulfur isotopic characteristics of discharging fluids over a distance of up to 40 km are controlled at depth in the plumbing system. The simplest explanation for the change in the $\delta^{34}S(H_2S)$ of discharging fluids of ocean-ridge systems is the model proposed by Styrt *et al.* (1981) and Bluth & Ohmoto (1986), which appeals for two sources of H_2S, one from leaching of sulfide sulfur in submarine basalt ($\delta^{34}S \approx +0.5‰$; Ohmoto 1986), and the other from reduction of seawater sulfate ($\delta^{34}S = +20‰$) by the ferrous iron component of basalt in the deeper part of the plumbing system. The temporal change from +1.7‰ to +5.0‰ for the $\delta^{34}S(H_2S)$ of hydrothermal fluids at 11°-13°N may be interpreted as an increased contribution of seawater-derived H_2S (from ~10% in the earlier fluids to ~25% in the recent fluids). Similarly, the temporal change of ~6‰ to ~1‰ for the $\delta^{34}S(H_2S)$ at 21°N may be interpreted as a decreased contribution of seawater-derived H_2S (from 30% to 5%) during the hydrothermal activity. A question, however, remains as to why the temporal change in the proportions of these two sulfur sources differs between the 11°-13°N system and the 21°N system.

SUMMARY

(1) The $\delta^{34}S$ values of sulfides at 11°-13°N average among the heaviest in hot-spring systems, including 21°N and the southern Juan de Fuca Ridge systems. The $\delta^{34}S(H_2S)$ values of vent fluids are similar to those at 21°N (which show a slightly larger range), but are generally lighter than values for the fluids from Juan de Fuca.

(2) There is little difference in $\delta^{34}S$ values between vent-fluid H_2S and sulfides which line the inner walls of the chimneys.

(3) The horizontal zonation of chimneys in this study typically shows either a slight decrease (11°N) or a central depletion (13°N) from the interior to the exterior. Two samples analyzed along their lengths show decreasing isotopic values toward the tops of the chimneys. These trends are rarely observed in other submarine hot-spring systems.

(4) The variation in the $\delta^{34}S$ values of vent-fluid H_2S and sulfide minerals within chimney walls is probably due to rapid chemical and isotopic reactions between hydrothermal fluids and chimney sulfides.

(5) The similarity in the $\delta^{34}S$ characteristics among vents at 11°N and those at 13°N suggests that the hydrothermal systems at 11°N, located over a 4-km distance, are connected at depth to a single magma chamber; those at 13°N are within a 40-km distance and may also be connected at depth. The $\delta^{34}S(H_2S)$ values of hydrothermal fluids at 11° and 13°N probably changed gradually, from ~1.7 in the earlier stages to ~5‰ in recent stages, because of an increased contribution of reduced seawater sulfate deep within the plumbing system.

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