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COMPUTATIONAL MODELING OF CHEMICAL AND SULFUR ISOTOPIC REACTION PROCESSES IN SEAFLOOR HYDROTHERMAL SYSTEMS: CHIMNEYS, MASSIVE SULFIDES, AND SUBJACENT ALTERATION ZONES

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ABSTRACT

Incremental reaction computations have been effectively used to model solution mixing, mineral precipitation, and rock-alteration processes in active seafloor hydrothermal systems. Simulation of ambient seawater mixing with hydrothermal solution for a variety of pathways, including approximately adiabatic and simple conductive heating or cooling, results in predicted temperatures of mineral precipitation, paragenetic sequence of minerals, and chemical composition that are consistent with observations from active vents. Coupled modeling of sulfur isotopic reaction paths produces $\delta^{34}S$ values of sulfide minerals of 1.5–4.5 per mil, in excellent agreement with observed values. Thus, the mixing calculations can accurately model the range of $\delta^{34}S$ values of sulfide minerals found in most seafloor vent systems. However, the reduction potential of the hydrothermal solution is not sufficient under any mixing conditions to produce $\delta^{34}S(H_2S)$ values above 4.5 per mil observed in some active vents. Fluid/solid interaction within and below seafloor sulfide deposits is also important. Simulated reaction of venting hydrothermal solution with previously formed sulfide minerals (± anhydrite and ambient seawater) significantly alters some metal concentrations but has only a very limited effect on the sulfur isotopic composition of sulfide in minerals and solution. In particular, computed models show that reaction of high-temperature solutions with massive sulfides may significantly remobilize Zn within the massive sulfide deposit. Sulfate-reduction reactions in hydrothermal stockworks have been modeled as fayalite + anhydrite ± pyrrhotite reaction with hydrothermal solution to form pyrrhotite + chalcopyrite + iron silicates ± magnetite assemblages. Such reactions seem to be the only near-surface processes which can result in the large positive $\delta^{34}S(H_2S)$ values of some active vent solutions. Near-surface hydrothermal reaction processes also have a subtle, but potentially important, effect on concentrations of H_2S, SiO_2, and Fe and pH in the emerging vent fluids. The results of subseafloor hydrothermal reactions are much more evident in massive sulfide deposits exposed on land, and are expressed as stockwork alteration zones and zoned metal-distributions in the ore lenses. However, sulfur isotope effects due to reaction with basalt in stockwork zones are insignificant on the scale of a large ore deposit. Reworking of massive sulfide lenses results in zoning effects which can be quantified using the computed models.

Keywords: massive sulfide deposits, hydrothermal modeling, sulfur isotopes, mineral stabilities, rock–water interaction.

SOMMAIRE

Des calculs du progrès des réactions chimiques ont été utilisés pour étudier le mélange de solutions, la précipitation de minéraux, et les processus d'altération des roches, phénomènes courants dans tout système hydrothermal actif dans les fonds marins. La simulation du mélange de l'eau de mer avec un fluide hydrothermal pour une variété de modèles qui supposent un réchauffement ou un refroidissement, soit approximativement adiabatique, soit par simple conduction, nous permet de prédire la température de précipitation des minéraux, leur paragenèse, et la composition chimique de l'eau; ces prédictions concordent avec les observations faites sur les évents actifs. Le couplage de ces calculs à l'étude du cheminement des réactions isotopiques mène à des valeurs de $\delta^{34}S$ des sulfures entre 1.5 et 4.5‰, ce qui est en très bon accord avec les mesures. Une simulation des mélanges peut donc reproduire les valeurs $\delta^{34}S$ observées dans les sulfures de la plupart des systèmes d'évents sous-marins actifs. Toutefois, le potentiel réducteur de la solution hydrothermale n'est pas suffisamment élevé, quelles que soient les conditions de mélange, pour reproduire les valeurs $\delta^{34}S$ du H_2S supérieures à 4.5‰ qui ont été signalées dans certains évents actifs. L'interaction du fluide avec les phases solides au sein et en dessous des gisements de sulfures sous-marins est aussi importante. Une réaction simulée entre solution hydrothermale émise et les sulfures déjà formés (± anhydrite et eau de mer ambiante) exerce un effet important sur la concentration de certains métaux, mais a une influence beaucoup plus subtile sur la signature isotopique des minéraux et de la solution. En particulier, les calculs montrent que la réaction d'une solution de haute température avec les sulfures massifs pourrait remobiliser le Zn dans ces gisements. Les réactions causant la réduction des sulfates dans les zones altérées ont été étudiées en utilisant la réaction modèle fayalite + anhydrite ± pyrrhotite avec solution hydrothermale, produisant pyrrhotite + chalcopyrite + silicates de fer ± magnétite. Parmi les réactions importantes près de la surface, seules ces dernières peuvent expliquer les valeurs élevées en $\delta^{34}S$ du H_2S dans le fluide de certains évents actifs. Les réactions hydrothermales près de la surface pourraient exercer une influence subtile, mais peut-être importante, sur les concentrations de H_2S, de SiO_2 et du Fe, et sur le pH des fluides des évents. L'influence des réactions hydrothermales actives en dessous du plancher océanique est beaucoup plus évidente dans les gisements de sulfures massifs qui affleurent maintenant sur terre. Ces réactions rendent compte des zones d'altération en stockwork et de la zonation dans la concentration des métaux dans les lentilles minéralisées.

Toutefois, les effets isotopiques dus à la réaction fluide - basalte dans les zones à stockwork sont insignificants à l'échelle d'un gros gisement. La remobilisation des lentilles de sulfures massifs cause des effets de zonation qui peuvent être quantifiés avec les modèles calculés.

(Traduit par la Rédaction)

Mots-clés: gisement de sulfures massifs, modèle hydrothermal, isotopes de soufre, stabilité des minéraux, interaction roche - eau.

INTRODUCTION

Investigations of venting hydrothermal solutions and sulfide deposits on ocean ridges have provided a rich source of information on chemical and physical conditions during formation of seafloor volcanogenic massive sulfide deposits (Macdonald *et al.* 1980, Albarede *et al.* 1981, Ballard *et al.* 1981, Welhan & Craig 1983, Haymon 1983, Lichtman & Eissen 1983, Koski *et al.* 1984, Michard *et al.* 1984, Sleep *et al.* 1983, Von Damm *et al.* 1985a,b, Tivey & Delaney 1986, Von Damm & Bischoff 1987, Shanks & Seyfried 1987, Woodruff & Shanks 1988). These well-constrained systems allow critical examination of chemical-reaction-pathway models and have significantly improved our understanding of the processes and constraints involved in dynamic hydrothermal systems (Janecky & Seyfried 1984, Bowers *et al.* 1985, Janecky 1988) and during intense subseafloor alteration (Seyfried & Janecky 1985, Alt *et al.* 1986, Seyfried 1987, Seyfried *et al.* 1988). As the number of sites sampled has expanded, it has become increasingly obvious that the process of massive sulfide formation is more complex than simple mixing of seawater with hydrothermal fluid in black-smoker vents (Von Damm & Bischoff 1987, Campbell *et al.* 1988). A variety of near-surface processes, including seawater entrainment and reaction with basalt or previously deposited sulfides (Fig. 1), affects hydrothermal solution composition and resulting deposits (Janecky 1988).

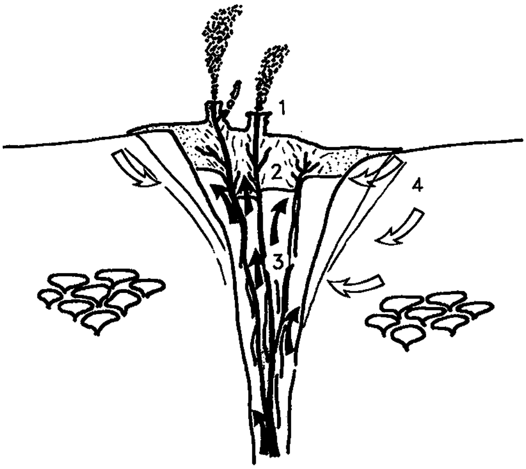

FIG. 1. Hypothetical cross-section of a volcanogenic massive sulfide deposit, showing near-surface zones of rock–water interaction and seawater mixing that contribute isotopically heavy sulfur to the hydrothermal system. Dynamic chemical reaction processes involving hydrothermal solution are generalized as follows: (1) ambient seawater mixing to form "black smoker" plumes, (2) massive sulfide autometamorphism and refining, and (3) stockwork hydrothermal alteration of wallrock basalts and previously precipitated hydrothermal sulfide. Ambient seawater entrainment (4) into the subjacent alteration zone or the massive sulfide deposit is also likely. After Janecky (1988).

Sulfur isotopic data for dissolved species and solid phases have shown that venting solutions and associated sulfides are not necessarily in gross equilibrium, but rather reflect evolving reaction processes (Kerridge *et al.* 1983, Shanks & Seyfried 1987, Woodruff & Shanks 1988). Moreover, chemically similar solutions, sampled at different vents or over time at a single vent, can have significantly different $\delta^{34}S$ values. Thus, sulfur isotopic data provide a sensitive tool for refining the reaction pathways of hydrothermal solutions in active seafloor systems.

Previous reaction-pathway modeling results

The potential effects of mixing, cooling, and chemical reactions on metal-bearing hydrothermal solutions have long been recognized with respect to formation of ore deposits, and a variety of attempts has been made to model such processes (Large 1977, Walshe & Solomon 1981, Reed 1983). Studies of the Red Sea geothermal system provided the first modern seafloor massive sulfide analog (Bischoff 1969) and led to improved modeling of ore-fluid evolution (Shanks & Bischoff 1977). However, realization that the brine in the Atlantis II Deep is a mixture of seawater and ore fluid (Zierenberg & Shanks 1986, 1988) has limited the utility of reaction-path computations, as have the high salinities. Collection of high-temperature hydrothermal solution samples from the East Pacific Rise (EPR) (particularly at 21°N) allowed the first relatively complete chemical and physical characterization of hydrothermal solutions which transport metals. The observation that some black-smoker fluids are clear at the chimney orifice, and therefore are unsaturated with metal sulfides, focused attention on processes of hydrothermal solution mixing with seawater as the primary cause of mineral precipitation from these pristine ore fluids. In addition to reactions involving seawater mixing with hydrothermal solution, two interrelated processes have largely been overlooked: sulfide-deposit reaction with hydrothermal solutions, and rock alteration in subjacent stockwork zones.

Computation of equilibrium and partial

equilibrium pathways for seawater mixing with 21°N EPR hydrothermal solution (Janecky & Seyfried 1984, Bowers *et al.* 1985) has demonstrated (Fig. 2) that mineral associations, temperature-related zonation in chimneys, and the composition of the massive deposits are all closely controlled by equilibrium processes, even though kinetics play an important role and the bulk deposit cannot be considered to be in overall equilibrium. For example, sluggish reaction-kinetics apparently preclude quartz precipitation and may inhibit sulfate–sulfide equilibration. Coupled temperature decrease *and* addition of Mg and SO_4 to the hydrothermal solution in a spatially limited zone of mixing are the critical changes which result in localization of sulfide deposition. Based on the mixing pathway models, Janecky & Seyfried (1984) and Shanks & Janecky (1984) suggested that sulfate-reduction reactions occurring during mixing could have a significant effect on the sulfur isotopic composition of the solutions and solid phases, depending on the amounts and direction both of chemical and isotopic reactions.

Relationships of sulfur isotopic compositions to precipitation process of sulfide and sulfate minerals have been generally focused on examination of equilibrium fractionation for mineral pairs, and on mineral-stability diagrams, primarily at constant temperature (Ohmoto 1972). These approaches are limited by the unconstrained solution-evolution pathway and the requirement that all solution species and minerals be in mutual equilibrium. Mixing and hydrothermal flow rates in the most active seafloor vents proceed at much faster rates than isotopic equilibration rates (Macdonald *et al.* 1980, Converse *et al.* 1984, Ohmoto & Lasaga 1982), limiting the applicability of strict equilibrium approaches. However, with the advent of reaction-pathway models, such as EQ3/6 (Wolery 1978, 1979, 1983), chemical reactions can be modeled explicitly, including consideration of bounding partial-equilibrium pathways, as functions of temperature and evolving-solution composition (Walshe & Solomon 1981, Janecky 1988). In this paper we examine results of initial models of near-seafloor fluid–chimney and fluid–rock interaction processes, and compare computed sulfur isotopic distributions for mixing models (including conductive cooling and heating) with the observed $\delta^{34}S$ values for the natural systems examined to date.

Sulfur isotopic composition of 21°N EPR and Juan de Fuca Ridge sulfides

Numerous investigators have measured $\delta^{34}S$ values of solution and solid samples from vent systems of the EPR and Juan de Fuca Ridge (Hékinian *et al.* 1980, Styrt *et al.* 1981, Arnold & Sheppard 1981, Kusakabe *et al.* 1982, Kerridge *et al.* 1983, Zierenberg *et al.* 1984, Shanks & Seyfried 1987, Woodruff & Shanks 1988). Results for seafloor sulfide deposits indicate a slight enrichment in ^{34}S over basaltic sulfur, and a relatively tight distribution (Fig. 3), but sulfate minerals have compositions very close to ambient seawater. Fewer $\delta^{34}S$ values of aqueous sulfide have been measured, but also indicate ^{34}S-enrichment over basaltic sulfide. Solution $\delta^{34}S(H_2S)$ values, both on average and for individual chimneys (Fig. 3), are generally higher than sulfide minerals (Kerridge *et al.* 1983, Shanks

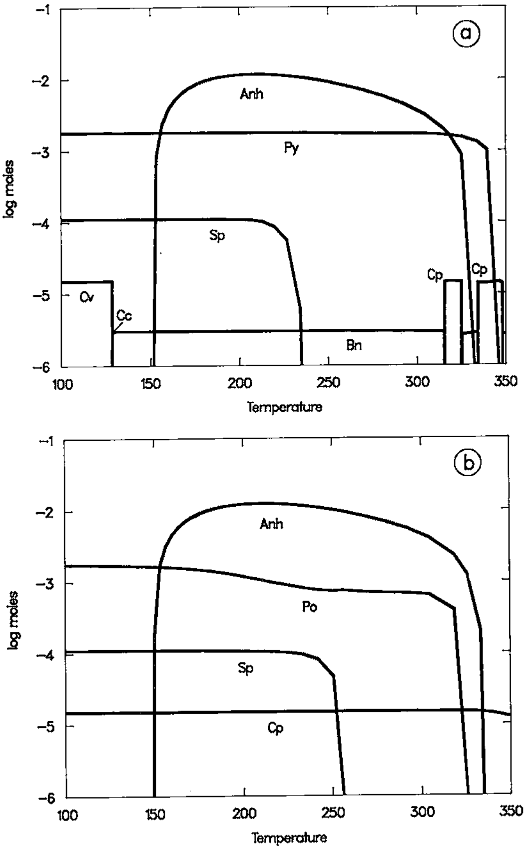

FIG. 2. Amounts (log moles) of mineral precipitates which are in equilibrium from 350°C to 100°C during adiabatic mixing of ambient seawater into 1 kg of hydrothermal solution (after Janecky & Seyfried 1984). In the sulfate–sulfide chemical equilibrium model (a), precipitation of silicate phase was suppressed. In the sulfate–sulfide chemical disequilibrium model (b), precipitation of pyrite and silicate phases was suppressed. Mineral abbreviations are: Cp chalcopyrite, Sp sphalerite, Po pyrrhotite, Py pyrite, Cc chalcocite, Cv covellite, Bn bornite, and Anh anhydrite. Relative mineral abundances and the sequences of mineral precipitation with respect to temperature are in good general agreement with observed paragenesis in seafloor chimney deposits.

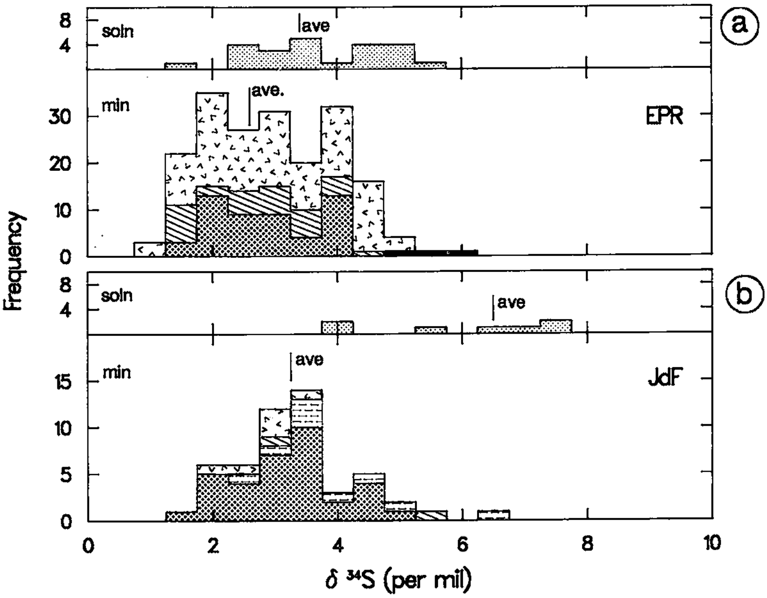

FIG. 3. Measured $\delta^{34}S$ values of minerals and solutions from (a) 21°N, EPR, and (b) Juan de Fuca Ridge (Kerridge *et al.* 1983, Shanks & Seyfried 1987, Woodruff & Shanks 1988). Mineral-separate analyses represented are: sphalerite (heavy stipple), pyrite (diagonal pattern), chalcopyrite (v pattern), bornite–chalcocite–covellite (solid fill), and pyrrhotite (horizontal dash pattern). Solution analyses are indicated by light dot fill. Most sulfide mineral samples fall into the range from 1.5 to 4.5 per mil, with Juan de Fuca Ridge samples being slightly ^{34}S-enriched with respect to 21°N. Vent-fluid $\delta^{34}S(H_2S)$ values are commonly higher than 4.5 per mil, as are $\delta^{34}S$ values of bornite-rich samples from 21°N.

& Seyfried 1987, Woodruff & Shanks 1988). Similarly, replacement of chalcopyrite in the outer zones of chimneys at 21°N involves formation of ^{34}S-enriched (to 5.2–6.2 per mil) bornite, chalcocite, and covellite, presumably due to seawater-sulfate reduction (Woodruff & Shanks 1988). The minimum $\delta^{34}S$ value, both of solids and solutions measured to date from seafloor volcanogenic systems, is approximately 1.0 per mil.

Experimental studies (Seyfried & Janecky 1985, Seyfried 1987, Seyfried *et al.* 1988) of basalt–seawater reactions, and direct measurements of vent fluids (Von Damm *et al.* 1985a), strongly indicate that dissolved sulfate is not significant in the deep source region of the hydrothermal system. Sulfate is thought to be lost from the system due to precipitation in the down-welling limbs of the convection cell during recharge. This has led Shanks *et al.* (1981), Shanks & Seyfried (1987), and Woodruff & Shanks (1988) to suggest that the $\delta^{34}S$ value of the fluid ascending from the deep portion of the system is very close to basaltic sulfide values (0–1 per mil). Bowers (1988) has reached a similar conclusion based on computational modeling of the deep portion of the system. Thus, for the purposes of modeling the modern vent systems, we assume the ascending fluid has a uniform $\delta^{34}S(H_2S)$ of 1 per mil as it enters the shallow (<500 m) subseafloor region. Seawater sulfate in these calculations was taken to have a $\delta^{34}S$ value of 21 per mil (Rees 1978).

COMPUTATIONAL PROCEDURES

Chemical reaction pathways

Chemical reaction-pathways have been computed using the EQ3/6 reaction-pathway modeling codes (Wolery 1978, 1979, 1983). Dissociation constants for aqueous species are from the 250-bars data base of Janecky (1982) and Janecky & Seyfried (1983, 1984). Mineral dissolution and redox reaction constants, and gas fugacity relations are calculated using SUPCRT and data from Helgeson *et al.* (1978), Helgeson & Kirkham (1974a,b, 1976), Helgeson *et al.* (1981), and Helgeson (pers. comm. of updates and corrections to the data). Sulfate and sulfide aqueous species and minerals are treated either as being in total equilibrium, or as two independent sets of sulfide and sulfate chemical components (see

Janecky & Seyfried 1984). The data base has been extensively tested for consistency against experimental and field data on mineral solubility in seawater-salinity solutions. Hydrothermal solution and seawater compositions are the OBS vent-fluid composition from 21°N, EPR (Von Damm *et al.* 1985a,b) as used by Janecky & Seyfried (1984), except where noted.

Sulfur isotopic modeling

Distribution of sulfur isotopes between aqueous species and minerals has been calculated using a new computer code EQPS (Janecky & Shanks, in prep.). The code, designed to operate as a post-processor to EQ6, calculates the total moles of all sulfur-bearing components in the system from data on tabular files output by EQ6, or input by the user. An isotopic data input file provides EQPS with fractionation-factor coefficients for each solution and mineral component relative to a reference solution species chosen to be H_2S, consistent with previous convention (Ohmoto & Rye 1979). The fractionation factors are used to calculate the composition ($\delta^{34}S_i$) of each component, with the isotopic composition of H_2S constrained by the composition and mass of the system and all other components.

Chemical reaction constraints of interest are: 1) redox equilibrium *versus* disequilibrium, especially whether sulfate reduction progresses appreciably or not; and 2) open *versus* closed system (*i.e.*, are precipitates available or unavailable for reaction with the evolving solutions). These types of chemical reaction constraints are implemented routinely when running the chemical reaction models using EQ3/6.

Isotopic reaction constraints of interest are: 1) sulfate–sulfide isotopic exchange equilibria or disequilibria independent of chemical equilibria — isotopic disequilibria in this paper refer to the special limiting case where 21 per mil seawater-derived sulfate is converted without exchange to a corresponding amount of 21 per mil H_2S, which is then added to the aqueous sulfide reservoir (H_2S and sulfide minerals isotopically equilibrate); 2) open *versus* closed isotopic exchange reactions between aqueous species and precipitated minerals — a more complex process than that considered for chemical reactions, because precipitated or saturated reactant phases (or both) may partly redissolve to equilibrate with solution, but may or may not simultaneously exchange isotopically with the solution; and 3) the extent to which mineral precipitation is coupled with redox processes during dissolution of a reactant phase — if chemical reduction occurs at a mineral surface, rather than homogeneously in solution, the resulting reduced sulfur may tend to be precipitated inhomogeneously, thus affecting the resulting mineral isotopic composition and apparent fractionation factors.

Estimates of rates of isotopic exchange between aqueous sulfate and sulfide, for systems near chemical equilibrium, have been examined by Ohmoto & Lasaga (1982), who assumed that chemical equilibration occurs at the same rates as isotopic equilibration. Comparison of observed mineral assemblages/parageneses (*e.g.*, containing pyrite, bornite–chalcocite–covellite, magnetite) and calculated mixing reaction pathways (Janecky & Seyfried 1984, Bowers *et al.* 1985), suggests that chemical equilibria are approached in mixed seafloor solutions. However, isotopic disequilibrium between sulfate and sulfide, similar to that described by Ohmoto & Lasaga (1982), is observed in seafloor massive sulfide samples, including those with assemblages that indicate approach to chemical equilibrium (Kusakabe *et al.* 1982, Kerridge *et al.* 1983, Zierenberg *et al.* 1984, Shanks & Seyfried 1987, Woodruff & Shanks 1988). In addition, flow rates and time scales of mixing in active seafloor vents (Macdonald *et al.* 1980, Converse *et al.* 1984) are very short compared to isotopic equilibration rates.

The EQPS code has been designed to allow independent examination of chemical and isotopic exchange disequilibria for sulfate–sulfide transformations. This is achieved by evaluating mass-balance and compositional constraints separately for sulfate-bearing and sulfide-bearing components of the system. Chemical oxidation and reduction processes are accounted for by examining the mass-balance relations and transferring the required masses and isotopic compositions between the two subsystems.

Open-system behavior between minerals and solution is computed by tracking the composition and masses of previously precipitated minerals separately from newly precipitated minerals. This results in sequential addition of isotopically evolving sulfide or sulfate to the solids as precipitation proceeds. For computational simplicity, and because minerals seldom dissolve regularly, dissolution of precipitated minerals is treated as a bulk average process. Inhomogeneous oxidation-/reduction-reaction processes occurring at a mineral surface have not yet been generalized and included in the code.

Accuracy of the computational procedure is most dependent on the step-size executed by EQ6, and is only slightly dependent on the step-size of the EQPS calculation. Given sufficient output points from EQ6, the calculations are more accurate than present analyses of sulfur isotopic compositions for several reasons. Firstly, EQPS calculations are sufficiently fast that small step-sizes are not a hindrance, especially when coupled to graphic output routines. Secondly, calculated EQ6 pathways are smooth and continuous between discontinuities, which are forced by EQ6 to be part of the output set of data points. This results in a typical computed $\delta^{34}S$ uncertainty of less than 0.05 per mil.

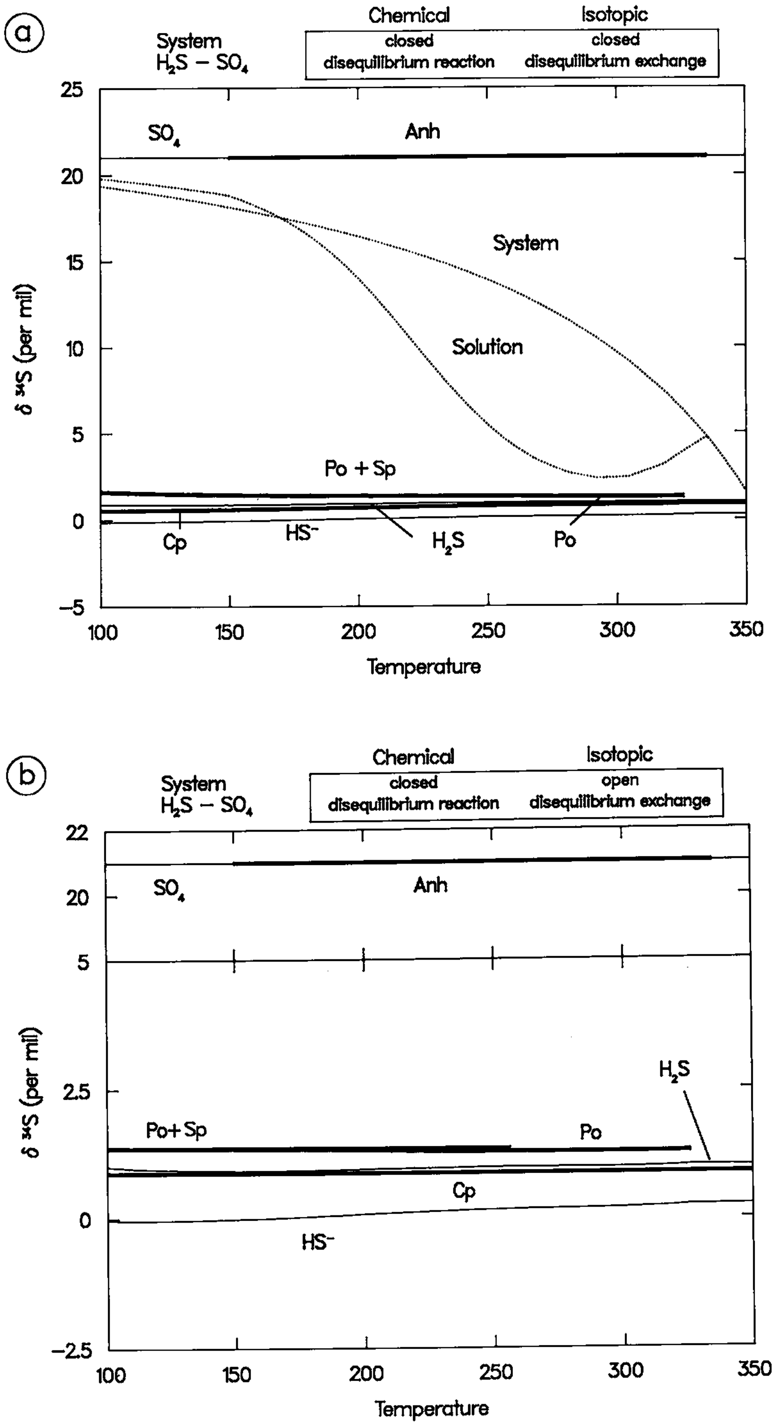

FIG. 4. Calculated $\delta^{34}S$ pathways during adiabatic mixing of seawater into hydrothermal solution from 350 to 100°C (Fig. 2b) for sulfate–sulfide chemical disequilibrium. Initial hydrothermal-solution sulfide and seawater sulfate were 1 and 21 per mil, respectively. Mineral compositions are shown as heavy lines (abbreviations from Fig. 2) and solution species as thin lines. Total mixed-system compo-

Modeling Results and Discussion

Adiabatic and non-adiabatic mixing reaction pathways

Previous computations have shown that mineral assemblages in seafloor chimneys can be modeled reasonably by mixing hydrothermal solution and seawater (Janecky & Seyfried 1984, Bowers *et al.* 1985), especially if kinetic effects on silicate precipitation, aqueous sulfate–sulfide equilibria, and stable *versus* metastable precipitation of sulfide minerals are incorporated (Janecky & Seyfried 1984). The effects of conductive heating of mixed solutions on reaction pathways have not been investigated extensively, and few conductively cooled reaction pathways have been studied. Such pathways, however, may be important in the formation of some chimney assemblages, such as chalcopyrite–bornite–chalcocite–covellite sequences observed in thin chimney walls (Haymon 1983, Woodruff & Shanks 1988).

Sulfur isotopic pathways for adiabatic mixing reactions. Examination of several possible isotopic reaction pathways for approximately adiabatic mixing (Fig. 2) provides a baseline model set for comparison to isotopic measurements from seafloor systems (Figs. 4, 5). The simplest isotopic pathway in an adiabatic mixing system is that associated with sulfate-sulfide chemical disequilibrium (Fig. 4), where sulfate-reduction and sulfide-oxidation reactions are inhibited. For a closed chemical system in which minerals isotopically re-equilibrate continually (Fig. 4a), sulfide-mineral $\delta^{34}S$ values diverge from solution composition by amounts controlled by the mineral–H_2S fractionation factors. Pyrrhotite, sphalerite, and chalcopyrite remain close to the 1 per mil initial hydrothermal solution composition. Alternatively, if mineral compositions are fixed as each increment precipitates, in an isotopically open system (Fig. 4b), much smaller ^{34}S-enrichment of pyrrhotite and sphalerite minerals occurs. Such pathways can produce the lowest $\delta^{34}S$ values measured from the seafloor vents, but not the values in the range from 2–4 per mil that are so commonly observed (Fig. 3).

Chemical-equilibrium adiabatic-mixing pathways, where sulfate reduction becomes quantitatively and isotopically important, are more complex; we have examined combinations of three types of constraints (Fig. 5). Complete sulfate–sulfide isotopic exchange equilibrium and chemical equilibrium in a closed system (Fig. 5a) result in generally decreasing $\delta^{34}S$ values for mineral and solution sulfides. Such isotopic compositions are not observed in active mid-ocean ridge seafloor systems (Fig. 3). Below approximately 200°C, sulfate–sulfide reactions are particularly inhibited (Ohmoto & Lasaga 1982), and thus the extremely negative values achieved by these models are not likely in natural systems without biological mediation.

For an isotopically open system that achieves chemical equilibrium and sulfate–sulfide isotopic exchange equilibrium (Fig. 5b), pyrite and Cu-mineral $\delta^{34}S$ compositions are more consistent with the range of measured seafloor values (Fig. 3). However, H_2S, sphalerite, and covellite have much lower $\delta^{34}S$ values than observed, due to lower temperature isotopic equilibration between sulfate and sulfide in solution.

Sulfate–sulfide isotopic exchange disequilibrium (where sulfate is reduced to sulfide without isotopic exchange, but sulfide minerals and H_2S isotopically equilibrate) in closed and open isotopic systems (Figs. 5c,d) gives isotopic compositions most generally consistent with the measured $\delta^{34}S$ values for all sulfide minerals. It is interesting to note that analyses of natural samples provide no evidence of systematic isotopic differences between pyrite, sphalerite, and chalcopyrite, as predicted by standard fractionation approaches and these calculated reaction pathways, possibly due to dynamic variations of mixing and precipitation on a local scale. In contrast to general agreement between models and measured compositions of most sulfide minerals, predicted $\delta^{34}S$ values of late covellite, chalcocite, and bornite are distinctly lower than H_2S and pyrite, whereas measured compositions of the Cu-rich phases that occur as replacements of chalcopyrite–isocubanite are ^{34}S-enriched (Woodruff & Shanks 1988).

Simple adiabatic mixing models thus are consistent with the observed 1.5–4.5 per mil range of most sulfide-mineral $\delta^{34}S$ values (Fig. 3). The maximum shifts in major sulfide mineral isotopic compositions require that sulfate–sulfide chemical equilibria are attained and sulfate–sulfide isotopic exchange disequilibrium prevails. In contrast, bornite and other Cu-rich sulfides are apparently produced by some more complex mechanism.

Solution sulfide $\delta^{34}S$ also increases in the models when chemical equilibria and sulfate–sulfide isotopic exchange disequilibria are coupled. *However, the maximum of such increases is only about 2 per mil above the initial value of 1 per mil due to the limited*

sition and bulk solution (sum of dissolved sulfate and sulfide components) composition as dotted lines. Results are similar under closed system (a) and open system (b) sulfate–sulfide isotopic exchange constraints, with resultant mineral and H_2S $\delta^{34}S$ values in the range from 0.5 to 1.5 per mil, which is the minimum observed in active-seafloor-vent sulfides.

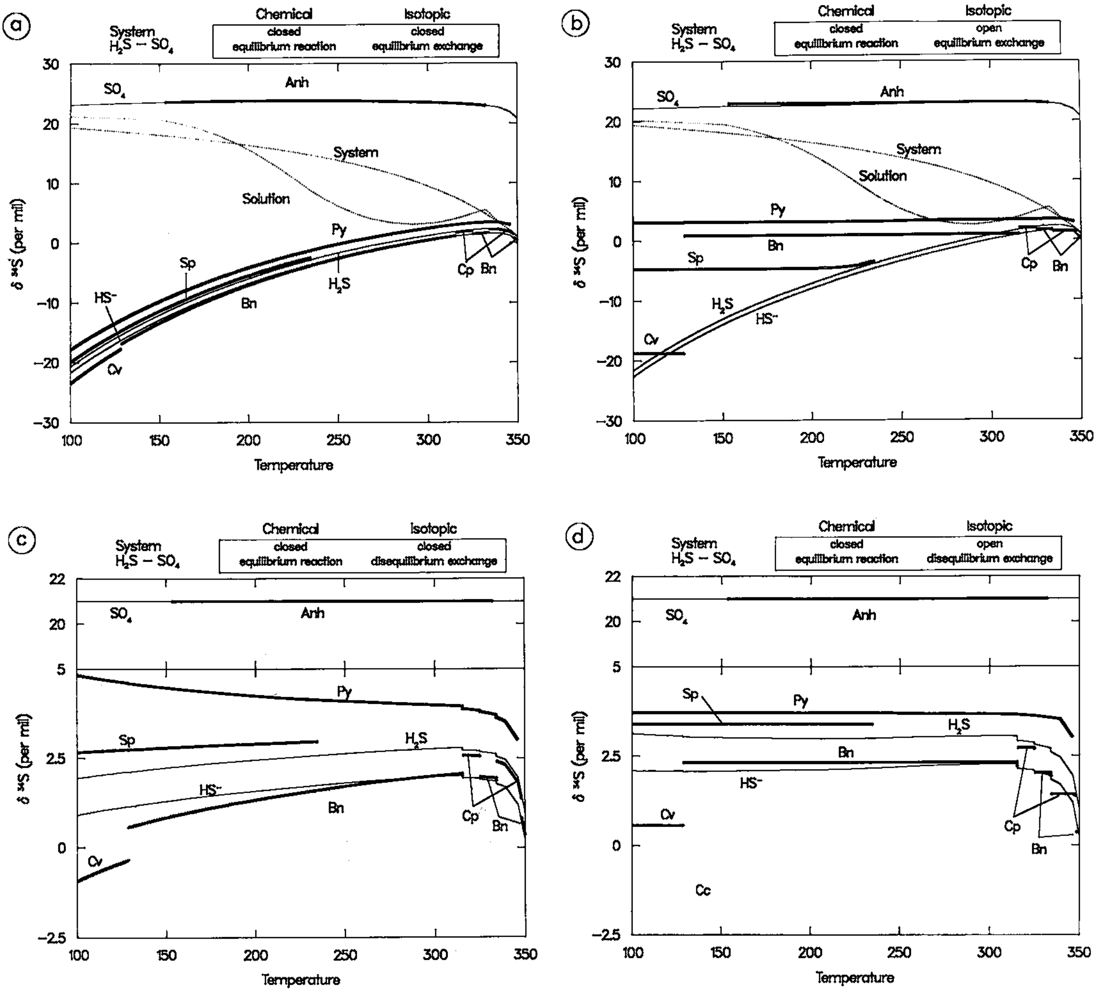

FIG. 5. Calculated $\delta^{34}S$ reaction pathways during adiabatic mixing of seawater into hydrothermal solution from 350°C to 100°C (Fig. 2a) for sulfate–sulfide chemical equilibrium. Four sets of constraints were modeled: (a) equilibrium sulfate–sulfide isotopic exchange in an isotopically closed system, (b) equilibrium sulfate–sulfide isotopic exchange in an isotopically open system, (c) disequilibrium sulfate–sulfide isotopic exchange (sulfate reduced is quantitatively converted to isotopically heavy sulfide, see text) in an isotopically closed system, and (d) disequilibrium sulfate-sulfide isotopic exchange in an isotopically open system. Labeling and line types as in Figure 4. Disequilibrium isotopic exchange in an isotopically open system best approximates the maximum of $\delta^{34}S$ values for common active-vent sulfides (Fig. 3).

reducing potential of the hydrothermal solution. Thus, reactions occurring during simple adiabatic mixing cannot explain solution-sulfide $\delta^{34}S$ as high as 4 to 7.5 per mil, as observed at both 21°N and Juan de Fuca, if the assumption of a relatively constant deep hydrothermal composition is correct. Such solutions may represent special processes even in seafloor vents, because they are not found to be precipitating significant amounts of sulfide minerals. Shanks & Seyfried (1987) and Woodruff & Shanks (1988) have argued that the lack of variation in vent-fluid chemistry from a given vent site, despite large variations in $\delta^{34}S$ values of H_2S relative to sulfide minerals, points to near-surface reactions modifying a relative uniform solution evolved at depth.

Non-adiabatic reaction pathways. Mineral-stability fields calculated for the full range of conductively cooled to conductively heated systems for mixing seawater into hydrothermal solution are summarized in Figure 6. The approximately adiabatic pathway of Figure 6 is identical to that of the sulfur equilibrium

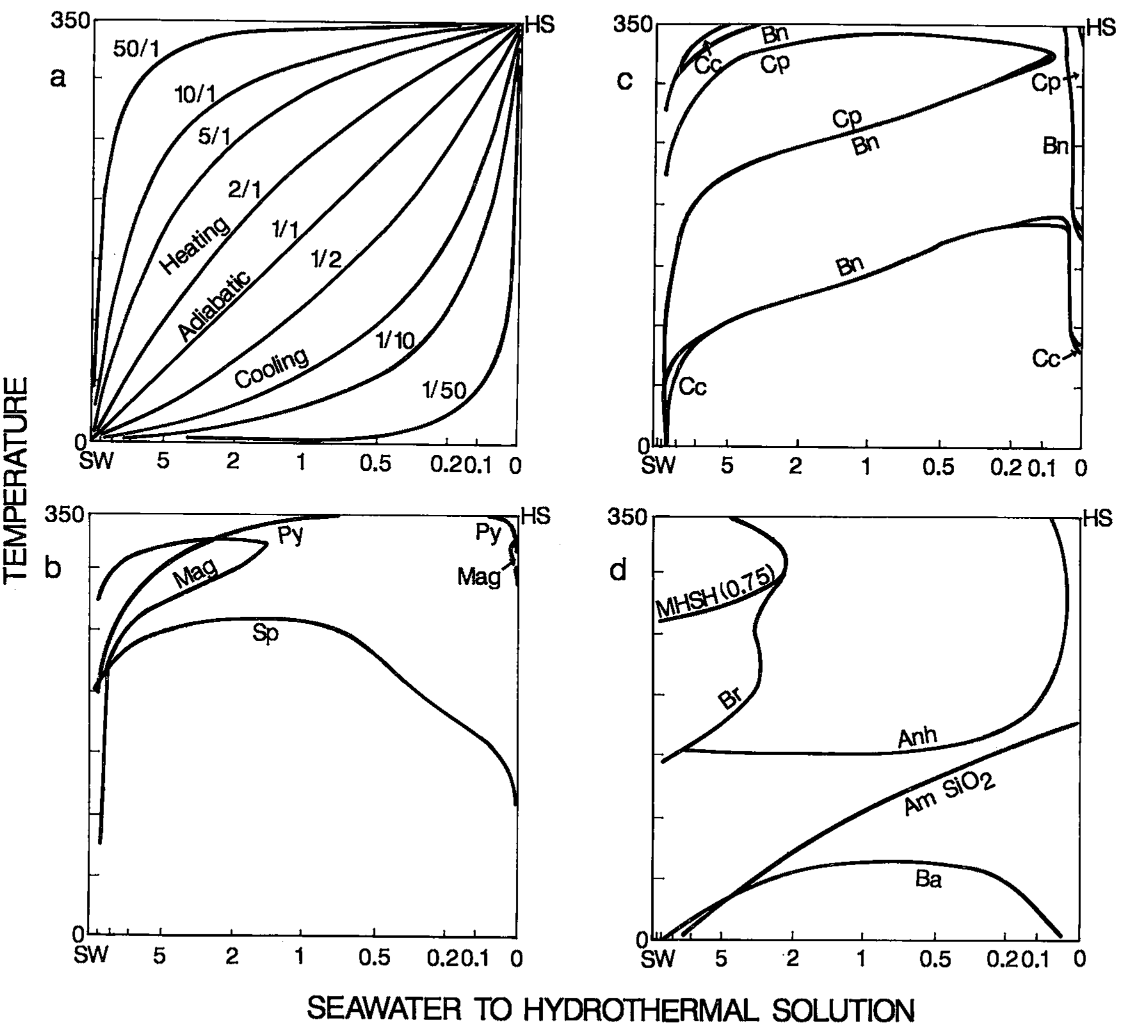

FIG. 6. Diagrams of simple mixing pathways (a) and corresponding mineral-product stability fields (separated for clarity in b, c, and d) for seawater mixing into hydrothermal solution, as a function of mixing ratio and temperature. The linear path from hydrothermal solution to seawater represents an approximately adiabatic path, whereas conductive cooling or conductive heating during the mixing process results in a nonlinear path, labeled with mixing ratio (R) of seawater to hydrothermal solution, relative to the adiabatic pathway ($R = 1$). Temperature of a mixed solution (T°C) at any point along the paths is a function of reaction progress (ξ) and mixing ratio (R) per unit reaction progress in the equation: $T = (350°\text{C} + R \cdot \xi \cdot 2°\text{C})/(1 + \xi)$, where the amount of 350°C hydrothermal solution in the model is 1 kg, and the amount of 2°C seawater mixed into the sytem is $R \cdot \xi$ kg. Mineral labels as in Figure 2, with the addition of Mag magnetite, MHSH(.75) magnesium hydroxysulfate hydrate (.75) (Janecky & Seyfried 1983) or caminite, Br brucite, Am SiO_2 amorphous silica, and Ba barite. Note that extensive magnetite stability occurs only under conditions of extreme conductive heating, as in thin chimney walls, and barite and amorphous silica only form under conditions of significant conductive cooling.

pathway shown in Figure 2a, whereas paths above and below it are conductively heated and cooled, respectively. Infinitely mixed and non-mixed pathways correspond to seawater heating and conductively cooled hydrothermal solution pathways, respectively.

It is apparent from the calculations (Fig. 6) that conductive cooling will favor final assemblages rich in barite, amorphous silica, and sphalerite. Conductive heating leads to anhydrite-rich deposits that may, in extreme cases, contain magnesium hydroxysulfate hydrate and magnetite. Only small amounts of conductive heating are required to make bornite and chalcopyrite the dominant copper sulfide minerals over most of the model mixing pathways.

At temperatures greater than about 200°C for most mixing ratios (Fig. 6), chalcopyrite *versus* bornite stability can be reversed or oscillate due to very slight variations in initial solution compositions, calculated activities of aqueous species, or the thermodynamic data. In fact, other Cu-bearing phases (*e.g.*, isocubanite) actually are found in the highest temperature zones of active chimneys and may be either the most stable Cu-bearing phases or may reflect inhibition of redox reactions necessary to precipitate chalcopyrite, bornite, and pyrite. However, the limited scope of the thermodynamic data base forces use of chalcopyrite and bornite as representatives of all such Cu-Fe-S phases.

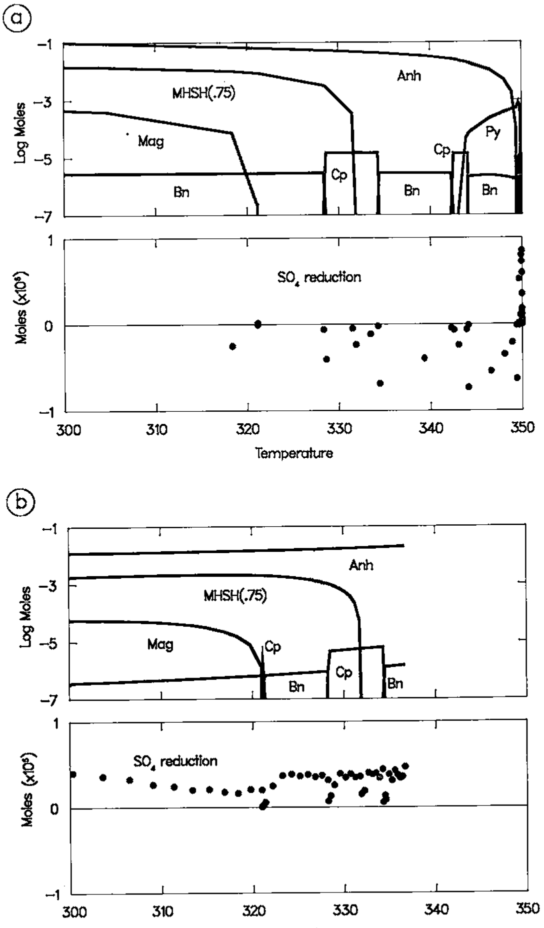

FIG. 7. 300–350°C segments of calculated conductive heating reaction path models (R = 48, Fig. 6) for (**a**) seawater mixing into hydrothermal solution (progressing from right to left) and (**b**) hydrothermal solution mixing into seawater (progressing from left to right). Upper panels show amounts of minerals in equilibrium with the mixed solution as the reaction proceeds. Lower panels indicate the amount of sulfate reduction or sulfide oxidation for each reaction step. Changing solution-sulfate concentration due to both mixing and precipitation of mineral phases causes the sawtooth shape in **a** and the wave pattern in **b**. Mineral abbreviations as in Figures 2 and 6. Sulfate reduction predominates only when hydrothermal solution is mixed into conductively heated seawater **b**. Conversely, mixing conductively heated seawater into hydrothermal fluid results mainly in sulfide oxidation (negative sulfate reduction, **a**).

Calculated isotopic pathways indicate that conductive heating or cooling does not produce significant variations in reduction of seawater-sulfate or mineral isotopic compositions, relative to the adiabatic path. Timing of chemical and isotopic reactions with respect to temperature may be significantly affected, however, allowing kinetics more influence on actual isotopic distribution.

^{34}S-enriched bornite-chalcocite-covellite assemblages. All the above model computations implicitly assume that sulfate reduction occurs homogeneously in solution, and complete mixing occurs in solution with dissolved sulfide. Precipitation from the mixed reservoir is then controlled by aqueous–solid isotopic fractionation factors. An additional possible reaction mechanism is reduction of sulfate at the mineral–solution interface, without mixing with the bulk solution reservoir of sulfide, such that chalcopyrite reacts to form a more oxidized assemblage and the reduced sulfate is totally incorporated in the solids, as in the following reactions (Janecky & Seyfried 1984, Woodruff & Shanks 1988):

$$\underset{\text{Chalcopyrite}}{CuFeS_2} + 0.4\,SO_4^{2-} + 1.2\,H_2 + 0.8\,H^+ = \underset{\text{Bornite}}{0.2\,Cu_5FeS_4} + \underset{\text{Pyrite}}{0.8\,FeS_2} + 1.6\,H_2O, \qquad (1)$$

and

$$\underset{\text{Chalcopyrite}}{CuFeS_2} + 0.073\,SO_4^{2-} + 0.146\,H^+ = \underset{\text{Bornite}}{0.2\,Cu_5FeS_4} + \underset{\text{Pyrite}}{0.64\,FeS_2} + \underset{\text{Magnetite}}{0.055\,Fe_3O_4} + 0.073\,H_2O, \qquad (2)$$

or

$$\underset{\text{Chalcopyrite}}{CuFeS_2} + 2.333\,Cu^+ + 2.667\,H^+ + 0.667\,SO_4^{2-} + 0.167\,Fe^{2+} = \underset{\text{Bornite}}{0.667\,Cu_5FeS_4} + \underset{\text{Magnetite}}{0.167\,Fe_3O_4} + 1.333\,H^+ + 2\,H_2O \qquad (3)$$

Magnetite is found in active chimneys in association with bornite that replaced chalcopyrite (Oudin 1983, Woodruff & Shanks 1988). Recently, a chimney from the southern Juan de Fuca Ridge containing a thick magnetite zone has been recovered (Woodruff &

Shanks 1988). Pyrite, in contrast, is generally absent from the zone of bornite formation. Reaction of chalcopyrite to form bornite and magnetite (Fig. 6) must occur under conditions of substantial conductive heating (about 48 times the seawater-to-hydrothermal-solution ratio of an adiabatic pathway at equivalent temperatures). Seawater mixing into hydrothermal solution along such conductively heated pathways results in chalcopyrite reaction to bornite *and* closely asociated magnetite stability at temperatures between 330 and 320°C (Figs. 6,7). These calculations also indicate that caminite (magnesium hydroxysulfate hydrate, MHSH) should also be an important component of such assemblages.

When conductively heated seawater mixes into hydrothermal solution, sulfate reduction occurs only with incipient mixing (Fig. 7a). In contrast, when hydrothermal solution is mixed into conductively heated seawater the calculations indicate oxidation of sulfide at low temperatures, and subsequent steady reduction of sulfate as the reaction proceeds (Fig. 7b). The latter scenario is consistent in many ways with the structure of thin chimney walls in that the inner "chalcopyrite zone" is a good heat conductor but relatively impermeable, whereas the outer "anhydrite zone" is relatively permeable (Tivey & McDuff 1987).

To examine the results of isotopic processes in this local chimney environment, we can assume that all reduced sulfate is incorporated in sulfides without fractionation. Chalcopyrite formed via chemical disequilibrium pathways has a $\delta^{34}S$ value of about 1.0 per mil (Fig. 4), and seawater sulfate has a $\delta^{34}S$ of 21 per mil (Rees 1978). For total consumption of chalcopyrite in reactions (1) and (3) above, the $\delta^{34}S$ compositions of the resulting bornite are 4.3 per mil and 6.0 per mil, respectively. For reaction (2), the resulting $\delta^{34}S$ value for bornite would be 1.7 per mil, a smaller but still significant increase. Thus, the observed increase in $\delta^{34}S$ of the Cu-rich minerals relative to most of the minerals and the bulk chimney may be controlled by reactions within the chimney, and the approximate conditions under which such reactions occur can be identified. More exact understanding of the process, in particular the extent of magnetite formation by reaction (3) and isotopic distribution between and within minerals, requires explicit modeling of coupled flow and chemical reactions and kinetics (Tivey & McDuff 1987), and more detailed analysis of the solid products using high-precision ion- or laser-probe techniques (Shanks & Criss 1988).

Reactions within chimneys and sulfide deposits

Various features of massive sulfide deposits and chimneys may be attributed to reaction between previously deposited sulfide materials and hydrothermal solution, with or without addition of ambient seawater. Of particular interest are metal zonations within deposits and individual chimneys, effects on isotopic and chemical composition of hydrothermal solution, and trends in $\delta^{34}S$ values of sulfide deposits. Qualitative models for development and growth of active chimneys reveal some of the chemical processes (Goldfarb *et al.* 1983, Haymon 1983, Tivey & Delaney 1986), including replacement of early low-temperature sphalerite–anhydrite assemblages by later high-temperature wurtzite–isocubanite/chalcopyrite assemblages. Increases in $\delta^{34}S$ values of sulfide minerals and fluids within a deposit could result from sulfate reduction by two general processes: (1) reheating of materials to temperatures above 250°C, leading to reduction of anhydrite sulfate; and/or (2) mixing of seawater with hot hydrothermal solution within the deposit, resulting in reduction of seawater sulfate. In either case, some mineral or minerals must act as the reducing agent.

Isothermal reaction of 350°C hydrothermal solution with minerals previously precipitated by seawater – hydrothermal solution mixing to 200°C represents one generalization of intra-deposit processes. Model results are represented in terms of reaction progress (Fig. 8), which may be viewed as either the amount of reaction in a particular region of the deposit with respect to time, or as the distribution of reaction products along a flow pathway at a particular time.

Dissolved Fe remains approximately constant during the reaction, until pH increases late in the calculation, while sulfide decreases as pyrite precipitates, and fO_2 increases only slightly (Fig. 8a). Most strikingly, Zn is increased significantly while Cu is depleted in the high-temperature solutions by reaction with massive sulfide materials, which has a considerable affect on the local bulk sulfide-mineral composition (Fig. 8b). The calculated reaction pathway also indicates that only minor dissolution of anhydrite in the model is necessary to saturate the hydrothermal solution (Fig. 8b). Similar processes may be important in the formation of Zn-rich, Cu-depleted solutions and deposits in active systems (Von Damm & Bischoff 1987).

The small increases in solution-sulfide isotopic composition which result from chimney – hydrothermal fluid reaction (Fig. 8c) are consistent with the limited solubility of anhydrite in hydrothermal solutions and with limited sulfate reduction. Furthermore, as reaction progresses and pyrrhotite continues to dissolve (Fig. 8b), $\delta^{34}S(H_2S)$ values return to that of the input hydrothermal solution. Thus, neither mixing between hydrothermal solution and seawater *nor* reaction within the sulfide mound is sufficient to increase $\delta^{34}S$ values to those observed in active systems on the seafloor, even though other solution and deposit characteristics can be attributed to such processes.

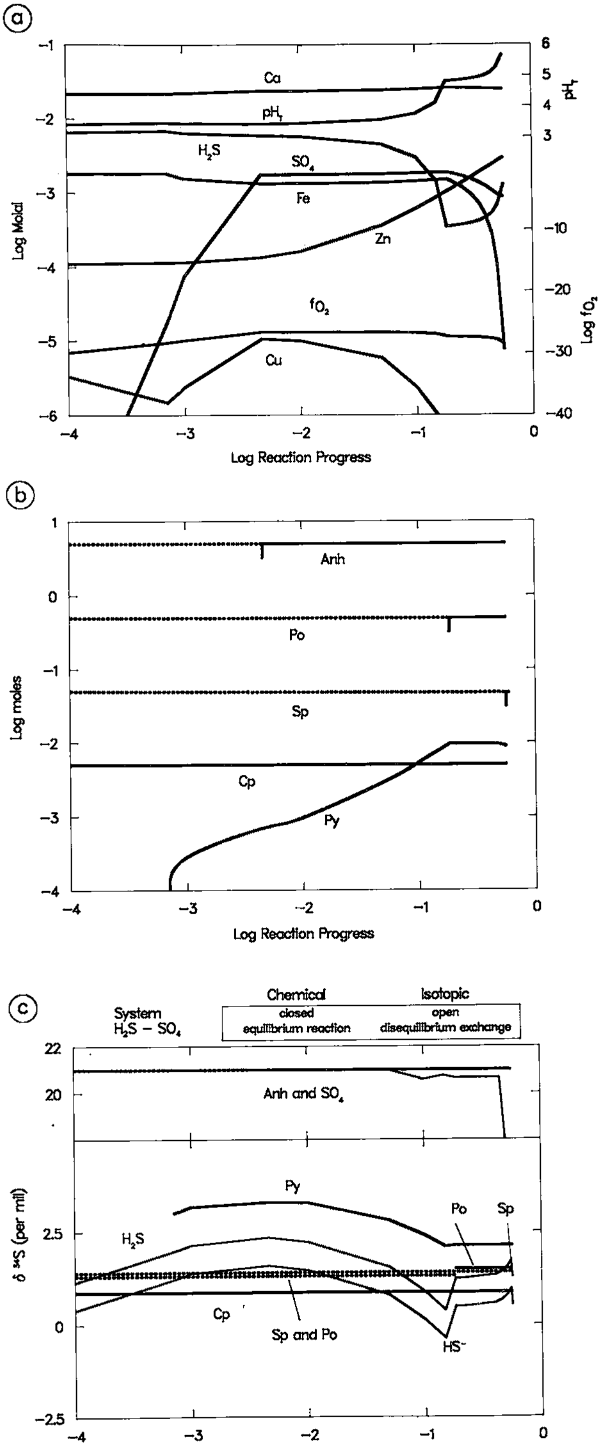

FIG. 8. Calculated 350°C isothermal reaction pathway of the 0.73 kg of bulk chimney materials formed during the adiabatic mixing simulation (Fig. 2b and Janecky & Seyfried 1984) with 1 kg hydrothermal solution, in a chemically closed system with chemical equilibrium. Plotted as a function of increasing reaction progress (from left to right) are (a) concentrations of selected solution components, pH at 350°C, and fO_2; (b) amounts of minerals present as reaction progresses (reaction products are shown as solid lines, and undersaturated reactants are shown by dashed lines with almost horizontal paths because the small fractions dissolved of the initial amounts are not apparent with the log scale of this Figure); and (c) corresponding $\delta^{34}S$ pathways of minerals and solution species for disequilibrium sulfate–sulfide isotopic exchange and an open isotopic system. Mineral abbreviations as in Figures 2 and 6. Resulting sulfide minerals have $\delta^{34}S$ values in the range of 1 to 3 per mil, similar to the natural systems. Uniform values for chalcopyrite and sphalerite are not consistent with the observed values in seafloor chimneys.

Reactions within the hydrothermal stockwork

Fossil massive sulfide systems have constrained our concepts of rock/water interaction effects in hydrothermal alteration zones that are inaccessible beneath the modern seafloor deposits (Franklin *et al.* 1981, Sawkins 1984, and references therein). Many of the subtle compositional and isotopic variations in the seafloor vent-fluids likely are due to such "feeder-zone" alteration. In the absence of drillhole sampling, theoretical modeling of fluid evolution is one of the most effective tools in assessing the consequences of subseafloor alteration.

Alteration due to reactions between basalt and hydrothermal solution (± ambient seawater) below the seafloor in massive sulfide ore deposits has been studied extensively, and the physical relationship of a hydrothermal flow zone to such deposits is understood in general terms (Franklin *et al.* 1981, Sawkins 1984, and references therein). However, the potential influence of chemical reactions in the stockwork zone on venting solutions and processes of formation of massive sulfide deposits has been largely unrecognized. The nature of the plumbing system near the seafloor (Roberts & Reardon 1978, Cathles 1983) may significantly influence the extent of alteration reactions, and consequently the composition of venting solution and deposit characteristics. For example, high permeability surrounding the hydrothermal upflow zone could increase seawater ingress, resulting in Mg metasomatism and sulfate reduction.

Crystalline tholeiitic basalt, initially composed of plagioclase, pigeonitic pyroxene, olivine, and minor oxide and sulfide minerals (Williams *et al.* 1954), commonly is replaced in stockwork zones by chlorite-rich assemblages (Franklin *et al.* 1981, Zierenberg *et al.* 1988). Stockwork-alteration pathways, particularly for individual flow paths though vein networks, probably are complex and both temporally and spatially dynamic. Alteration of olivine and pyroxene in such rocks will release ferrous iron which may result in enhanced reducing potential (see Shanks *et al.* 1981) beyond that attributable solely to pristine hydrothermal solution, as in the following reaction:

$$\begin{aligned}&1.563\ \underset{\text{Labradorite}}{Na_{0\cdot4}Ca_{0\cdot6}Al_{1\cdot6}Si_{2.4}O_8} + 6\ \underset{\text{Fayalite}}{Fe_2SiO_4} + 2.5\ H^+\\ &+ 8\ H_2O = \underset{\text{Chlorite}}{Fe_{12}Al_{2\cdot5}Si_{5\cdot5}O_{20}(OH)_{16}} + 4.25\ SiO_2(aq)\\ &+ 0.625\ Na^+ + 0.938\ Ca^{2+} + 1.25\ H_2(aq) \qquad (4)\end{aligned}$$

Observations from altered basalts indicate that olivine is generally more reactive than pyroxenes, consistent with experimental and theoretical constraints (Janecky & Seyfried 1986, Murphy & Helgeson 1987, Seyfried 1987). In addition, relative reaction rates between plagioclase and olivine favor olivine alteration. Thus, to examine the implications of stockwork alteration with respect to redox potential, we have simplified the basalt alteration process to that of fayalite reacting to form iron silicates. Both fayalite and the iron silicates actually are solid-solution components in phases with Mg-dominated compositions.

Stockwork alteration may have two general consequences: (1) stabilization of the more reduced sulfide phases in the stockwork and massive sulfide deposit, and (2) reduction of seawater sulfate introduced through the surrounding rocks (Fig. 1). The latter process is of most interest with respect to resultant $\delta^{34}S$ values of fluid and minerals, and will be examined using a simplified hydrothermal solution reaction model with fayalite + anhydrite ± Fe sulfide representing basalt, seawater-derived sulfate, and earlier hydrothermal precipitates, respectively. Quartz precipitation is inhibited, as it apparently is within seafloor massive sulfide deposits (Haymon & Kastner 1981, Janecky & Seyfried 1984). Two types of bounding pathways are calculated, based on the presence or absence of secondary magnetite (Figs. 9, 10). Solution compositions along the reaction paths illustrate the relatively buffered state of the hydrothermal solution. Decreases in Fe or H_2S (Figs. 9a and 10a, respectively) only occur following extensive reaction, in response to increased pH. Significant variations in dissolved SiO_2 concentrations can also occur, depending on the alteration minerals formed. Magnetite precipitation stabilizes pyrrhotite with respect to pyrite, and limits formation of iron-silicate minerals (Figs. 9b and 10b, respectively). With better constraints on the reaction of all basalt components and consideration of broader metasomatic effects, including more stable aluminosilicate minerals than those of this limited subsystem, the computed pH increase would not occur until even greater amounts of reaction progress. However, stockwork alteration occurs under conditions of focused flow and at high water/rock ratios; thus, the extreme amounts of reaction attendant to the pH increases are not likely to be attained.

In spite of the limitations of the simplified models, the consequences for $\delta^{34}S(H_2S)$ values are significant (Figs. 9c, 10c). Even before the strong Fe and sulfide concentration decreases (Figs. 9a, 10a), $\delta^{34}S$ of H_2S in solution increases by about 3.5 per mil in the magnetite-absent model, and exceeds 5 per mil where magnetite is allowed to precipitate to equilibrium. The latter reaction continues to increase $\delta^{34}S(H_2S)$ to greater than 15 per mil (Fig. 10c). Comparison of a variety of similar computed reaction pathways to the available data on H_2S concentrations and $\delta^{34}S(H_2S)$ values from 21°N and Juan de Fuca Ridge vent sites (Fig. 11) confirms that the models accurately constrain the processes that cause large variations in vent compositions, even for substantially different initial compositions. Perhaps, using the $\delta^{34}S$ data as a guide and more thoroughly investigating stockwork-alteration processes, we can attain a better understanding of subtle differences observed in vent-fluid compositions and measured temperatures (Campbell *et al.* 1988, Von Damm *et al.* 1985a, Von Damm & Bischoff 1987). In addition, such reactions may have consequences for other geochemical and geophysical characteristics of these systems, such as the potentially profound effect of secondary magnetite on the magnetic signature of active vent systems (Tivey & Johnson 1985).

IMPLICATIONS FOR VOLCANOGENIC MASSIVE SULFIDE ORE DEPOSITS

The computational models for active seafloor massive sulfide deposits can be compared to volcanogenic massive sulfide ore deposits in three primary areas: (1) chemical composition and zoning; (2) sulfur isotopic relationships; and (3) influence of stockwork alteration. We recognize that many ancient massive sulfide deposits have different source-rock compositions, profoundly different plumbing systems, and that ore-fluid salinity may have varied by a factor of about three. Nonetheless, water/rock interaction with seawater-derived fluids is not particularly sensitive to the mineralogy and bulk composition of the source rock (Shiraki *et al.* 1987, Seyfried 1987), and some general applications of the present calculations can be developed.

Chemical composition and zoning

Active chimney and ancient ore-deposit compositions have been compared to those predicted for the bulk sulfide phases from the simple mixing models by Janecky & Seyfried (1984), who found reasonable agreement. Autometamorphism and reworking of ore deposits by the hydrothermal solutions have been considered to explain widespread development of large-scale zoning from Cu-rich cores to Zn-rich margins in ancient deposits (Franklin *et al.* 1981, Eldridge *et al.* 1983), and can be quantitatively examined with respect to the interaction between hydrothermal solution and previously precipitated massive sulfide observed in seafloor chimneys and modeled above (Fig. 8). Although many previous workers have considered evolution of solution composition in space and time to explain such features, experimental studies of basalt–seawater interaction indicate that metal-bearing solutions can be developed only under a narrow range of conditions near 400°C and 400 bars in mid-ocean ridges (Seyfried & Janecky 1985, Seyfried 1987). It follows that, where sphalerite is absent, ophiolitic massive sulfide materials probably have experienced post-depositional reaction with hydrothermal solution at temperatures >250°C (Fig. 2) and at bulk solution-to-rock mass ratios of greater than approximately 25 (Fig. 8b). Thus, initial sulfide precipitation, coupled with later *in situ* zone-refining of massive sulfide, can produce the major-metal zonation observed in many deposits without requiring depositional fractionation from buoyant plumes (Solomon & Walshe 1979), or gross evolution of the ascending hydrothermal solution composition through time (Ohmoto *et al.* 1983). Such processes are also consistent with descriptions of veins that cut otherwise stratified Kuroko deposits (Eldridge *et al.* 1983), which probably represent "black and white smoker" feeders within a larger context of diffuse flow (East Pacific Rise Study Group 1981).

Sulfur isotopes

Ore deposits allow examination of $\delta^{34}S$ variations with respect to geologic time, as pointed out by Sangster (1968), who noted the general tracking of temporal variations in seawater-sulfate $\delta^{34}S$ by contem-

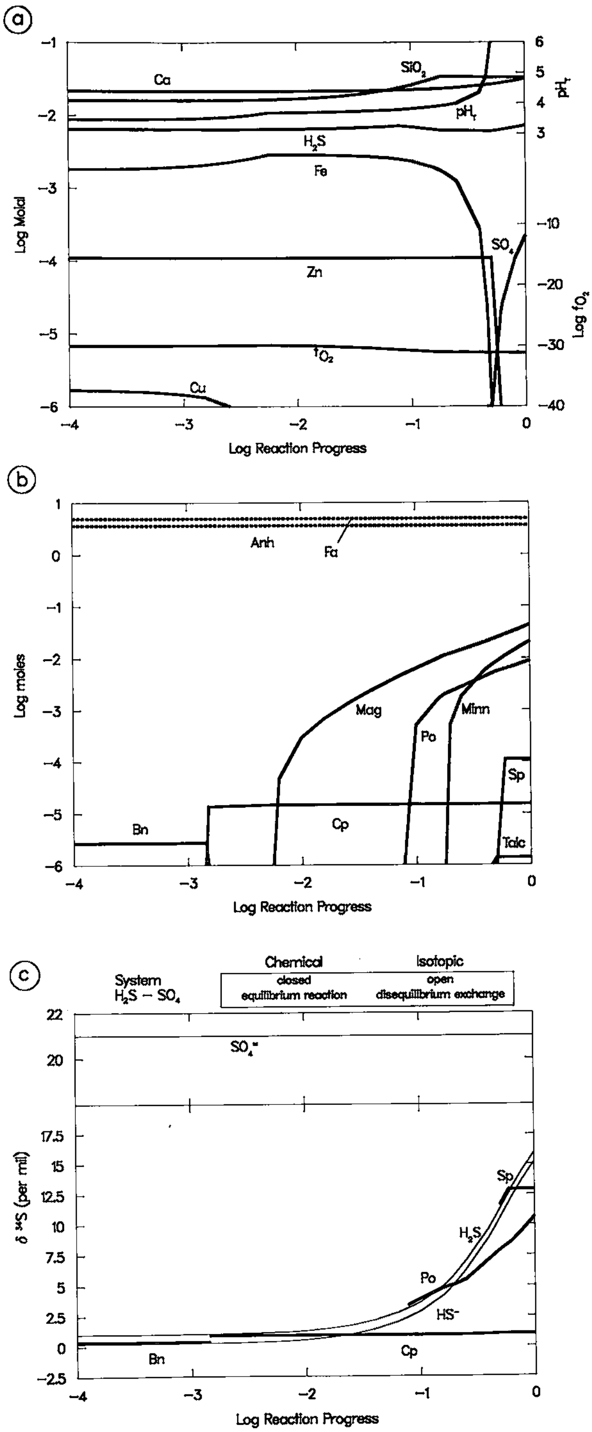

FIG. 9. Calculated isothermal (350°C) reaction of 1 kg of hydrothermal solution with anhydrite and fayalite, with magnetite precipitation permitted. Plotted as a function of increasing reaction progress are: (a) concentrations of selected solution components, pH at 350°C, and fO_2; (b) amounts of minerals present as reaction progresses (reaction products are shown as solid lines, and undersaturated reactants are shown by dashed lines with nearly horizontal paths because the small fraction dissolved of the initial amounts are not apparent with the log scale of this Figure), and (c) corresponding $\delta^{34}S$ pathways of minerals and solution species for disequilibrium sulfate–sulfide isotopic exchange and an open isotopic system. Mineral abbreviations as in Figures 2 and 6, with addition of Fa fayalite, and Minn minnesotaite. $\delta^{34}S$ results indicate large increases to greater than 15 per mil, as the reaction progresses. $\delta^{34}S(H_2S)$ values of 7.5 per mil, the maximum ^{34}S-enriched vent fluids sampled, are obtained with only subtle alteration of fluid chemistry.

poraneous massive sulfide deposits (Fig. 12). In addition, the accessibility of ore-deposit samples in three dimensions, and the accurately characterized relationships between samples, provide a more complete picture of the full range and character of sulfur isotopic variations.

Only part of the regional and temporal $\delta^{34}S$ variability of individual deposits can be explained by sulfur isotopic compositional variations in seawater. Equilibrium temperatures calculated using $\delta^{34}S$ values of sulfide–sulfide mineral pairs from Kuroko deposits are generally,but not universally, consistent with other temperature indicators (*e.g.*, fluid-inclusion filling temperatures), whereas sulfate–sulfide mineral pairs are far from equilibrium (Franklin *et al.* 1981 and references therein). Although equilibrium fractionation approaches cannot explain these observations (Ohmoto & Lasaga 1982), the reaction-path computations discussed above have considerable potential for modeling the dynamic processes involved in ancient-deposit evolution, when placed in geologic context.

Sulfur isotope values of sulfide minerals in volcanogenic massive sulfide ore deposits characteristically are close to 0 per mil, or are enriched somewhat in ^{34}S (Fig. 12), similar to active seafloor vents. Sulfate minerals in ancient massive sulfide deposits commonly are enriched in ^{34}S, to values approximating contemporaneous seawater sulfate. Ranges of $\delta^{34}S$ values of sulfide minerals are often similar for different deposits within the same district, with individual deposits and distinctive ore types within individual deposits often having narrower $\delta^{34}S$ ranges. Where examined, sulfide $\delta^{34}S$ values in a given orebody often have a poorly defined trend of decreasing $\delta^{34}S$ values upward (Kajiwara 1971, Franklin *et al.* 1981, Rye *et al.* 1984). Generally upward-decreasing bulk $\delta^{34}S$ values in massive sulfide ore deposits may result from a combination of limited reducing potential of the hydrothermal solution and sulfide deposit (Figs. 4, 5, 8), combined with progressive exclusion of seawater from the deposit as it grows.

Sulfide isotopic compositions of ancient massive sulfide deposits and the apparent disequilibrium fractionation between sulfate and sulfide minerals is generally consistent with the results of mixing reactions under the varying constraints described above

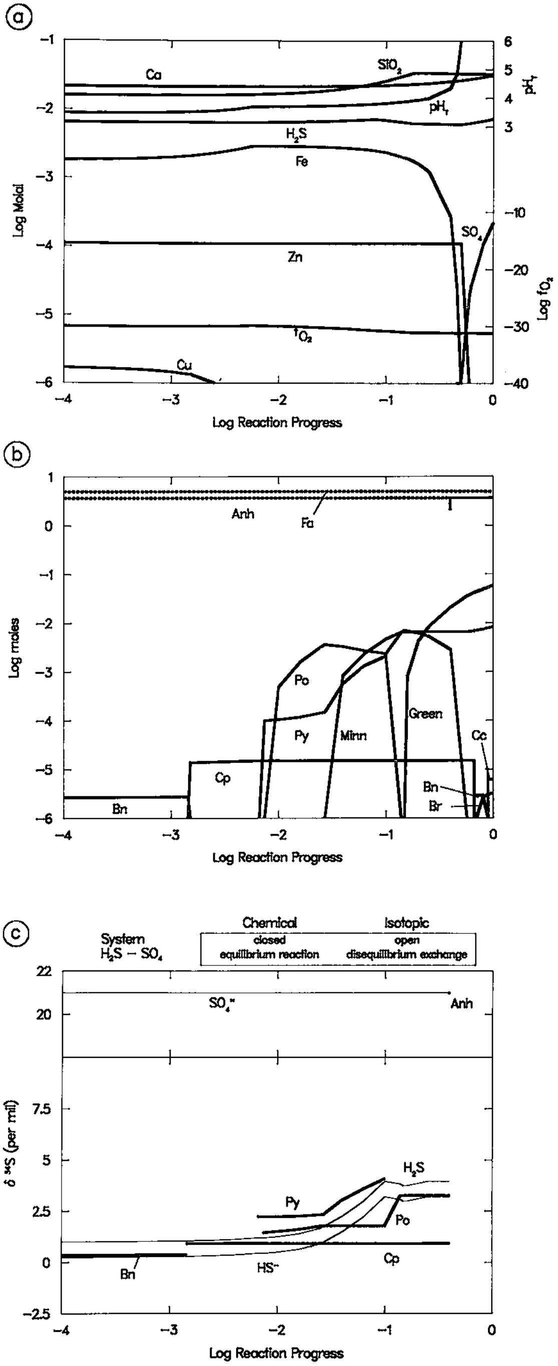

FIG. 10. Calculated isothermal (350°C) reaction of 1 kg of hydrothermal solution with anhydrite and fayalite, with magnetite precipitation suppressed. Plotted as a function of increasing reaction progress are: (a) concentrations of selected solution components, pH at 350°C, and fO_2; (b) amounts of minerals present as reaction progresses (reaction products are shown as solid lines, and undersaturated reactants are shown by dashed lines with nearly horizontal paths because the small fraction dissolved of the initial amounts are not apparent with the log scale of this Figure); and (c) corresponding $\delta^{34}S$ pathways of minerals and solution species for disequilibrium sulfate–sulfide isotopic exchange and an open isotopic system. Mineral abbreviations as in Figures 2, 6, and 9, with addition of Green greenalite. $\delta^{34}S$ values of solution sulfide can be shifted to 4 per mil, without substantial variations in fluid chemistry.

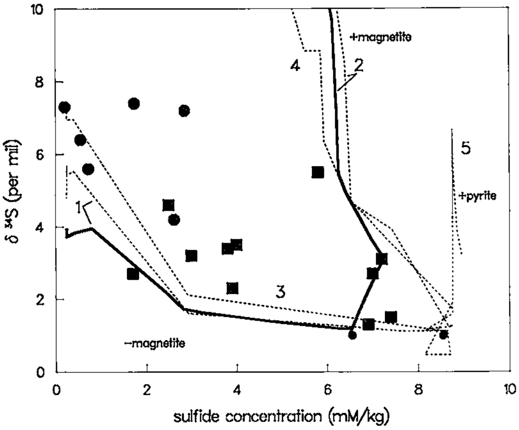

FIG. 11. $\delta^{34}S$ of solution sulfide *versus* sulfide concentration for data from active 21°N EPR (solid squares) and Juan de Fuca (large solid circles) hydrothermal-vent solution samples (Shanks & Seyfried 1987, Woodruff & Shanks 1988) with respect to selected model computation results. Pathways from calculated stockwork alteration models in Figures 9 and 10 are shown as solid lines, with an initial H_2S concentration of 6.5 m*M*. Dashed lines represent a set of reaction pathways calculated using hydrothermal solution compositions (8.5 m*M* H_2S) from Hanging Gardens site, 21°N, EPR (Von Damm *et al.* 1985a). Hydrothermal-solution reaction pathways illustrated are (1) anhydrite + fayalite reactants with suppression of magnetite and all silica polymorphs; (2) anhydrite + fayalite reactants with magnetite precipitation allowed and suppression of all silica polymorphs; (3) anhydrite + fayalite + pyrrhotite reactants with suppression of magnetite and all silica polymorphs; (4) anhydrite + fayalite + pyrrhotite reactants with magnetite and quartz precipitation allowed; and (5) anhydrite + fayalite + pyrite reactants with magnetite precipitation allowed and suppression of all silica polymorphs. Restriction of the solution H_2S and $\delta^{34}S(H_2S)$ data to within the bounds of the calculated reaction pathways strongly suggests that subseafloor basalt alteration is the process which produces the $\delta^{34}S$-enriched H_2S values.

(Figs. 4, 5). However, most individual deposits show a significant range of sulfide $\delta^{34}S$ values (Franklin *et al.* 1981, Ohmoto & Rye 1979, and references therein), usually larger than the ranges observed in modern deposits on sediment-free ridge crests. Large massive sulfide ore deposits often have experienced a complex history of precipitation and replacement reactions, with some replacement reactions occurring at temperatures considerably lower than peak temperatures. If lower temperature sulfide replacements precipitate in equilibrium both chemically and isotopically, leading to more negative $\delta^{34}S$ values (Fig. 5a,b), then broader overall $\delta^{34}S$ ranges should result. In fact, a number of the deposits with large $\delta^{34}S$ ranges (Fig. 12) have samples which extend the range to negative $\delta^{34}S$ values, supporting the hypothesis that lower temperature reactions have the effect of extending the $\delta^{34}S$ range. Modern deposits on the ridge crests studied to date are too small, too young, and too incompletely sampled to show these effects.

Stockwork-alteration effects

Although significant shifts in solution H_2S isotopic compositions at active vents are attributable to stockwork alteration, how significant are such processes likely to be in the formation of a large ore deposit? A rough estimate can be made by calculating the effect of fayalite alteration in a stockwork on the minimum amount of hydrothermal solution necessary to form a substantial ore deposit. For a stockwork pipe 500 m^2 in area and 0.5 km deep ($\sim 7.5 \times 10^8$ kg basalt), the amount of fayalite component available for alteration is $\sim 2.3 \times 10^7$ moles (~ 15 mole % of olivine, which is ~ 3 wt.% of the basalt; Williams *et al.* 1954). In the model computations of Figure 9, hydrothermal solution $\delta^{34}S$ (H_2S) values are shifted by 5 per mil at a reaction progress of 0.16 (equivalent to 0.016 moles of fayalite reacted with 1 kg hydrothermal solution). Thus, 1.4×10^9 kg of hydrothermal solution can be shifted by 5 per mil in such a stockwork. An estimate of the amount of hydrothermal solution necessary to form a representative ore deposit with 1 wt.% Cu and 1 million metric tons of ore (Franklin *et al.* 1981) can be made by assuming that all Cu carried by the hydrothermal solution is trapped in the massive sulfides. The model computations use a Cu concentration of 0.015 m*M*/kg for the hydrothermal solution (Von Damm *et al.* 1985a,b), which results in a minimum estimate of approximately 10^4 kg of solution to form 1 kg of massive sulfide, or 10^{13} kg of solution to form 1 million metric tons of ore. Thus, 1.4×10^5 kg of ^{34}S-enriched massive sulfide is produced in a 1 million metric ton deposit, or <0.02 wt.% of the ore deposit. Even this is probably a high estimate because it was assumed that excess seawater-sulfate is available to all solution passing through the 0.5-km-deep pipe, and that all Cu carried by the solution is trapped in the deposit.

Sulfate reduction resulting in sulfide isotopic shifts in active seafloor hydrothermal vents, therefore, provides important insight into the chemical reaction processes affecting the solution composition near the seafloor. Such shifts, however, must be transient occurrences during the formation of a large and economic ore deposit. Sulfur isotopic composition of large ore deposits, like the seafloor chimneys, must be dominated by sulfide derived from source rocks deep in the hydrothermal system. Minor modification (1-3 per mil $\delta^{34}S$ increase) results from addition of ^{34}S-enriched sulfate by mixing at the vent site. Thus, apparent correlations between $\delta^{34}S$ variations

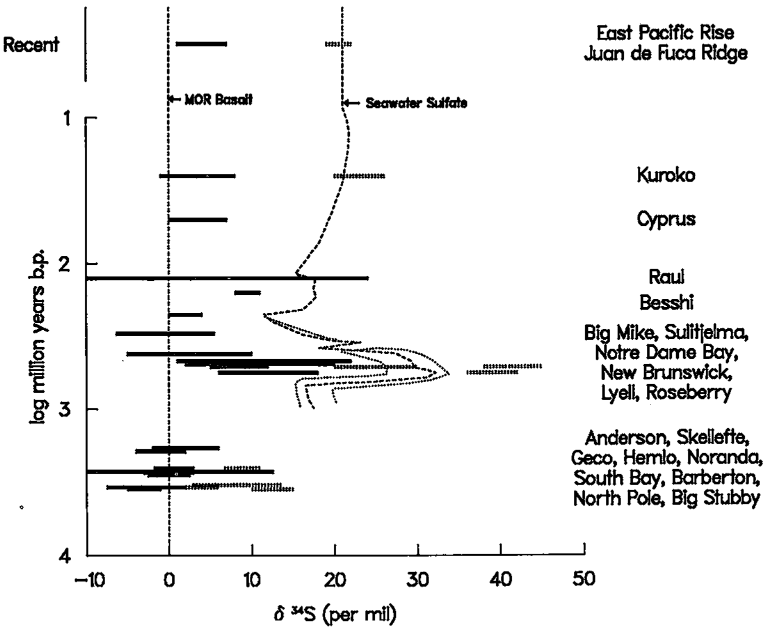

FIG. 12. Measured $\delta^{34}S$ ranges for selected massive sulfide ore deposits (Franklin *et al.* 1981, Rye *et al.* 1984, Cameron & Hattori 1987) and sulfide and sulfate mineral samples from 21°N, EPR and Juan de Fuca active hot springs (Shanks & Seyfried 1987, Woodruff & Shanks 1988, Kerridge *et al.* 1983). Sulfide and sulfate composition ranges are shown as solid and dashed lines, respectively. Seawater sulfur isotopic evolution curve after Claypool *et al.*(1980). $\delta^{34}S$ values of massive sulfide deposits tend to track contemporaneous seawater–sulfate value, averaging about 17 per mil less than sulfate $\delta^{34}S$, similar to the modern deposits. Ancient massive sulfide deposits generally have larger $\delta^{34}S$ ranges than the modern deposits; the larger ranges are only partly attributable to reactions associated with seafloor venting.

in seawater sulfate and massive sulfide $\delta^{34}S$ compositions (Sangster 1968) (Fig. 12) must be due to variations in source-rock composition and/or deep reduction of seawater sulfate by processes which are *not* occurring in sampled mid-ocean ridge sytems, because processes near the seafloor do not have the potential to reduce the quantities of sulfate necessary.

CONCLUSIONS

Examination of chemical reactions and coupled sulfur isotopic distribution using the results of EQ6/EQPS pathway computations provides significant insight into the processes and compositions of materials at active seafloor hydrothermal vent sites. The computations allow examination of systems which simultaneously change in chemical composition, temperature and bulk $\delta^{34}S$. In addition, reaction pathways that include isotopic or chemical disequilibium and closed or open systems can be compared.

Simple adiabatic mixing models, using 350°C end-member solution compositions from 21°N, EPR, and ambient seawater, produce mineral assemblages similar to those observed in seafloor chimney deposits (Figs. 5, 6). Adiabatic mixing reactions produce $\delta^{34}S$ values similar to the range generally observed in chimneys (1.5–4.5 per mil) only if a full range of equilibrium and disequilibrium paths occurs (Figs. 5, 6). Increases of 4.5 per mil in $\delta^{34}S$ values require chemical equilibrium with respect to sulfate reduction, open isotopic systems, and sulfur isotopic disequilibrium (no exchange between sulfate and sulfide components) for the batch sulfate-reduction process.

Bornite–chalcocite–covellite replacements of chalcopyrite–isocubanite that are ^{34}S-enriched to $\delta^{34}S$ values of 5.2–6.2 per mil cannot form by simple adiabatic mixing processes. Such $\delta^{34}S$ values require reduction of seawater sulfate, and selective concentration of the derived sulfide. This can be modeled by reaction of chalcopyrite with seawater and hydrothermal solution in thin-walled chimneys where conductive heating creates fluid composition and temperature characteristics such that magnetite is stable and pyrite is not. Observed sulfur isotope distributions are modeled reasonably by reaction of chalcopyrite during conductively heated fluid mixing to form bornite and minor magnetite (reaction 3).

Sulfide $\delta^{34}S$ values above 4.5 per mil in solution samples from both Juan de Fuca Ridge and 21°N *cannot* have formed by mixing reactions under any combination of constraints. The hydrothermal solutions do not have the reducing capacity to cause enough sulfate reduction to produce sulfide $\delta^{34}S$ values higher than 4.5 per mil. Similarly, reaction with previously deposited chimney minerals contributes little additional reducing capacity. Incipient reaction in feeder-zone basalts immediately underlying seafloor deposits, which produces a stockwork alteration zone, is required to account for the observed ^{34}S-enriched sulfide in solution. Reaction pathways based on consumption of the fayalite component of olivine from the basalt and seawater-derived sulfate (from subsurface mixing or previously deposited anhydrite) can produce $\delta^{34}S(H_2S)$ increases of 5 per mil and greater. All measured $\delta^{34}S(H_2S)$ values from 21°N and Juan de Fuca Ridge vent fluids are bounded by the presence or absence of secondary magnetite in the model reaction. The fact that feeder-zone basalt alteration is required to account for some sulfur isotope values of vent fluids and sulfide minerals in chimneys should be considered in any assessment of spatial and temporal variations of vent-fluid chemistry.

Mass-balance considerations indicate that stockwork alteration will have relatively little effect on the bulk $\delta^{34}S$ composition of large massive sulfide ore deposits. Models of hydrothermal solution reaction with massive sulfides provide a mechanism for development of metal zoning within massive sulfide ore deposits which does not require that metal-bearing hydrothermal compositions vary substantially with time, consistent with experimental evidence (Seyfried 1987). Ranges of $\delta^{34}S$ values that the models produce are also consistent with ranges observed in ore deposits, especially if equilibrium isotopic fractionation during lower temperature replacement reactions are important.

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