

SULFUR AND BASE METAL TRANSPORT IN THE SALTON SEA GEOTHERMAL SYSTEMMichael A. McKibben¹, C. Stewart Eldridge², and Alan E. Williams¹¹Geothermal Resources Program, Institute of Geophysics and Planetary Physics, University of California, Riverside, California, 92521 USA²Geology Department, and Research School of Earth Sciences, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601, AustraliaABSTRACT

Sulfur isotope data demonstrate that H₂S in the SSGS brines is generated by partial hydrothermal reduction of SO₄²⁻ derived from dissolution of lacustrine sulfate minerals in the host sediments. No magmatic input of sulfur is indicated. SO₄²⁻ reduction is promoted by interaction of the sediments with an upwelling diapir of Fe²⁺-rich hypersaline brine. Base metals are carried in the brines as the chloride complexes PbCl₃⁻, ZnCl₂⁰, CdCl₂⁰, CuCl₃²⁻, and MnCl₂⁰. Fe is probably carried as both FeCl₃⁻ and FeCl₄⁻ complexes. Vein sulfide precipitation within the reservoir occurs during brine dilution and oxidation at an interface between the hypersaline brines and overlying, more oxidized lower-salinity fluids.

INTRODUCTION

The hypersaline reservoir brines of the SSGS are very deficient in sulfur relative to metals, so that the availability of reduced sulfur remains the major limitation on sulfide deposition in the reservoir (Skinner et al., 1967). In order to identify sulfur sources and more accurately model metal transport in the SSGS reservoir brines, we have conducted a systematic investigation of the sulfur isotopic variations in minerals and hydrothermal fluids from this active ore-forming geothermal system. These studies have been made possible by new drillcores provided by the Salton Sea Scientific Drilling Project (Elders and Sass, 1988). We have also determined the nature of the complexes transporting base metals in the brines, allowing more accurate calculation of metal sulfide solubilities in brines.

SULFUR ISOTOPE STUDIES

A few early $\delta^{34}\text{S}$ values of ≈ 0 permil for vein sulfides and pipe scales tentatively suggested a magmatic origin for the reduced sulfur in the brines (White, 1968). However, significant amounts of metamorphosed lacustrine evaporites, rich in CaSO₄, are now known to be present in the SSGS host rocks at 1–3 km depth (Herzig et al., 1988; McKibben et al., 1988a; Osborn et al., 1988). This occurrence adds another possible mechanism of generating reduced sulfur for ore genesis: hydrothermal reduction of evaporite-derived SO₄.

We have performed 46 conventional analyses and 219 SHRIMP (Eldridge et al., 1987) analyses of $\delta^{34}\text{S}$ for sulfide and sulfate minerals in host rock sediments, veins, and

igneous rocks. Fourteen samples of aqueous H₂S and SO₄ were collected from flow-tests of 9 geothermal wells and analyzed for $\delta^{34}\text{S}$. The results and interpretation summarized here are being published in more detail elsewhere (McKibben and Eldridge, 1988).

Stratiform gypsum and anhydrite

Sulfate minerals in the deltaic-lacustrine host sediments range from disseminated stratabound crystals and nodules in mudstones to stratiform bedded accumulations of evaporitic gypsum and anhydrite (McKibben and Elders, 1985; McKibben et al., 1988b; Herzig et al., 1988). The $\delta^{34}\text{S}$ data lie chiefly between 0 and 20 permil with a mean for all sulfate analyses of 10 permil (Figure 1), compositions that are consistent with those found in lacustrine evaporites precipitated from sulfate derived from continental sources. Sulfate input into the Salton Basin has been dominated largely by Colorado River water, but punctuated by variable contributions from local streams and storm runoff from the mountain ranges surrounding the Salton Trough.

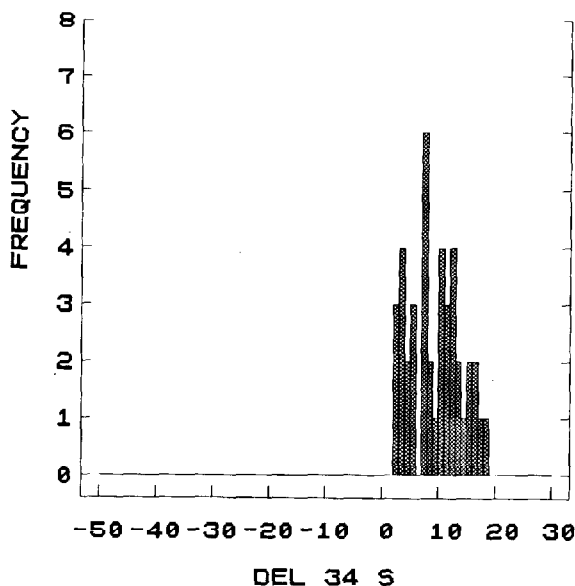


FIGURE 1. Histogram of $\delta^{34}\text{S}$ values for sedimentary anhydrite in the SSGS host sediments. Mean is 10 permil.

Pyrite in sediments

Pyrite typically occurs as framboids (5–50 μm), cubes (5–100 μm), and rarely as pyritohedrons (up to 0.1 mm) in stratiform diagenetic layers and lenses that may locally comprise up to a few volume percent of a sample of sediment (McKibben and Elders, 1985). In general these pyrites are isotopically light, ranging widely from –48 to 6 permil (Figure 2). The mean isotopic composition of pyrite in sediments (≈ -10 permil) indicates that the kinetic fractionation effect for the biogenic reduction of SO_4 in the lacustrine sediments was generally around 20 permil (k_1/k_2 of Ohmoto and Rye (1979) = 1.020).

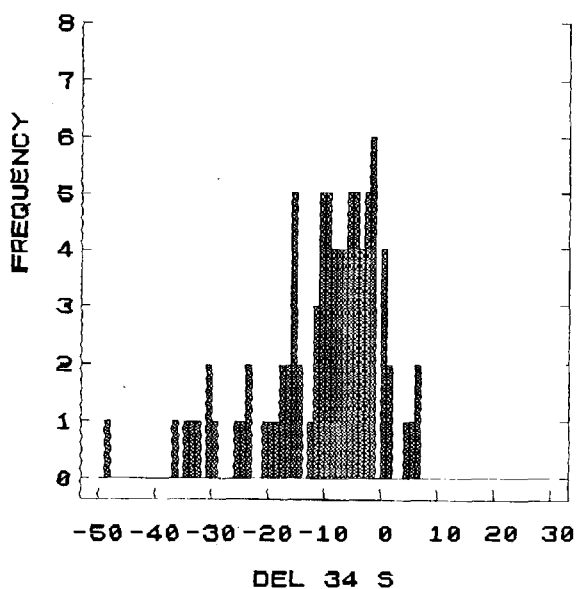


FIGURE 2. Histogram of $\delta^{34}\text{S}$ values for sedimentary pyrite in the SSGS host sediments. Mean is –10 permil.

Sedimentary anhydrite–pyrite isotopic fractionation

The apparent sulfur isotopic fractionation between intergrown sedimentary anhydrite and pyrite can be quite variable (Figure 3). The comparison of measured Δ values with those expected at equilibrium illustrates that there has been no consistent movement toward equilibrium isotope partitioning between sulfate and sulfide in the Pleistocene and younger sediments at temperatures up to 350°C, implying that the isotopic compositions of stratiform sulfate and sulfide still reflect those of the initial shallow lacustrine depositional environment.

Pyrite in igneous rocks

An altered diabase sill and its lower contact zone were cored at a depth of 2.9 km in the well S2–14 (Elders, 1987; Herzig and Elders, 1988). Brecciated metasediments and stringers of diabase within the contact zone contain abundant secondary pyrite crystals. The pyrite in the diabase stringers replaces plagioclase phenocrysts and groundmass. Pyrite is also found as coarse-grained cubes in hydrothermal veins that clearly cut and post-date the main mass of the diabase sill. The $\delta^{34}\text{S}$ values of all of these pyrites (–7 to 2 permil) fall entirely within the range

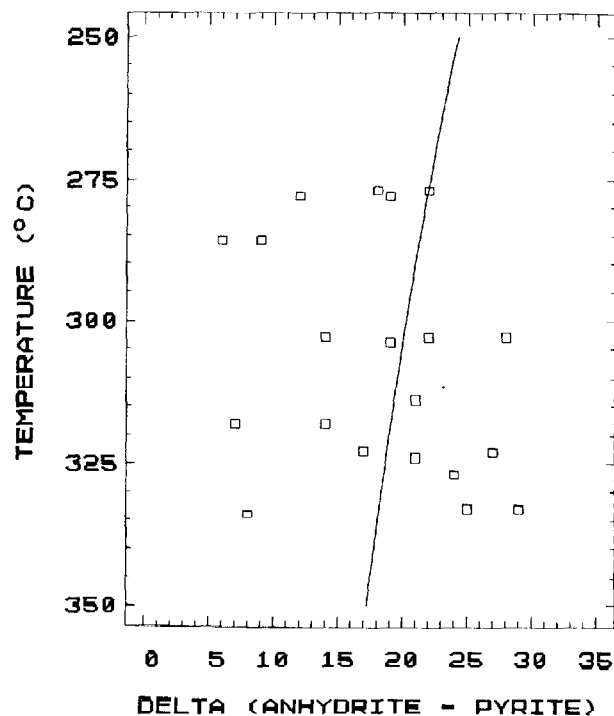


FIGURE 3. Plot of S isotopic fractionation between intergrown sedimentary anhydrite and pyrite (Δ) versus measured downhole temperature. Curve is for equilibrium $\text{SO}_4\text{--H}_2\text{S}$ fractionation from Ohmoto and Lasaga (1982).

noted for the vein mineralization (see below), indicating that the sill is overprinted by later hydrothermal events.

Vein sulfides

Vein mineralization in the SSGS is most abundant in the depth interval 2000–5000 ft (610–1524 m) (McKibben et al., 1988a). With the exception of one vein, vein sulfides have a fairly limited range of sulfur isotopic compositions from –9 to 9 permil, with a mean of ≈ 0 permil (Figure 4). Variation in the $\delta^{34}\text{S}$ values of the vein sulfides probably reflects some variability in the source of sulfide, the redox state of the brine, or possibly the metal/sulfide ratio of the fluid.

In those samples containing both hydrothermal and sedimentary pyrite, the hydrothermal pyrite does not have isotopic values shifted significantly toward the very light sedimentary compositions. Therefore, the sulfur-poor, metal-rich brines are not deriving reduced sulfur from leaching of sedimentary sulfides in the host rocks.

Fluid precipitates and pipe scales

There are two types of SSGS fluids, recognizable by their differing salinities and chemistries, which appear to be density-stratified (McKibben et al., 1987, 1988a; Williams and McKibben, 1988). They are referred to as the deep hypersaline brines, which have measurable amounts of both H_2S (10–15 ppm) and SO_4 (5–120 ppm), and the shallow lower-salinity geothermal fluids, which do not generally contain measurable amounts of H_2S and often have high SO_4 contents (500–2000 ppm). The

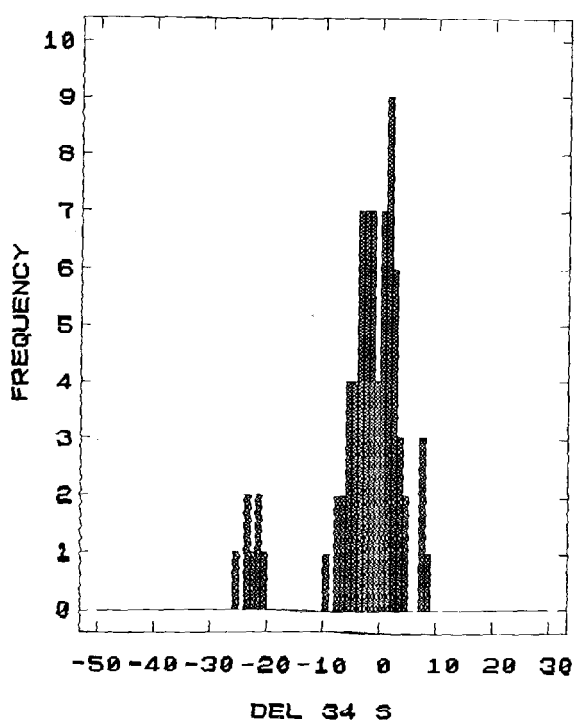


FIGURE 4. Histogram of $\delta^{34}\text{S}$ values for veins sulfides in the SSGS. Mean of the main population is 0 permil.

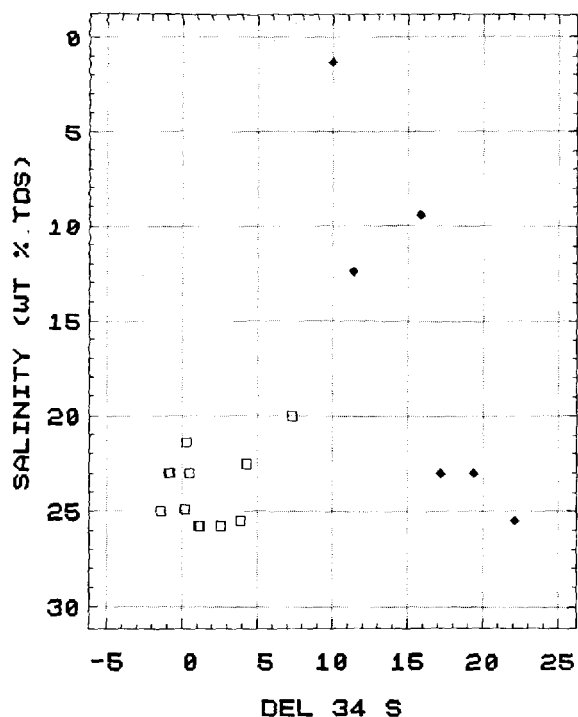


FIGURE 5. Plot of $\delta^{34}\text{S}$ values for aqueous SO_4^{2-} (solid diamonds) and aqueous H_2S (open squares) versus flash-corrected salinity for SSGS reservoir fluids.

subhorizontal interface between the two fluid types generally coincides with the domal shape of the 250°C isotherm in the SSGS (Williams and McKibben, 1988), which varies in depth from 2000–5000 ft (606–1515 m) across the geothermal field. Figure 5 shows $\delta^{34}\text{S}$ values of H_2S and SO_4 samples from these fluids plotted versus reservoir fluid salinity.

The total range (6–22 permil) in $\delta^{34}\text{S}$ values for aqueous SO_4 is significantly greater than that found for H_2S (–1.4 to 7.3 permil). The highest values for SO_4^{2-} (17–22 permil) are from the deep hypersaline brines (>20 wt % TDS) and the lower values for SO_4^{2-} (9–16 permil) are from shallow lower-salinity fluids (<10 wt % TDS) or from well-bore mixtures of low-salinity and hypersaline fluids produced from multiple flow-zones over large uncased intervals in wells (Williams and McKibben, 1988). The $\delta^{34}\text{S}$ values of SO_4 generally appear to increase with increasing salinity (and temperature) as the fluid interface is approached and crossed (Figure 5).

Comparison of the isotopic compositions of aqueous SO_4 and sedimentary anhydrite (Figures 5 and 1) shows that the maximum $\delta^{34}\text{S}$ value of the SO_4 from the deep hypersaline brines exceeds that of any anhydrite found by 3 permil and is enriched in ^{34}S relative to the mean anhydrite value (10 permil) by 12 permil.

Paired samples of fluid H_2S and SO_4 were collected from hypersaline flow-zones in three wells:

Well	Sample	Salinity	Temp	$\delta^{34}\text{S}$	Δ
1	steam H_2S	25.5 wt %	310°C	3.9 ‰	18.2
	fluid SO_4	25.5	310	22.1	
2	steam H_2S	23.0	299	–0.9	18.1
	fluid SO_4	23.0	299	17.2	
3	steam H_2S	23.0	300	0.5	19.5
	steam H_2S	23.0	300	–0.8	
	fluid SO_4	23.0	300	19.4	

The reservoir temperatures of all three brines fell within 300–310°C and differences in isotopic composition between reduced and oxidized sulfur species was remarkably consistent at 18–20 permil.

The observed sulfur isotopic fractionation between aqueous H_2S and SO_4 in the deep hypersaline brines agrees very well with the experimentally determined equilibrium fractionation (19–20 permil, Ohmoto and Lasaga, 1982) for dilute solutions. Therefore, the equilibrium sulfur isotopic fractionation between reduced and oxidized aqueous sulfur species is not strongly affected by the very high salinities of these brines at this temperature. It is not surprising that equilibrium has been attained, as the residence times for brines in the SSGS appear to be 10^2 to 10^3 years (Zukin et al., 1987) whereas only 140 days would be required to establish equilibrium for Salton Sea reservoir brine conditions (McKibben and Elders, 1985; Ohmoto and Lasaga, 1982).

Sources of aqueous sulfate and sulfide

The similarity between the mean $\delta^{34}\text{S}$ values of SO_4 in low-salinity geothermal fluids and sedimentary gypsum and anhydrite (≈ 10 permil) is consistent with the notion that SO_4 in these shallow fluids is derived directly from

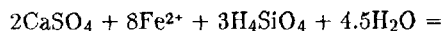
dissolution of sedimentary sulfate. However, the contrast between $\delta^{34}\text{S}$ values for sedimentary sulfates and SO_4 in the deep hypersaline brines (≈ 20 permil) suggests that simple dissolution of stratiform anhydrite is not likely to be the sole process influencing the isotopic composition of aqueous SO_4 in the deep brines. The ^{34}S enrichment of aqueous SO_4 in the deep hypersaline brines must reflect high temperature partial reduction of SO_4 dissolved from stratiform anhydrite in the deeper parts of the hydrothermal system.

This hypothesis can be evaluated using the mass balance (Ohmoto, 1986):

$$\delta^{34}\text{S}_{\Sigma\text{S}} = \delta^{34}\text{S}_{\text{H}_2\text{S}} + \Delta_{\text{SO}_4-\text{H}_2\text{S}} (R/(1+R))$$

where R is the mole ratio of sulfate and sulfide in solution. For conditions of 300°C applicable to the SSGS reservoir brines, the resulting values of $\delta^{34}\text{S}_{\Sigma\text{S}}$ average 10 permil, in perfect agreement with the mean $\delta^{34}\text{S}$ value for sedimentary anhydrite in the host sediments. SO_4 derived from dissolution of anhydrite in the reservoir rocks (≈ 10 permil) therefore could have undergone $\approx 50\%$ reduction to yield H_2S (≈ 0 permil) and ^{34}S -enriched SO_4 (≈ 20 permil) in the deep hypersaline brines.

The deep hypersaline reservoir brines are rich in Fe and Mn (1000–2000 ppm each) and have high $\text{Fe}/\text{Zn}+\text{Pb}$ and $\text{H}_2\text{S}/\text{SO}_4$ ratios relative to the overlying less saline fluids, implying that these deep brines have a relatively reduced oxidation state (McKibben et al., 1987; Williams and McKibben, 1988). Therefore, interaction of these reduced thermally-upwelling brines with the reservoir of evaporitic SO_4 in the host sediments could promote reduction and H_2S generation. Replacement of sedimentary anhydrite by epidote and amphibole has been observed in the SSGS (Osborn et al., 1988), implying that reactions of the type:



may be responsible for partial hydrothermal SO_4 reduction to generate H_2S . Such a reaction is consistent with the epidote-hematite paragenesis of veins (McKibben et al., 1988a).

In addition to variations caused by different degrees of SO_4 reduction, fluctuations in the isotopic composition of aqueous H_2S and hence of vein sulfides (i.e., 0 ± 9 permil) could conceivably have been generated by several processes. Partial reduction of anhydrite sulfate along with dissolution of some intergrown diagenetic sulfide could result in a fluid with $\delta^{34}\text{S}$ values less than 0 permil. Fluid H_2S isotopic compositions could also be made either more positive or negative during vein sulfide precipitation if the fluid contained more metals than sulfur. Precipitation of sulfides could then significantly reduce the H_2S content of the fluid, making it isotopically lighter if pyrite were precipitated or isotopically heavier if galena were precipitated (Ohmoto, 1986). Local reduction of aqueous SO_4^{2-} or partial oxidation of H_2S to sulfanes at the site of deposition (fluid interface) could also produce the observed $\delta^{34}\text{S}$ variations in vein sulfides.

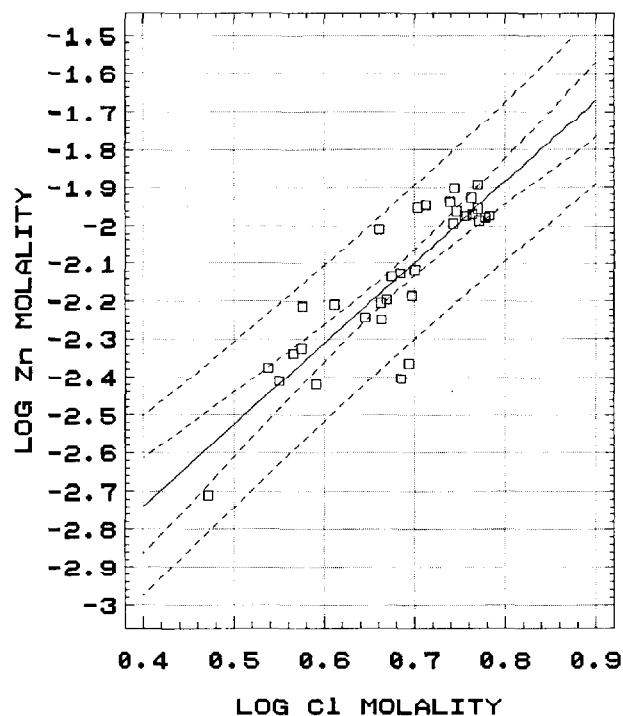
FIGURE 6. Regression of log total Zn molality versus log total Cl molality for SSGS hypersaline brines ($\approx 300^\circ\text{C}$). Slope is 2.1, indicating that ZnCl_2^0 complex is dominant.

METAL TRANSPORT

Few experimental data exist to evaluate the speciation and thermodynamics of metal chloride complexes in saline fluids at elevated temperatures appropriate for the SSGS. Therefore, it is necessary to determine such information empirically. Our database from the Salton Sea geothermal system includes a series of 44 nearly isothermal ($\approx 300^\circ\text{C}$) Na–Ca–K–Cl brine analyses covering a range of total chloride concentrations from 3–6 molal (Williams and McKibben, 1988). In such brines only 4–9 water molecules exist per ion, and the low dielectric constant of water further reduces the degree of ionization. Consequently, the predominant metal chloride species in these brines should be neutral or high ligand number chloride complexes.

Published thermodynamic data on alkali chloride solutions indicate that activity coefficients remain relatively constant at high salinities at elevated temperatures. Therefore, isothermal plots of log total metal molality versus log total chloride molality will yield slopes corresponding to the mean ligand number of the metal chloride complexes, assuming that a single mineral controls a given metal's solubility and that pH and mH_2S remain relatively constant over the salinity range.

From such plots we have determined the mean ligand numbers for several metal chloride complexes in the Salton Sea brines (McKibben and Williams, 1988). For Zn, our data yield a mean ligand number of 2.1 (Figure 6), in excellent agreement with the lower-salinity experimental data of Ruaya & Seward (1986) and Bourcier & Barnes (1987). Similar determinations for all base metals indicate that the dominant chloride complexes are: PbCl_3^- , ZnCl_2^0 , CdCl_2^0 , CuCl_3^{2-} , and MnCl_2^0 . Fe data are complicated by the presence of both Fe^{2+} and Fe^{3+} in the brines, yielding a mean ligand number of 4.4. This implies that Fe is carried by mixtures of FeCl_3^- and FeCl_4^- complexes.



These empirical speciation data allow more accurate calculation of metal sulfide solubilities in the SSGS brines, with obvious applications to scaling problems.

Vein mineral precipitation mechanisms

Sulfide vein mineralization is most concentrated at depths of 2000–5000 ft (610–1524 m) which happens to be the interval occupied by the interface between an upwelling hypersaline brine diapir and overlying lower-salinity fluids (McKibben et al., 1987, 1988a; Williams and McKibben, 1988). This interval is also a zone of abundance of evaporitic sulfate occurrences (Figure 1). Coincidence of the brine interface and abundance of vein mineralization suggests that the main mechanism involved in ore mineral precipitation is simple cooling and dilution of the H₂S- and metal-bearing hypersaline brine. H₂S, derived chiefly from partial reduction of sedimentary anhydrite at depth, could rise with the hot brines and be precipitated as sulfides during destabilization of metal chloride complexes at the fluid interface. This process could also be enhanced through partial reduction of sulfate contained in the shallow low-salinity fluids, due to interaction with Fe²⁺ in the reduced hypersaline brines. Precipitation by partial oxidation of H₂S to sulfanes (S₂²⁻ in pyrite, S₃²⁻ in chalcopyrite) at the fluid interface could also account for some of the ⁶³⁴S variations of the vein sulfides.

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