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Sulphur isotopic variations in nature

11. Sulphur isotope ratios of sulphides from the Broadlands geothermal field, New Zealand

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Sulphide minerals separated from cores in the Broadlands geothermal field normally appear, from textural evidence, to be in chemical equilibrium with one another, other hydrothermal minerals, and the geothermal fluids at temperatures between 160 and 285°c. In Bore 16, average sulphur isotopic ratios ($\delta^{34}S$ values Cañon Diablo Troilite) are: pyrite $+5.2‰$, sphalerite $+4.6‰$ and galena $+2.7‰$, compared to equivalent values of $3.9‰$, $3.7‰$ and $1.4‰$ from Bore 7. The slightly more negative values in sulphides from Bore 7 may result from the different fluid composition and greater permeability. Isotope temperatures derived from the sulphide pairs are, with two exceptions, higher than (including error limits) the measured borehole temperatures, probably indicating incomplete attainment of isotopic equilibrium. Only at temperatures above 260°c do 2 sphalerite–galena pairs show good agreement with measured temperatures. Isotopic exchange between pyrite, pyrrhotite, sphalerite, and the solution appears to be slow, whereas galena exchange is fast. Although the $\delta^{34}S$ values are within the range of those for magmatic sulphur, the origin of the sulphur may be sulphate leached from the basement rocks and partly reduced to H_2S.

INTRODUCTION

Within the Broadlands geothermal field, Taupo Volcanic Zone, New Zealand, small quantities of sphalerite, galena, and chalcopyrite have been found in cores and cuttings from 6 drillholes at depths where temperatures vary from 120 to 298°c (Browne 1969, 1971). The host rocks are Quaternary–Recent silicic lavas, tuffs, ignimbrites, volcanic sediments, and underlying Mesozoic greywackes and argillites. Other hydrothermal minerals associated with the sulphides include quartz, K-feldspar, albite, K-mica, chlorite, and calcite. Textural evidence suggests that the sulphides and hydrothermal minerals in the base-metal zones are in equilibrium with one another and with the present-day deep hydrothermal fluids (Browne 1971). However, galena and sphalerite from 302–323 m in Bore 16 show pitting and evidence of corrosion by hydrothermal fluids; this depth is thought (Browne 1971) to be a zone where thermal fluids mix with river water.

The importance of these and other sulphide occurrences associated with geothermal activity (Skinner et al. 1967; Degens & Ross 1969) lies in their similarity to some ore deposits (e.g. Robinson 1974). Current research has concentrated on determining temperatures of ore formation and the nature of ore-forming fluids (Groves et al. 1970; Robinson & Ohmoto 1973). In particular, sulphur isotope geothermometry, as discussed in the next section, and fluid inclusion studies have been responsible for many major findings. Active geothermal fields, where temperatures can be measured, provide an opportunity to test such geothermometric methods. This paper reports such a study on the sulphur isotope

geothermometry of coeval base-metal sulphides from the Broadlands geothermal field. Although limited by availability of sample material, we believe this is the first report on the isotopic composition of base-metal sulphides in cores from an active hydrothermal area.

Sulphur Isotope Thermometry

For the isotope exchange reaction:

$$Pb^{34}S + Zn^{32}S = Pb^{32}S + Zn^{34}S \tag{1}$$
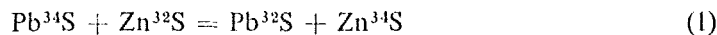
with equilibrium constant K, theory predicts that $\ln K$ varies in proportion to $1/T$ at low temperatures and to $1/T^2$ at high temperatures, and approaches zero at very high temperatures (Urey 1947). Calculations of the partition function ratios to determine equilibrium constants between metallic sulphides at high temperatures have been made by Sakai (1968) and Hulston & Elcombe (personal communication).

The relative enrichment of one isotope in A with respect to B is given by the enrichment factor, ϵ, where:

$$\epsilon_{AB} = \alpha - 1 \text{ or } \Delta_{AB} = 1000 (\alpha - 1) \tag{2}$$

and α is the fractionation factor. In δ terminology* it can be shown that:

$$1000 (\alpha - 1) = (\delta_A - \delta_B)/(1 + \delta_B/1000) \tag{3}$$

Hence:

$$\Delta_{AB} \approx \delta_A - \delta_B \tag{4}$$

Fractionation factors obtained from theoretical calculations are usually expressed in the form of $1000 \ln \alpha$ which can be expanded to the following approximation:

$$1000 \ln \alpha \approx \delta_A - \delta_B \tag{5}$$

For simple isotope exchange reactions such as (1), $\alpha = K$ when isotopic equilibrium is attained.

In addition to theoretical calculations, equilibrium constants for sulphide exchange reactions have been experimentally determined at high temperatures by many workers (reviewed by Czamanske & Rye 1974). The most extensive work is by Kajiwara & Krouse (1971), who studied different sulphide systems by exchanging sulphur vapour. On the other hand, Czamanske & Rye (1974) determined equilibrium constants for the sphalerite–galena system by hydrothermal transport and precipitation of the sulphides. However, agreement between these calibration curves is not good. Theoretical calculations and the curve of Kajiwara & Krouse (1971) give larger fractionation factors than the curve of Czamanske & Rye (1974). The magnitude of sulphur isotope fractionation appears to depend on the bond strength of the particular sulphide (Bachinski 1969). At equilibrium, sulphides display the following $\delta^{34}S$ trend: pyrite > pyrrhotite $\geqslant$ sphalerite > chalcopyrite > galena.

Experimental Techniques and Results

Drillhole temperatures were measured after well completion by an electric geothermometer which is accurate to $\pm 2°c$. Measured temperatures may differ from pre-drilling and

*The isotopic composition of a sample (*i*) and the differences between samples are reported in parts per thousand deviation from a standard (*s*):

$$\delta_i(‰) = [(R_i - R_s)/R_s]10^3$$

where R is the ratio of the heavy to light isotope.

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Table 1—Sulphur

	Measu	
	Depth (m)	Py
Bore 16	302–323	4.9
	815	5.5
	1053	5.1
	1354	
Bore 15	1842	
Bore 7	845	3.9

*The $\delta^{34}S$ values have an e
Py, pyrite; Sl, sphalerite; G
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mineral deposition temperatures (Eslinger & Savin 1973), but below about 600 m, measured temperatures are probably closer to pre-drilling temperatures because of higher formation permeability.

The sulphide phases were separated by hand from the lightly crushed cores. Galena and sphalerite samples were acid-evolved to silver sulphide (Rafter 1957b), which together with pyrite and pyrrhotite, was burnt in a stream of pure tank O_2 at 1100°c to give SO_2 (Rafter 1957a). Analyses of this gas were performed using the mass spectrometric techniques described by Hulston & Shilton (1958). Mixing and memory effects of the mass spectrometer were negligible, and since differences in $\delta^{34}S$ values are used for temperature determinations no further corrections need be considered. All the analyses are given with respect to the Cañon Diablo Troilite (CDT) standard (Jensen & Nakai 1963) and have a reproducibility of $\pm 0.2\%_0$ or better. Where sufficient material was available the samples were run in duplicate (Table 1). Sphalerite and galena from Bore 7, 845 m, were analysed by Czamanske & Rye (1974) who obtained the same $\delta^{34}S$ difference as this study.

Results of the analyses are shown in Table 1 together with apparent temperatures for pyrite–galena, pyrite–pyrrhotite, pyrite–sphalerite and sphalerite–galena pairs, using the curves of Kajiwara & Krouse (1974) and for sphalerite–galena pairs using the curve of Czamanske & Rye (1974). Measured borehole temperatures are also given and it can be seen that there is good agreement between the isotope and measured temperatures only for the sphalerite–galena pairs (Bore 16, 1354 m, and Bore 7, 845 m). In spite of confirming the equilibrium $\delta^{34}S$ sequence, all other pairs give temperatures much higher than those measured.

TABLE 1—Sulphur isotope analyses and temperatures for Broadlands sulphide samples

		Measured $\delta^{34}S$ values (‰)*				Isotope Temperatures (°c)†					Measured borehole temperature (°c)
	Depth (m)	Py	Sl	Gn	Po	Py–Gn K&K	Py–Po K&K	Py–Sl K&K	Sl–Gn K&K	Sl–Gn C&R	
Bore 16	302–323	4.9	4.2‡	2.7‡		430		380	460	410	160
	815	5.5	4.8‡	2.8		370		380	360	320	216
	1053	5.1	4 3	2.6		390		340	410	370	254
	1354		5.0	2.7					320	280	267
Bore 15	1842				3.6						285
Bore 7	845	3.9	3.7	1.4	3.6	390	>500	>500	320	280	274

*The $\delta^{34}S$ values have an error of $\pm 0.2\%$ or better and are reported relative to Cañon Diablo Troilite. Py, pyrite; Sl, sphalerite; Gn, galena; Po, pyrrhotite.
†The isotope temperatures are determined from the differences in $\delta^{34}S$ values and the calibration curves of K&K (Kajiwara & Krouse 1971) and C&R (Czamanske & Rye 1974).
Total errors vary from about ± 50 to ± 100°c for the lower to the higher temperatures respectively.
‡Average of duplicate analyses.

DISCUSSION

Duration of activity

The life of the Broadlands geothermal system is thought to be of the order of ½ million years (Browne 1973) and it is therefore pertinent to consider temperature variations with time. This has been done by Browne *et al.* (1975), who measured the filling temperatures of two-phase primary fluid inclusions in quartz crystals associated with the sulphides. These are close to present-day borehole temperatures, indicating that there has been an extremely stable heat flow regime in the area, at least since the deposition of the hydrothermal minerals.

Isotope exchange kinetics

The rates of attainment of isotopic equilibrium within the sulphide minerals should be considered; they indicate the equilibrium $\delta^{34}S$ trend and thus must at least be approaching equilibrium $\delta^{34}S$ values. The reaction rates of sulphur isotope equilibrium between PbS and HS$^-$ and between ZnS and HS$^-$ have been reported (Kiyosu 1973) to be fast (half-life of the order of hours) in a concentrated NaHS solution at pH 10. Moderately fast reaction rates (half-life of the order of days) have been reported for the H_2S–HSO_4^- system (Robinson 1973) and between sulphides and sulphur vapour (Kajiwara & Krouse 1971), both at high fS_2 conditions. Thus the attainment of isotopic equilibrium is probably a function both of temperature and the activity of sulphur. Puchelt (1969) has further demonstrated that sulphur in galena equilibrates more rapidly with sulphur in another galena or with free sulphur than does sulphur in sphalerite, whereas that in pyrite is very difficult to exchange (Salomons 1971). Indicated temperatures below 100°c have been reported for galena–sphalerite pairs from a Mississippi Valley-type deposit (Pinkney & Rafter 1972) showing that low temperature equilibrium can be achieved. In the Wairakei geothermal system, Steiner & Rafter (1966) show that pyrite and anhydrite are not in isotopic equilibrium. Also sulphate and H_2S are out of chemical and isotopic equilibrium (Kusakabe 1974). An isotopic temperature of 350°c is indicated by the H_2S/HSO_4^- sulphur isotope fractionation, but the maximum measured temperature is 270°c. A similar approach to, but incomplete attainment of, isotopic equilibrium may also take place at Broadlands, affecting all but the high-temperature galena–sphalerite pairs. In Bore 16, equilibrium between galena and sphalerite seems only to be reached when the sphalerite $\delta^{34}S$ value is a maximum, the galena $\delta^{34}S$ values remaining nearly constant. Thus these sulphides do indeed appear to have different exchange rates. The composition of the deep Broadlands waters are: 3000 ppm salinity, pH 6.0 (at 260°c) and total sulphur $= 4 \times 10^{-3}$M (Browne & Ellis 1970). Under these conditions, the isotopic equilibrium rates with the solution appear to be galena > sphalerite > pyrite.

Conditions of sulphide deposition in Bores 7 and 16

The $\delta^{34}S$ values of the sulphides in Bore 7 are lower, by about 1‰, than values in Bore 16. Bore 7 discharges 33000 kg/h water, 10400 kg/h steam and 2200 kg/h gas (mainly CO_2) at 10.2 bars pressure and this is mainly drawn from a fracture zone between 700 m and 900 m (Dench 1968). Boiling occurs at this depth and causes deposition of calcite, quartz, and adularia from CO_2 loss and a consequent pH increase (Browne & Ellis 1970). The base-metal sulphides in this bore, therefore, occur in a zone known to have good permeability, and this may help in attaining a more rapid isotopic equilibrium. This contrasts with Bore 16 where permeability is much less and the subsurface fluids have a more restricted circulation. Quartz crystals from several Broadlands bores (including Bores 7 and 24) contain both vapour-dominant and liquid-dominant fluid inclusions trapped from boiling solutions (Browne *et al.* 1975). Eslinger & Savin (1973) determined the oxygen isotope composition of quartz, illite and whole rocks of cores from Bore 16. Although they found oxygen isotopic equilibrium was attained between coexisting silicate phases where the clay mineralogy was simple, they also showed that the temperature inversion between about 400 m and 800 m (Browne 1971) in Bore 16 was probably a post-drilling feature and that the undisturbed temperature profile probably showed a regular increase with depth. However, the maximum difference between the oxygen isotope temperature and the measured bore temperature is only 80°c (at 616 m). The difference in chemistry between Bores 7 and 16 could account for the small differences in absolute $\delta^{34}S$ values (Ohmoto 1972).

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Sulphur source

In the Broadlands system, absolute $\delta^{34}S$ values and the small variations are similar to those observed for sulphides in the Wairakei geothermal system (Steiner & Rafter 1966) and the Tui Mine, Te Aroha (Robinson 1974). In these two situations the origin of the sulphur is thought to be Jurassic sea-water sulphate leached from the Mesozoic basement rocks and partly reduced to H_2S (Kusakabe 1974; Robinson 1974). Although the $\delta^{34}S$ values are close to those for sulphur of magmatic origin ($\delta^{34}S \approx 0\permil$), a similar sea-water sulphate origin for the Broadlands system is possible. Inorganic reduction of sulphate by hydrogen in hydrothermal condition has been suggested by Malinin & Khitarov (1969). Because of temporary closure of the Broadlands bores it has not yet been possible to sample sulphur species from the waters; this will be attempted later.

CONCLUSIONS

For the chemical conditions of the Broadlands fluids the attainment of isotopic equilibrium between sulphides appears to be slow. Only 2 galena–sphalerite pairs give isotopic temperatures close to the measured temperatures. The limiting step appears to be the attainment of sphalerite–solution equilibrium above about 260°C. The calibration curve of Czamanske & Rye (1974) for the sphalerite–galena pair may be applicable to natural hydrothermal systems when the temperature and sulphur activity are sufficiently high to promote rapid isotope exchange. Small inter-bore variations of absolute $\delta^{34}S$ values may result from slight differences in solution chemistry possibly resulting from different permeabilities. It is suggested that the source of the sulphur in the system is sulphate leached from underlying rocks and partly reduced to H_2S.

ACKNOWLEDGMENTS

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