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SULFUR ISOTOPE MINERALOGY OF SULFIDES

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ABSTRACT

Sulfur from the troilite phase in meteorites exhibits a remarkably uniform S^{32}/S^{34} composition of 22.21 ± 0.02, which value is taken as a reference standard for δS^{34} measurements. Primordial sulfur is identical to or at least very near this composition; nevertheless, sulfide minerals, even juxtaposed sulfides of the same species, are known to vary by more than 5% from this value, although no evidence has yet been found to indicate that specific sulfide species are characterized by specific isotopic compositions, even though sulfates are generally enriched in S^{34}. Information, therefore, on the processes by which this isotopic fractionation occurs is of assistance in determining the genesis of the sulfur in sulfide minerals.

For example, a large δS^{34} variation for sulfides in one deposit is indicative of a biogenic rather than a magmatic hydrothermal origin for the sulfur in the sulfides. Biogenic sulfur is derived from hydrogen sulfide gas evolved from anaerobic bacteria of the *Desulfovibrio* genus. Sulfides in concretions, "red beds" copper deposits, and sandstone-type uranium deposits exhibit broad δS^{34} variations, suggesting that they contain sulfur derived almost entirely from this biogenic process. The sulfur in magmatic hydrothermal sulfides, on the other hand, is quite uniform in its δS^{34} composition. It is suggested that the reason for such is that as magmatic hydrothermal solutions become more and more concentrated in a cupola zone during progressive crystallization of their host or parent magma, the solutions become well mixed, resulting in a homogenization of what isotopic variations there may have been.

Further δS^{34} studies corroborate the inference that one mechanism of sulfide replacement and exsolution is by diffusion of the smaller cations through the framework of the larger sulfur anions because the replacing sulfide exhibits the same original isotopic composition of the replaced sulfide. Even supergene sulfides form by this same mechanism of replacement, as indicated by δS^{34} analyses plus the additional realization that sulfates are reduced to sulfides only at temperatures of several hundred degrees C. in the presence of an effective reducing agent such as carbon. Enrichment of S^{34} (a common feature of sulfates) in sulfides, which has been noted for a few sulfide deposits, in correlation with geologic data, is rather suggestive of this source of sulfur.

Mass spectrometric measurements of the stable sulfur isotopic composition of sulfide minerals is an additional important mineralogical step in determining the composition and variation in composition of sulfide minerals.

THERMODYNAMIC STUDY OF PYRRHOTITE AND PYRITE

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ABSTRACT

Through the use of the electrum tarnish method (Barton and Toulmin, 1959; Toulmin and Barton, 1960) the following equation has been found to interrelate the composition of pyrrhotite, fugacity of sulfur, and temperature:

$$\log_{10} f_{S_2} = (70.03 - 85.83N)\left(\frac{1000}{T} - 1\right) + 39.301\sqrt{1 - 0.99808N} - 11.9113. \tag{1}$$

In this equation f_{S_2} is the fugacity of sulfur relative to the ideal diatomic gas at 1 atm, N is the mole fraction of FeS in pyrrhotite (in the system FeS-S_2), and T the absolute temperature. The experimental uncertainty in the equation is 0.002 in N. Substituting equation 1 into the Gibbs-Duhem equation and inte-

grating leads to the following expression for the activity of FeS (a_{FeS}) relative to the pure substance at the temperature of consideration:

$$\log_{10} a_{FeS} = 85.83 \left(\frac{1000}{T} - 1 \right) (1 - N + \ln N) + 39.301\sqrt{1 - 0.99808N} - 39.226 \tanh^{-1} \sqrt{1 - 0.99808N} - 0.0024. \qquad (2)$$

The electrum tarnish method has permitted us to determine the f_{S_2} *vs* T curve for the univariant assemblage pyrrhotite-pyrite-vapor from 743° to 325° C. (a considerably greater range than previously studied). The curve passes through the points indicated in the table below. Our determinations of the composition of pyrrhotite are in excellent agreement with the results of Arnold (1958). The activity of FeS in pyrite-saturated pyrrhotite is very different from unity (Table 1), a fact that greatly influences the interpretation of some other phase equilibrium studies involving pyrrhotite and their application to sulfide mineral assemblages, but has little effect on the more general calculations of composition of hydrothermal or magmatic fluids.

TABLE 1. POINTS ALONG THE SMOOTHED PYRITE-PYRRHOTITE CURVE

t° C.	N_{FeS}	$\log f_{S_2}$	a_{FeS}
743	0.8993	$+0.76$	0.375
599	0.9202	-2.00	0.455
514	0.9298	-4.00	0.496
410	0.9395	-7.00	0.536
354	0.9440	-9.00	0.554
325	0.9462	-10.17	0.564

Combining these data with the well-known standard free-energy of the reaction Fe $(\alpha)+\frac{1}{2}S_2(g, 1 \text{ atm}) = \text{FeS}$ (pyrrhotite), we calculate the standard free energy of formation of pyrite from the elements (Fe, S_2) at 1 atm:

$$\Delta G^\circ = -71{,}260 + 47.09\,T \text{ cal (T in degrees K)} \qquad (3)$$

The temperature coefficient of equation (3) is in excellent agreement with calorimetric data.