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SULFUR ISOTOPE GEOCHEMISTRY AND FRACTIONATION BETWEEN COEXISTING SULFIDE MINERALS

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Abstract

The study of sulfur isotope abundances in nature is rewarding because of the ubiquity of the element and the variety of chemical forms in which it is found. Theoretical calculations and laboratory investigations of sulfur isotope fractionation in chemical, microbiological and mineralogical systems lead to an understanding of the isotope distribution patterns in nature and give information regarding the modes of formation and subsequent histories of many kinds of sulfur bearing materials.

A broad distinction may be made between biogenic and primary sulfur. Biogenic sulfur is characterized by a wide range of isotope ratio values as a result of the variable fractionation introduced during the reduction of sulfate to sulfide by anaerobic bacteria, while primary sulfur tends to have a comparatively narrow range of isotope ratio values. The simple nature of these patterns may be altered either by homogenization of isotope ratios by metamorphic heating events or by contamination with sulfur from other sources.

There is considerable current interest in the comparison of the sulfur isotope ratios in coexisting sulfide minerals. The difference in isotope ratios between mineral types may represent equilibrium sulfur isotope effects or may be related to kinetic isotope effects during the emplacement of the minerals with later modification by metamorphic heating events. In either case such differences can be used as a geothermometer by utilizing the predictable and measurable temperature dependences of sulfur isotope exchange equilibria. The types of observational, theoretical and experimental studies performed to date are mentioned, as are some of the problems which remain to be solved in order to develop this method of geothermometry.

Introduction

Isotope geochemistry has as its basis the small differences in chemical behavior shown by the isotopes of an element. The concept of an isotope was introduced by Soddy (1910) and Fajans (1911) as a consequence of radioactivity in heavy elements and isotopes were considered to be element pairs which could not be separated chemically. For twenty years all attempts at chemical separation failed. It was the discovery of the isotopes of the light elements around 1930, particularly that of deuterium by Urey *et al.* (1932) that lead to success in this endeavour. Since then differences in the chemical properties of the isotopes of hydrogen, carbon, nitrogen, oxygen, sulfur, and other elements have been both calculated using the methods of statistical mechanics and measured experimentally. These differences can lead to significant isotope fractionation in chemical reactions, both in nature and in the laboratory, and are the cause of changes in the relative isotope abundances of these elements from sample to sample.

Since the war extensive studies have been made of natural isotope abundance variations and, together with theoretical and laboratory work, such studies have been used to help in the solution of a wide variety of geochemical problems. Sulfur isotope geochemistry has proved to be a particularly rewarding field because of the reasonably large percentage mass difference between the two principal isotopes, the variety of the chemical forms of sulfur and their widespread occurrence in such diverse materials as sea water, sedimentary rocks, petroleum, primary igneous rocks, volcanic gases and mineral deposits. Studies with sulfur isotopes have been concerned with such problems as the isotope fractionation in the biological sulfur cycle and in the sulfur bearing gases of volcanoes, the isotopic composition of present day and ancient oceans, the possible origins of oil and the modes of formation and post depositional histories of sulfide mineral deposits.

Sulfur has four stable isotopes ($^{32,\,33,\,34,\,36}S$) whose percentage abundances are approximately 95.0, 0.75, 4.20 and 0.017 respectively. Isotope abundance variations are generally considered in terms of the abundance ratio, $^{34}S/^{32}S$, of the two principal isotopes, although for special purposes, such as the measurement of cosmic ray effects in meteorites, use may be made of variations of both $^{33}S/^{32}S$ and $^{36}S/^{32}S$ ratios (Hulston and Thode, 1965). The range of variation of $^{34}S/^{32}S$ in nature is approximately 10% and when referring to differences of isotope abundance ratios between samples it is common practice to use the "del" notation where

$$\delta^{34}S = \left(\frac{(^{34}S/^{32}S)\text{sample}}{(^{34}S/^{32}S)\text{standard}} - 1\right)$$

$(\delta^{34}S) \times 1000$, therefore, gives the permil difference in isotope ratio between a sample and a standard.

The generally accepted standard is the $^{34}S/^{32}S$ ratio of troilite from the Canyon Diablo meteorite. There are several reasons for expressing sulfur isotope ratios in this manner. First, the mass spectrometric techniques used for sulfur isotope abundance measurements make the determination of differences of $^{34}S/^{32}S$ between samples much more precise than the determination of the absolute value of $^{34}S/^{32}S$ for either sample. Using a few mg of sulfur as sulfur dioxide or sulfur hexafluoride it is possible to compare samples with a precision of the order of 0.1 $^0/_{00}$. Second, the use of troilite from Canyon Diablo as a standard makes the interlaboratory comparison of results much easier than if a number of personal standards are used. Finally, the ratio $^{34}S/^{32}S$ is remarkably uniform in meteorites (Macnamara and Thode, 1950; Vinogradov, 1958; Thode *et al.*, 1961; Kaplan and Hulston, 1965) and there is a considerable body of evidence to suggest that the primordial, or initial, terrestrial value of $^{34}S/^{32}S$ is the same as that of Canyon Diablo troilite. Thus this value represents a logical base level from which to measure fractionation effects in nature.

Isotope geochemistry then involves observations of sulfur isotope distribution patterns in nature, theoretical calculations of equilibrium and kinetic isotope effects and laboratory measurements of isotope effects in chemical, biological, and mineralogical processes. All these studies are important in the interpretation of natural isotope distribution patterns and in the solution of geochemical problems. This paper deals briefly with these various aspects of sulfur isotope geochemistry and discusses specifically recent work with coexisting sulfide minerals.

THE THEORY OF ISOTOPE EFFECTS

Predictions of the differences in behaviour of isotopic substances are made in two ways. For systems in equilibrium the calculations involve the properties of the equilibrating substances but do not depend on the particular pathways or mechanisms involved in the achievement of equilibrium. For systems undergoing change, as in unidirectional chemical reactions, the situation is somewhat more complicated and attention must be paid to the reaction mechanism and possible intermediates involved in the formation of the final product material.

Equilibrium isotope effects. Equilibrium constants for isotope exchange reactions may be calculated in terms of the characteristic vibrational frequencies of the various isotopic species. A typical isotope exchange reaction may be written

$$A_1 + B_2 \leftrightarrows A_2 + B_1$$

where the subscripts 1 and 2 indicate that the molecules A and B with one element as a common constituent contain only the light and heavy isotope respectively of that element.

Using statistical mechanics the isotope equilibrium constant may be expressed in terms of the partition functions, Q, of the equilibrating species:

$$K = \frac{Q(A_2)}{Q(A_1)} \bigg/ \frac{Q(B_2)}{Q(B_1)} .$$

The equilibrium constant then is simply the product or quotient of two partition function ratios, one for the two isotopic species of A, the other for B. The partition function of a molecule is given by:

$$Q = \sum_i g_i \exp(-E_i/kT).$$

Here the summation is over all the allowed energy levels of the molecules, and g_i is the statistical weight of the i^th^ level E_i. It has been shown (Bigeleisen and Mayer, 1947; Urey, 1947) that for the purpose of calculating partition function ratios of isotopic molecules, other than H_2 for which rotational energies must be taken into account, it is sufficient to consider a modified partition function, Q', such that

$$Q' = \prod \nu_i \sum \exp(-E_{\text{vib}}/kT)$$

where ν_i is the i^th^ zero order vibrational frequency and E_{vib} is a vibrational energy state of the molecule.

If the harmonic oscillator approximation is used for molecular vibrations then:

$$Q' = \prod u_i \exp(-u_i/2)/(1 - \exp(-u_i))$$

where

$$u_i = h\nu_i/kT.$$

For many molecules only the observed fundamental frequencies are known. If, however, zero order frequencies and anharmonicity coefficients are available then more precise estimates of Q' may be made. The harmonic oscillator approximation is most seriously in error at high temperatures where vibrational energy levels other than the ground state have appreciable populations.

The calculation of a partition function ratio for a pair of isotopic molecules thus requires a knowledge of the vibrational frequencies of each of them. When fundamental vibrational frequencies (and possibly zero order frequencies and anharmonicity coefficients) are obtained from infrared and Raman spectroscopy for the most abundant isotopic species it is possible to set up a force constant model of the molecule and to write equations relating the vibrational frequencies, force constants, atomic masses and bond angles. Force constants are invarient under isotopic substitution so that once they are determined it is possible to evaluate the vibrational frequencies for the rare isotopic species by simply substituting the appropriate masses in the force constant equations. Then with the vibrational frequencies of the two species, the one measured, the other calculated, the partition function ratio for the two isotopic species is determined.

Using these methods the equilibrium constant K for the exchange reaction

$$H_2{}^{34}S + {}^{32}S\,O_2 \leftrightarrows H_2{}^{32}S + {}^{34}S\,O_2$$

has been calculated to be 1.008 at 500°C indicating that under equilibrium conditions there is 8°/oo more ^{34}S in the SO_2 than in the H_2S (Cragg *et al.*, in prep.). Thus the departure of this equilibrium constant from unity is a measure of the difference in the equilibrium properties of the two isotopes in this process.

When solid materials are considered the evaluation of partition function ratios becomes more complicated. It is no longer sufficient to consider the independent vibrations of each molecule, instead the lattice vibrations must be taken into account and the phonon spectrum of the lattice determined. This topic will be considered in more detail in a later section.

Kinetic isotope effects. The isotope fractionation introduced in the course of a unidirectional reaction may be considered in terms of the ratio of rate constants for the isotopic substances. According to the transition state theory of reaction kinetics (Eyring, 1935; Evans and Polanyi, 1935), reactant molecules are in equilibrium with molecules in a transition state through which reaction proceeds from reactants to products. Using the framework of this theory the ratio of rate constants, k_1/k_2, for two competing isotopic reactions:

$$A_1 \xrightarrow{k_1} B_1$$

and

$$A_2 \xrightarrow{k_2} B_2$$

may be written (Bigeleisen, 1949; Bigeleisen and Wolfsberg, 1958):

$$\frac{k_1}{k_2} = \left[\frac{Q'(A_2)}{Q'(A_1)} \Big/ \frac{Q'(A_2\ddagger)}{Q'(A_1\ddagger)}\right] \cdot \frac{\nu_1}{\nu_2} \,.$$

The ratio of rate constants for the reaction of light and heavy isotopic species is therefore expressed, as in the case of equilibrium constants, simply in terms of two partition function ratios, one for the two isotopic reactants species A, and one for the two isotopic species of activated complex or transition state $A^\ddagger$. The factor ν_1/ν_2 in the expression is a mass term ratio for the two isotopic species. ν may be related to a vibrational mode in the activated complex which becomes imaginary as the reaction coordinate is traversed and a bond broken. The determination of the ratio of rate constants is therefore formally the same as the determination of an equilibrium constant, although the calculations are not so precise because of the need for detailed knowledge of the transition state. However, by making certain assumptions concerning the nature of the transition state estimates for the ratio of rate constants for two competing isotopic reactions can be made.

Fractionation factors. For the purpose of understanding isotope abundance variations it is important to distinguish between the simple process fractionation factors given by equilibrium constants, or by ratios of rate constants in unidirectional reactions, and fractionation factors observed for systems where the simple process factor may have been multiplied many times. Commercial processes for the separation of isotopes depend on this kind of multiplication. Where such systems occur in nature isotope fractionation factors will be observed that are significantly larger than those calculated or measured for the simple processes.

A batch process or batch distillation is one such system that can give rise to large fractionation factors. For example, in the chemical reduction of sulfate to hydrogen sulfide the isotopic cases may be written as:

$$^{32}SO_4^{2-} \xrightarrow{k_1} H_2{}^{32}S$$

and

$$^{34}SO_4^{2-} \xrightarrow{k_2} H_2{}^{34}S$$

The ratio of rate constants, k_1/k_2, is about 1.024 at room temperature (Harrison and Thode, 1957). Since the $^{32}SO_4^=$ species reacts 24 °/₀₀ faster than $^{34}SO_4^=$ the H_2S produced at any instant is enriched in ^{32}S, or depleted in ^{34}S by this amount (24 °/₀₀) relative to the remaining $SO_4^=$.

The isotope effects resulting from this reaction may be estimated using the mathematical treatment of the Rayleigh distillation process. For small fractions of reaction the sulfide formed will be at −24°/₀₀ with respect to the starting material, but as the reaction proceeds to completion this difference will decrease until at the time of complete reaction the sulfide produced must of course have the same isotopic composition as the initial sulfate. Similarly for small fractions of reaction the residual sulfate isotopic composition will be virtually unaltered, but as the reaction proceeds, because of the continuing preferential reduction of $^{32}SO_4^=$, the remaining sulfate will become more and more enriched in $^{34}SO_4^=$. Thus the residual material will attain higher and higher $\delta^{34}S$ values relative to the starting material. After 75 percent of the sulfate has reacted, it may be shown that the residual material has a del value of +35°/₀₀ so that a ratio of rate constants of 1.024 has here produced a fractionation factor of 1.035.

Clearly batch processes of this type can occur in nature and give rise to a variety of observable fractionation factors which will depend upon the degree of completeness of reaction. This must be taken into account in interpretations of the natural isotope distribution pattern.

THE SULFUR ISOTOPE DISTRIBUTION IN NATURE

Figure 1 shows the ranges of $\delta^{34}S$ values found in nature for a number of different forms of sulfur. It may be seen that the overall range is about 100°/₀₀. It is this total

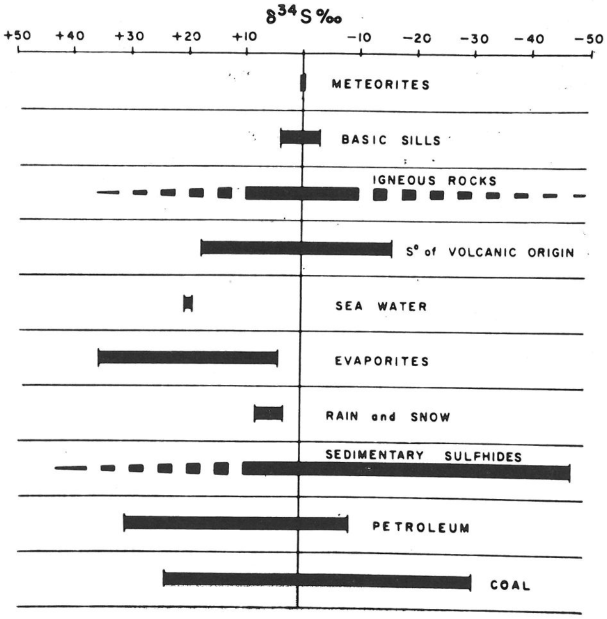

FIG. 1. The sulfur isotope distribution in nature.

spread and its fine details which must be explained in terms of isotope fractionation effects.

The two most common forms of sulfur in the earth's crust are sulfates and sulfides. The isotope exchange between sulfate and sulfide may be written

$$^{32}SO_4^{2-} + H_2{}^{34}S \rightleftarrows {}^{34}SO_4^{2-} + H_2{}^{32}S$$

and the theoretical value of the exchange constant is 1.075 at 25°C (Tudge and Thode, 1950). Therefore if this exchange takes place or is partially established in nature it should lead to sulfides being in general depleted in ^{34}S relative to sulfates by amounts up to 75°/₀₀. Although no simple mechanism for the establishment of this exchange is known spreads in isotope ratios of this order of magnitude are seen to occur. Evaporites represent the largest concentration of sulfates and they have $\delta^{34}S$ values ranging from +35°/₀₀ to +5°/₀₀ while sedimentary sulfides mave $\delta^{34}S$ values ranging from +40°/₀₀ to −50°/₀₀. This gives an overall spread of 85°/₀₀ between sulfates and sulfides. Since complete oxidation of a sulfide or the complete reduction of a sulfate will not result in any change in isotopic composition it is possible in special situations to have sulfate depleted, or sulfide enriched, in ^{34}S. A case in point is the pyrite of the Onwatin Slate in the Sudbury basin which has $\delta^{34}S$ values of up to around +30°/₀₀ (Thode *et al.*, 1962).

The types of material which exhibit the widest spread of $\delta^{34}S$ values are secondary in nature, that is to say they have been involved in the sedimentary cycle. Other forms of sulfur bearing materials such as basic sills, primary igneous rocks and volcanic gases show distinctly narrower ranges of $\delta^{34}S$ values which tend to be disposed symmetrically about zero (see Fig. 1). This distinction provides a basic diagnostic tool in sulfur isotope geochemistry. When an igneous rock is found which displays a wide range of $\delta^{34}S$ values or a narrower range well removed from zero it is possible to state with some certainty that the sulfur is not solely of primary origin but contains at least a component of reworked sedimentary sulfur.

The wide spread in $\delta^{34}S$ values for cyclic sulfur is the result of biological activity. The major biological process involving sulfur isotope fractionation is the reduction of sulfate to sulfide by the bacterium *Desulphovibrio desulphuricans* in the muds or developing sediments on the sea bottom (Thode *et al.*, 1951). Many laboratory experiments have been performed to elucidate the fractionation produced by these bacteria.

Experiments on the chemical reduction of sulfate to sulfide (Harrison and Thode, 1957) have shown that the fractionation in this case may be adequately explained if it is assumed that the step in the reaction which controls the isotope fractionation produced is one involving the cleavage of a sulfur-oxygen bond in the sulfate ion.

The situation for the bacterial reduction of sulfate is much more complex. In the course of experiments where such parameters as temperature, hydrogen donor type and concentration, sulfate concentration and bacterial population density were varied (Jones and Starkey, 1957; Harrison and Thode, 1958; Nakai and Jensen, 1964; Kaplan and Rittenberg, 1964) it was found that the measured fractionation factor introduced during the conversion of a small fraction of the available sulfate to sulfide could vary from 0.996 to 1.050. In a recent paper, Kemp and Thode (1968) list the possible steps that are involved in the reduction process as: (a) the uptake of sulfate, (b) the organic complexing of sulfate, (c) the reduction to organically bound sulfite and (d) the production of hydrogen sulfide. Under different conditions the net isotope fractionation produced will depend on the isotope effects in each of these steps, the relative speeds of the steps and the extent to which the sulfate reservoir is depleted. When the bacteria are extremely active, and the speeds of steps (b), (c), and (d) do not limit the rate of sulfide formation, it is the isotopic competition in step (a) which regulates the net isotope fractionation produced. Under these circumstances the isotope fractionation is small and fractionation factors between sulfate and sulfide of the order of unity are likely to be found.

The other extreme occurs when the bacteria produce sulfide under conditions of very low metabolic rate and when the uptake of sulfate is no longer the slow step in the overall reduction process. Under such circumstances it seems likely that the net isotope fractionation produced is the superimposition of an equilibrium isotope effect between bound sulfate and bound sulfite and the kinetic isotope effect involved in step (d). In this case overall fractionation factors produced can approach the upper limit of 1.050. However, in case of intermediate metabolic rates, a condition prevailing most often in laboratory experiments and in nature, intermediate fractionation factors are obtained (1.010 to 1.025).

Sulfate is reduced to sulfide in nature in two distinct situations, open and closed systems. In the open system, the sulfate reducing bacteria are in good contact with sea water and the sulfate which they reduce is constantly replenished. In such circumstances the product sulfide will have a $\delta^{34}S$ value removed from that of the ocean by an amount corresponding to the ratio of the rates of production of $H_2{}^{32}S$ and $H_2{}^{34}S$. In a closed system the bacteria are not in contact with the ocean sulfate reservoir. This may be caused by the isolation of a small volume of sea water from the well mixed ocean or by the overlaying of still active bacteria by muds holding interstitial sulfate. In such cases the $\delta^{34}S$ values of the sulfide produced and of the residual sulfate depend on the extent of reaction of the available sulfate as in the batch processes mentioned previously.

$\delta^{34}S$ values are remarkably constant for all present-day oceans and seas and it is reasonable to assume that they have been geographically uniform at any particular time in the past. Thus the $\delta^{34}S$ value of the ocean provides a convenient base level from which fractionation effects in the formation of sedimentary sulfides can be reckoned. The study of marine evaporites which were associated

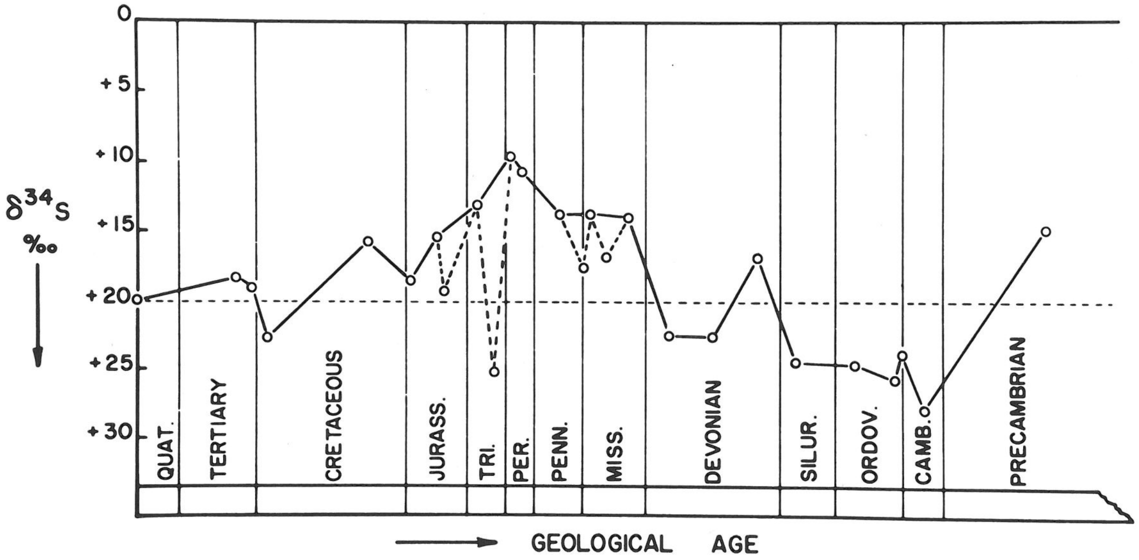

FIG. 2. The variation of the sulfur isotopic composition of the ocean over geological time.

with ancient oceans (*e.g.* Thode and Monster, 1965; Holser and Kaplan, 1966) shows that the $\delta^{34}S$ value of sea water sulfate has varied widely over geological time between approximately +30 and +10°/₀₀ as in Figure 2. This variation may be understood (Rees, 1970) in terms of the competition between evaporite formation and sulfide formation. Evaporite formation introduces only small isotope fractionation, while that in sulfide formation can be appreciable. In eras when evaporite formation was negligible ^{32}S was removed preferentially from the oceans by sulfide formation causing them to become enriched in ^{34}S relative to the input of sulfur from rivers. When evaporite formation was the dominant removal mechanism, the isotopic compositions of the input, the ocean reservoir and the output would all approach the same value. In eras of intermediate evaporite formation intermediate values of $\delta^{34}S$ would be established for the ocean.

There is a considerable range of $\delta^{34}S$ values for sulfur of volcanic origin (Rafter *et al.*, 1958a, 1958b; Rafter *et al.*, 1960; Sakai and Nagasawa, 1960). Much of the spread is caused by isotope exchange between various sulfur compounds in volcanic gases. At high temperatures the reaction

$$3S + 2H_2O \rightleftarrows 2H_2S + SO_2$$

goes to the right (Evans and Wagman, 1952) so that the reaction of elemental sulfur and water vapour can give rise to considerable quantities of hydrogen sulfide and sulfur dioxide. This same reaction, because of its reversibility, provides a mechanism for sulfur isotope exchange between sulfur dioxide and hydrogen sulfide according to the isotope exchange reaction:

$$^{32}SO_2 + H_2\,{}^{34}S \rightleftarrows {}^{34}SO_2 + H_2\,{}^{32}S.$$

This reaction has been studied experimentally and it is found that, in fair agreement with theory, the isotope exchange constant is 1.007 at 500°C with SO_2 becoming enriched in ^{34}S relative to H_2S (Cragg *et al.*, in press).

As the gases emerge from the volcano the reduction in temperature is responsible for a further isotope effect. At lower temperatures the reaction

$$3S + 2H_2O \rightleftarrows 2H_2S + SO_2$$

proceeds to the left so that H_2S and SO_2 together form sulfur. A study has been made of the kinetic isotope effect involved in this conversion of SO_2 to S° (V. A. Grinenko and H. G. Thode, publication in preparation). It was found that the ratio of rate constants for the conversion of the light and heavy species $^{32}SO_2$ and $^{34}SO_2$ was of the order of 1.015. This kinetic isotope effect further tends to enrich the residual SO_2 in ^{34}S.

The narrowest range of $\delta^{34}S$ values is found for basic rocks. Vinogrador *et al.* (1957) and Vinogradov (1958) reported small fluctuations in the isotopic content of sulfides in acid and basic rocks, although for ultrabasic rocks such as pyroxenite and dunite the range was very narrow indeed, around the $\delta^{34}S$ equal to zero or primordial value. Ault and Kulp (1959), on the basis of the average $\delta^{34}S$ value from a limited number of mafic rocks, granitic plutonic rocks including pegmatites, and hydrothermal deposits reported in the literature, concluded that the average $\delta^{34}S$ value for the earth's crust and mantle is +3.6°/₀₀ rather than 0.0°/₀₀

In contrast to this, on the assumption that sulfur occurring in ultrabasic or basic flat-lying intrusives might give an idea of the composition of sub-crustal or mantle material, Shima, Gross and Thode (1963) investigated four such large sills in considerable detail. The sills ranged from 1000 to 4000 feet in thickness and showed varying degrees of differentiation. Weighted mean values of $\delta^{34}S$ were 0.95, +1.0, +0.7 and +0.1°/₀₀. From these results it would appear that the average sulfur isotope ratio for basic magmas is very close to that for meteorites, *i.e.* $\delta^{34}S$ equal to zero.

The isotope ratios found in granitic intrusives and sulfide ore bodies have to be interpreted in terms of the fractionation patterns mentioned so far. This is not always simple, although detailed sulfur isotope studies have permitted the classification of sulfur in specific instances as primary or secondary or mixed, and has given evidence for subdividing many hydrothermal deposits into magmatic hydrothermal, metamorphic hydrothermal and ground water hydrothermal (Jensen, 1957, 1959).

Because of the complexities involved it is difficult to lay down strict rules for determining the origin of mineral deposits. Each particular case must be treated separately with due regard being given to the local geological conditions.

As the techniques of mass spectrometry have improved so has the range of problems which isotope geochemists may usefully study. In sulfur isotope geochemistry it was the large fractionation effects, such as in the bacterial reduction of sulfate, that were first investigated but as the precision of measurement of $\delta^{34}S$ values improved it became possible to investigate systems such as ultrabasic rocks and the meteorites where only small isotope fractionation effects are found.

The latter part of this paper is devoted to the isotope fractionation between coexisting sulfide minerals. The isotope effects involved are rarely greater than 5°/₀₀ so that measurement of these important effects requires careful sample preparation and precise mass spectrometry.

FRACTIONATION BETWEEN SULFIDE MINERALS

Observation of fractionation effects. In 1957 in the course of a broad survey of sulfur isotopes in nature Sakai (1957) suggested that isotopic fractionation between different metallic sulfides would bring about a slight variation of their isotope ratios during their deposition. The observational data he presented seemed to support this view, for among nine sulfide pairs he examined, in three cases out of three marcasite was enriched in ^{34}S relative to chalcopyrite, and in three cases out of three pyrite was enriched in ^{34}S relative to sphalerite. In one case sphalerite was enriched relative to galena and the remaining two cases were enrichment and depletion of sphalerite relative to chalcopyrite. However, Sakai was obliged to state that no firm conclusions could be drawn from these data since the magnitudes of the effects noted were at the limits of the precision of the measurements. Since 1957 many cases of sulfur isotope fractionation bewteen coexisting sulfide minerals have been noted.

Gavelin, Parwel and Ryhage (1960) in the course of a critical study of the isotope fractionation involved in sulfide mineralization noted that for sulfides in a single hand specimen there was a sequence pyrite-sphalerite-galena from higher values of $\delta^{34}S$ to lower values.

In two studies of the Heath Steele Ore deposits of Newcastle, New Brunswick, Dechow (1960) and Tupper (1960) noted possible isotope fractionation between sulfides. Dechow suggested that there was a tendency for pyrite to have a higher $\delta^{34}S$ value than chalcopyrite while remarking that this trend was not statistically significant. Tupper noted that the group means of $\delta^{34}S$ values for pyrite and chalcopyrite were very similar and that both were higher than those for sphalerite and galena.

Buschendorf *et al.* (1963) in a study designed to determine the origins of sulfide ore bodies at Meggen, Germany, again noted a high to low $\delta^{34}S$ trend for pairs among the three minerals, pyrite, sphalerite and galena.

Smitheringale and Jensen (1963) in a study of sulfides from igneous rocks and genetically associated mineral deposits of the Triassic Newark group of the Eastern United States noted that with coexisting pyrite and chalcopyrite there was a clear tendency for the pyrite $\delta^{34}S$ value to be high.

Friedrich, Schachner and Nielsen (1964) in their study of ore deposits in the Sierra de Cartagena, Spain, noted that the $\delta^{34}S$ values of the different coexisting sulfides differ only slightly from one another but that a high to low sequence could be written FeS, FeS_2, ZnS, PbS.

The work reported by Tatsumi (1965) seems to be the first study specifically concerned with sulfur isotope fractionation between sulfides. Taking his data from about a dozen suites of coexisting sulfide minerals from Japanese metallic deposits, he was able to say that $\delta^{34}S$ values for pyrite tend to be high, those for galena low, and those for chalcopyrite, sphalerite, bornite and tetrahedrite intermediate. The fractionation factors that he noted between pyrite-sulfide and sulfide-galena pairs ranged from 1.001 to 1.003, with deposits genetically connected with Tertiary volcanism giving higher factors than those of contact metasomatic or regionally metamorphic origin. The degree of fractionation is higher in the ore deposits formed at lower temperatures, which is in accord with the theory of isotope exchange equilibrium. This suggested that equilibrium had been established and that these effects might be used as a geothermometer. The principle of such a thermometer is based on the temperature dependence of the isotope equilibrium constant for reactions such as:

$$Fe^{32}S + Pb^{34}S \rightleftarrows Fe^{34}S + Pb^{32}S$$

Measurement of the fractionation factor, which at equilibrium would be equal to the isotope equilibrium constant, would give a measure of the temperature at which equilibrium of the two sulfides took place. Such a geothermometer would be of particular interest and utility, since, because of the nature of isotope effects, it would be pressure independent.

Speelman and Schwarcz (1966) have examined the sulfur isotope composition of coexisting pyrite-pyrrhotite pairs in metamorphic rocks in the Hailburton-Madoc area, Ontario. In 90 percent of their samples pyrite has a higher $\delta^{34}S$ value than pyrrhotite by between 0 and 1.4°/₀₀.

In a study of the origins of the Quemont ore body in Northwestern Quebec, Ryznar, Campbell and Krouse

(1967) noted two isotope effects connected with sulfides. Firstly, there is a tendency for the group mean $\delta^{34}S$ value of pyrite plus pyrrhotite to be higher than that for chalcopyrite plus sphalerite and that, secondly, the difference between the group means increases slightly with depth in the ore body. These effects are explained by the authors in terms of isotope fractionation during the course of mineralization from a sulfide melt. That is to say the isotope abundance patterns involved are the result of kinetic isotope effects associated with mineralization and not directly related to the equilibrium isotope effects between minerals.

The possibility of depositional effects is also mentioned by Stanton and Rafter (1967). For samples of coexisting sphalerite and galena from Broken Hill, New South Wales, they note that in general sphalerite has a higher $\delta^{34}S$ value than galena and that the difference between pairs is related to the degree of metamorphism which the minerals have experienced. They point out that this might represent purely metamorphic partitioning (an equilibrium isotope effect) or a substantial depositional partitioning (a kinetic isotope effect) that has been lessened by aging and metamorphism.

Lusk and Crocket (1969) in a new study of sulfur isotopes from the Heath Steele B-1 orebody of New Brunswick and from five other stratiform deposits in the area have made careful observations of the difference in $\delta^{34}S$ values between pairs of sulfides. They note that the fractionation factors between given pairs of sulfide minerals are relatively constant throughout all six deposits and that for pyrite-sphalerite, sphalerite-galena and pyrite-galena have mean values of 1.001, 1.002 and 1.003 respectively. From these observations they conclude that sulfur isotope equilibrium was closely approached at a fairly uniform temperature and that the deposits studied have undergone low temperature regional metamorphism which has generated the observed fractionations and caused localized isotopic homogenization with respect to given minerals.

Sasaki and Krouse (1969) in their study of the Pine Point lead-zinc mineralization again raise the suggestion that the isotopic composition of sulfides may be determined more by the circumstances of their emplacement than by post-emplacement equilibration. They point out that the previously reported studies on coexisting sulfide minerals seem to include many examples of successive mineralization as opposed to coprecipitation but that even so the observed isotopic trend is in accord with the minerals in question being in sulfur isotopic equilibrium. They suggest that this might be an indication that the sulfur isotope composition of the ore forming fluid in these deposits may have been comparatively uniform during the course of mineralization and that in such circumstances the isotope ratio variations among different sulfide species would have the same trend as if the minerals had formed at the same time and under conditions of isotopic equilibrium.

Further examples of isotope fractionation between coexisting sulfides have been reported following studies on ore bodies in Tasmania (Solomon, Rafter, and Jensen, 1969; Both *et al.*, 1969). These studies reinforce the previously observed ordering of $\delta^{34}S$ values with pyrite, sphalerite, chalcopyrite and galena forming a high to low sequence. The authors point out again that this trend is consistent with either depositional or later metamorphic effects.

The existence of systematic differences in $\delta^{34}S$ between coexisting sulfides in nature is now well established as is the idea that these differences reflect in some way the thermal histories of the sulfides in question. The theoretical and experimental work that has been done and is now in progress is largely concerned with the determination of the variations with temperature of sulfur isotope exchange constants for pairs of sulfides and the application of such data to geothermometry.

Theory. The first theoretical study of sulfur isotope fractionation between metallic sulfides was made by Sakai (1968). In addition, Bachinski (1969) has reported a study of the bond strengths of sulfide minerals and their relationship to isotope fractionation.

It is possible to make qualitative estimates of the fractionation to be expected between coexisting sulfides by using the simple idea that the process of equilibration is one where the total free energy of a system is minimized. If the rearrangement of isotopes between two phases is considered, it may be shown that in order to bring about this free energy minimization the heavier isotopes will tend to accumulate at sites with higher bond energies. Thus in order to predict the way in which sulfur isotopes will partition themselves in a multiple mineral assembly, it is necessary to have some knowledge of the force constants of the mineral lattices. These atomic scale parameters are reflected in many ways in the macroscopic properties of a crystal, for example volume compressibility, heat capacity at constant volume, free energy and heat of formation, lattice energy, solid state reaction rate and activation energy of diffusion.

Sakai and Bachinski have between them considered all the above macroscopic properties for a number of metallic sulfides with a view to determining the expected order of increasing $\delta^{34}S$ values in equilibrated sulfide mixtures. Bachinski has pointed out the use of such indicators is most successful for minerals with identical structures, but useful information may still be obtained for minerals of different structures in cases where the differences in the chosen macroscopic parameters are so large as to outweigh effects due to structural distortions.

Using these techniques it may be shown that in an equilibrium mixture the sequence in order of decreasing $\delta^{34}S$ value for the more important sulfide minerals should be:

$$\text{pyrite} > \text{sphalerite} > \text{chalcopyrite} > \text{galena}$$

This is in agreement with the trends noted for naturally occurring samples.

TABLE 1. VALUES OF $(K-1)\times 1000$ FOR SULFIDE-SULFIDE PAIRS. FROM SAKAI (1968)

Temp. °K	300	400	500	600	700	800
Pyrite Galena	14.8	8.9	5.7	3.9	3.0	2.2
Sphalerite Galena	10.7	6.0	3.9	2.7	2.0	1.5
Pyrite Sphalerite	4.1	2.9	1.8	1.2	1.0	0.7

In order to employ the isotope fractionation between sulfides as a geothermometer it is of course necessary to determine quantitatively the isotope equilibrium constants for pairs of sulfides and the variations of these equilibrium constants with temperature. As was mentioned earlier, in order to do this, it is necessary to know the phonon spectra of the lattices involved.

Sakai has gone part of the way to determining the necessary parameters by adopting a simplified model for lattice vibrations. He assumes firstly that the phonon spectrum of a sulfide mineral is made up of Einstein and Debye frequencies, corresponding to atomic and lattice vibrations. By further assuming the Debye frequency spectrum to be replaced by a single frequency he then develops simplified expressions for partition function ratios which may be related to measurable parameters such as the Debye temperatures of the crystals. The values of equilibrium isotope effects (K-1) he determines in this way, which are shown in Table 1, are only likely to be semi-quantitative because of the simplifying assumptions made but at least give some indication of the magnitudes and temperature dependences which may be expected.

According to a recent paper by Bottinga (1969), in order to determine explicitly the phonon spectrum of a lattice it is necessary to choose a physically plausible potential which describes the atomic interactions in the unit cell as a function of interatomic distances and angles. Then the equations of motion of the particles in the unit cell may be written and solved. As a check on the correctness of the assumed interparticle potential, the specific heat at constant volume must be calculated as a function of temperature and compared with the measured values. If agreement is not satisfactory, then the constants in the assumed interparticle potential must be adjusted and the calculations repeated. Bottinga has followed these procedures for graphite and diamond with respect to ^{12}C and ^{13}C isotope effects. Where experimental results are available, his calculations appear to be reasonably accurate. It seems likely that if precise calculations are to be applied to sulfur isotope fractionation between sulfide minerals, then it will be necessary to use this sort of technique.

At the present time then the equilibrium isotope effects between coexisting sulfide minerals can be understood in a qualitative way and the calculations performed so far give at least an indication of the magnitudes of the effects and of their temperature coefficients. More work is required, however, before theoretical estimates of the isotope equilibrium constants can be used with any degree of confidence.

Experimental work. Because of the difficulties and uncertainties involved in the calculation of partition function ratios for sulfides it seems that the best method of determining isotope exchange constants and thus calibrating the geothermometer is by laboratory experiments. A number of such studies are currently under way.

Ideally, binary mixtures of minerals in intimate contact (direct method) should be used for such determinations; but in order to obtain accurate results, it is essential to effect complete separation of the two components after equilibration. Anything less than 100 percent separation will lead to spuriously low values of estimated equilibrium constants. In order to overcome this problem, two essentially similar approaches have been used. The first, or indirect approach, is to have both sulfides present in the equilibration vessel but to keep them physically separated and to effect isotope exchange between them via transport of sulfur vapour. This may be written as:

$$M_1\text{S} \rightleftarrows \text{S} \rightleftarrows M_2\text{S}.$$

The second, or separate approach, is to measure the isotope exchange constants of individual minerals with elemental sulfur separately. If two such exchanges are written:

$$M_1{}^{32}\text{S} + {}^{34}\text{S} \overset{K_1}{\rightleftarrows} M_1{}^{34}\text{S} + {}^{32}\text{S}$$

$$M_2{}^{32}\text{S} + {}^{34}\text{S} \overset{K_2}{\rightleftarrows} M_2{}^{34}\text{S} + {}^{32}\text{S}$$

then the sulfide-sulfide exchange may be written as:

$$M_1{}^{32}\text{S} + M_2{}^{34}\text{S} \overset{K_{12}}{\rightleftarrows} M_1{}^{34}\text{S} + M_2{}^{32}\text{S}$$

If K_1 and K_2 are isotope exchange constants for the two separate sulfide-sulfur exchanges, then the isotope exchange constant for the two coexisting metallic sulfides will be simply:

$$K_{12} = \frac{K_1}{K_2}\,.$$

Before discussing briefly the results of such experiments it is worthwhile to mention a study of a similar nature in preparation by H. Puchelt and G. Kullerud in which the isotope effect in the formation of PbS from lead and sulfur was studied. The results of the series of experiments are shown in Figure 3.

Without going into the details of the mechanisms involved, it may be seen qualitatively that there is a kinetic isotope effect involved in the formation of lead sulfide and that ^{32}S reacts faster than ^{34}S so that the δ^{34}S value of the product sulfide is less then that of the starting material at $\delta=0$. Also, because of the preferential reaction of ^{32}S, the remaining unreacted sulfur becomes enriched in ^{34}S, this enrichment reaching a maximum as the last of the lead reacts. After this the excess free sulfur and the lead sulfide start to equilibrate and with time the difference between their δ^{34}S values decreases to finally reach a value corre-

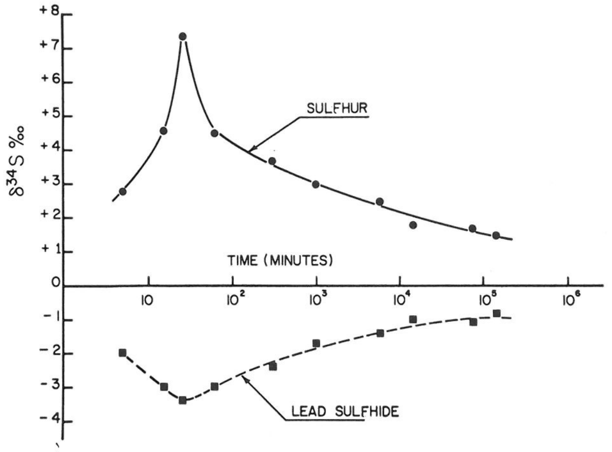

FIG. 3. Sulfur isotope fractionation during the reaction $Pb + S \rightleftarrows PbS$.

sponding to the isotope ecxhange constant of the reaction:

$$Pb^{32}S + {}^{34}S \rightleftarrows Pb^{34}S + {}^{32}S.$$

The important point to note concerning these experiments is that the reaction in nature of elemental sulfur with lead could under special circumstances produce appreciable isotope effects.

The results of some experiments designed to measure sulfide-sulfide equilibrium constants (as a function of temperature) are shown in Figures 4, 5, and 6. (In each case, the equilibrium isotope effect (K-1) is plotted against $1/T_2$ where T is given in degrees absolute.) The theoretical values are from Sakai (1968). The values ascribed to Grootenboer and Schwarcz (1969a, b) were obtained during their experiments with single sulfides equilibrating with sulfur (indirect method). H. P. Schwarcz (priv. commun.) has mentioned the possibility that some of the measurements on the pyrite-sulfur equilibrium may have been influenced by the presence of pyrrhotite. The experiments of Kajiwara Krouse, and Sasaki (1969), (see also Kajiwara, 1969) were performed with physically separated minerals which were equilibrated by the passage of sulfur vapour between them (indirect method).

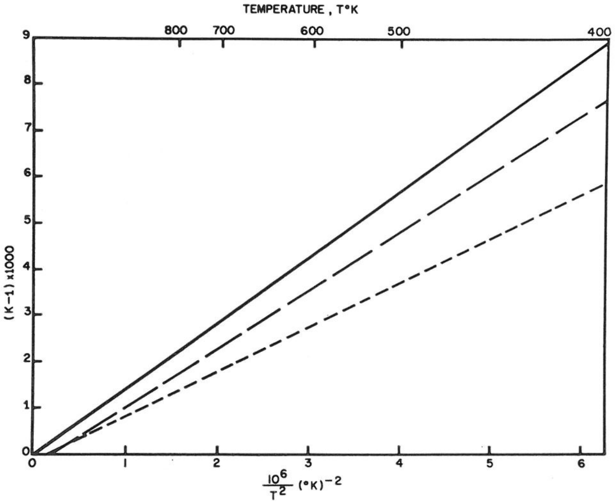

FIG. 4. Temperature variation of the sulfur isotope equilibrium constant for the pair pyrite-gelana.

——— Sakai (1968)
— — — Kajiwara *et al.* (1969)
- - - - Grootenboer and Schwarcz (1969a)

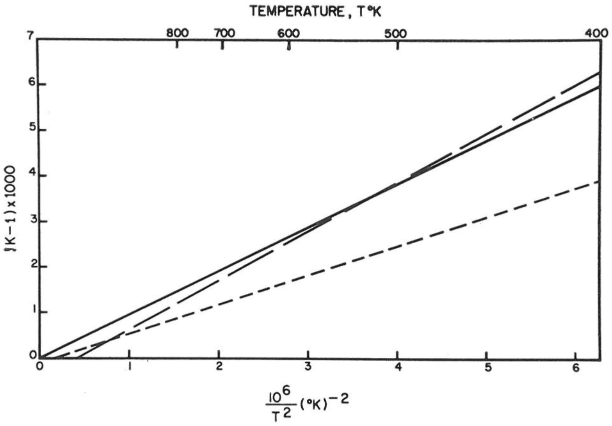

FIG. 5. Temperature variation of the sulfhur isotope equilibrium constant for the pair sphalerite-galena.

——— Sakai (1968)
— — — Kajiwara *et al.* (1969)
- - - - - - Grootenboer and Schwarcz (1969a)

It should be noted that the best straight line fits for both sets of experimental determinations do not pass through the origin. This does not necessarily indicate experimental error as has been demonstrated recently by Stern *et al.* (1968).

It is not surprising that there should be some discrepancy between the experimental values and the theoretical values of Sakai, in view of the approximate nature of his calculations. What is perhaps surprising is the lack of agreement between the different experimental determainations. It is clear that if the sulfide-sulfide geothermometer is to be usefully employed then it is necessary that these discrepancies be resolved.

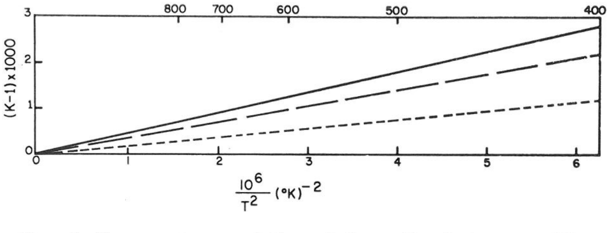

FIG. 6. Temperature variation of the sulfur isotope equilibrium constant for the pair pyrite-sphalerite.

——— Sakai (1968)
— — — Kajiwara *et al.* (1969)
- - - - - - Grootenboer and Schwarcz (1969a)

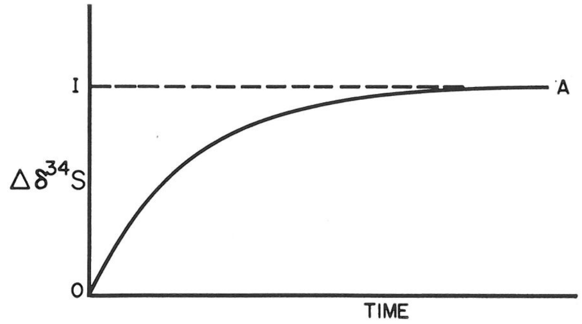

FIG. 7. The approach of a two component system to equilibrium. At equilibrium $\Delta\delta^{34}S = K - 1$.

In both sets of experimental determinations the criterion used for assessing the attainment of equilibrium was that the $\delta^{34}S$ values of the various components had reached steady values. Figure 7 shows the type of measurement which is required in these studies. *OA* represents the idealised variation of the difference in $\delta^{34}S$ values for two equilibrating phases. *IA* is the asymptote of this variation and the desired equilibrium constant is determined from the intercept *I*. With a typical array of experimental points with associated errors it may be appreciated that there are considerable difficulties associated with determining whether or not the experimental line *IA* is truly horizontal.

A possible improvement in experimental technique could be implemented as follows. Figure 8 indicates that there should be two sets of experiments, one as before and the other deliberately arranged so that the $\delta^{34}S$ values of the initial materials are such that equilibrium is approached from the opposite direction. As equilibrium is approached, one set of data gives upper limits and the other set lower limits for the isotope equilibrium constant. Since the presentation of this paper Rye and Czamanske (1969) have reported their results of sphalerite-galena exchange studies. They, in fact, did approach equilibrium from both directions and obtained results in good agreement with Grootenboer and Schwarcz (1969a).

H. Puchelt and G. Kullerud have performed experiments (publication in preparation) which are instructive when considering the experimental approach to isotopic equilibrium. This work is concerned with the sulfur isotope homogenization between similar sulfides (*e.g.* $(PbS)_1$, $(PbS)_2$) with initially different $\delta^{34}S$ values. The approach to isotopic equilibrium is followed, as in experiments with dissimilar sulfides, by studying the differences in $\delta^{34}S$ values as a function of time. However, in this situation there is no doubt as to when equilibrium has been established since of course when this is the case the difference in $\delta^{34}S$ values will be zero. Their results indicate that the times required for isotope homogenization to take place vary widely with temperature and mineral type. The homogenization time decreases with increase of temperature, while the time required for isotopic homogenization of lead sulfides is much less than that required for homogenization of zinc sulfides, which is in turn less than that required for iron sulfides (FeS2).

In passing it may be mentioned that there is a factor in the experiments which may be upsetting the determination of the isotope equilibrium constants. Measurements of the isotope equilibrium constant of an exchange reaction such as:

$$M^{32}S + {}^{34}S \rightleftarrows M^{34}S + {}^{32}S,$$

where *M*S is a metal sulfide and S represents liquid sulfur, may be made invalid by the presence in the system of another form of sulfur. If there is water vapour present in the system, its reaction with elemental sulfur would give rise to both sulfur dioxide and hydrogen sulfide. Also, elemental sulfur itself will exist in the liquid and vapour forms.

In such cases, the chemical exchanges taking place may be written as

$$MS \rightleftarrows S \rightleftarrows (X),$$

where (*X*) represents the other form (or forms) of sulfur. This situation would introduce no difficulties if the sampling of the two phases MS and S could be made under the actual experimental conditions of the equilibration. However, for practical reasons the technique used is to sample these phases after quenching the system by reducing its temperature to a point where no further exchange occurs. If at low temperatures one may write:

$$(X) \rightarrow S,$$

as is the case for the possible forms of (*X*) mentioned above, then it is not the isotopic composition of the liquid sulfur in the high temperature equilibrium mixture which is measured but rather the isotopic composition of the system (S+*X*). This system will only have the same isotopic composition as the liquid sulfur if the isotope equilibrium constant of the exchange:

$$^{32}S + {}^{34}X \rightleftarrows {}^{34}S + {}^{32}X$$

is unity.

One further problem must be mentioned. If the sulfur isotope fractionation between coexisting sulfide minerals is to be used as a geothermometer the temperature being measured must be defined. Two hypothetical cases il-

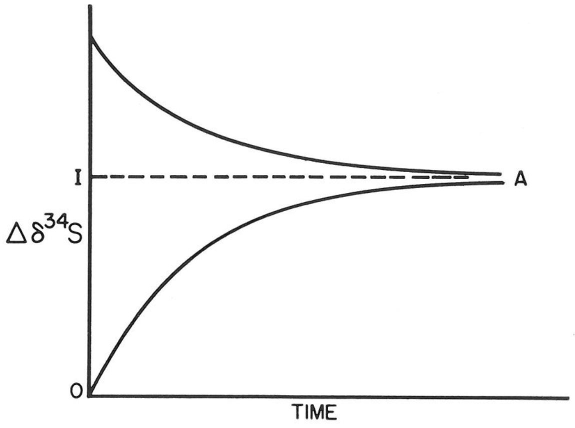

FIG. 8. The approach of a two component system to equilibrium. By proper choice of the $\delta^{34}S$ values of the starting materials equilibrium may be approached from either side.

lustrating this point are shown in Figure 9. In case A, the temperature stays at some value T long enough for isotope equilibrium to be established among coexisting sulfides. At time t the temperature falls sharply to a value where no further exchange takes place. This case is straight forward and clearly the 'temperature' measured by the geothermometer is T.

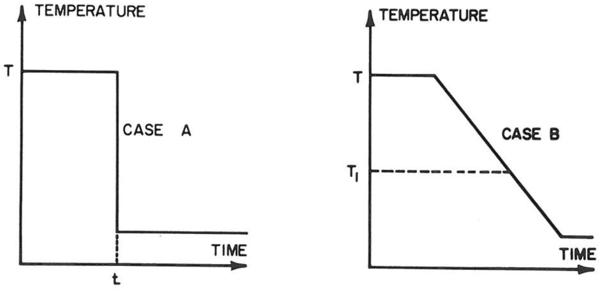

FIG. 9. Hypothetical temperature variations with time for sulfide mineral deposits.

In case B, the temperature again stays at temperature T long enough for equilibrium to be established, but then starts to decrease very slowly. The decrease is so slow that isotopic equilibrium continues to be maintained, until a temperature T_1 is reached at which there is no longer a mechanism or pathway available to permit exchange to continue and the exchange system becomes 'frozen'.

Other more complicated cases may be envisaged. For example, it may be that a pyrite-galena geothermometer and a sphalerite-galena geothermometer might under certain circumstances give different answers for the very good reason that because of their different rates of exchange they become 'frozen' at different temperatures.

CONCLUSIONS

The fractionation of the sulfur isotopes between coexisting sulfide minerals has been discussed from the point of view of the observation of such effects in nature and the theoretical and experimental work done so far on the determination of isotope equilibrium constants for such systems.

Work in this area is largely directed towards the development of a geothermometer for sulfide ore bodies. Before such a geothermometer can be successfully used a number of problems must be solved.

The differences in isotopic composition of coexisting sulfides may result either from simple equilibrium isotope effects or from depositional isotope effects followed by partial or complete equilibration. It is commonly supposed that concordance between two or more sulfide geothermometers is a necessary and sufficient condition for the recognition of isotope equilibrium, but it seems likely that the assumptions underlying this criterion will need critical examination in the future.

Theoretical values of isotope equilibrium constants for coexisting sulfides have so far been evaluated only in a qualitative or semiquantitative fashion. Much remains to be done in this type of approach.

The experimental determination of equilibrium constants performed so far do not agree well with each other. Before such determinations can be used as satisfactory calibrations of geothermometers it is clearly necessary that the discrepancies be removed.

Because of the foregoing considerations, no attempt has been made here to list the instances where individual workers have used such techniques to determine sulfide temperatures for specific ore bodies. Clearly until there is agreement on the calibrations of the temperature scales there will be no agreement on the temperature determined. It is felt that such applications, except when made in a qualitative manner, are somewhat premature.

However, with the wealth of observational material available, and the wide interest being shown in the technique by many isotope geochemists it seems likely that with time the problems outlined will be overcome and the technique developed into a satisfactory and useful method of pressure independent geothermometry.

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