EQUILIBRIUM FRACTIONATION

OF

SULFUR ISOTOPIES
EQUILIBRIUM FRACTIONATION OF SULFUR ISOTOPES

BETWEEN

PYRITE, SPHALERITE AND GALENA

By

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A Thesis

Submitted to the School of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Doctor of Philosophy

McMaster University

November 1969
TITLE: Equilibrium Fractionation of Sulfur Isotopes between Pyrite, Sphalerite and Galena as a function of Temperature.

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NUMBER OF PAGES: xv, 270.

SCOPE AND CONTENTS:

The existence of significant and consistent fractionation of sulfur isotopes in natural coexisting sulfide mineral pairs is demonstrated. Such fractionations are shown to depend exclusively on the mineralogy of the assemblage and temperature of equilibration, consistent with a process of fractionation during equilibrium exchange of sulfur isotopes between the sulfide phases. The fractionation of sulfur isotopes between galena, sphalerite and pyrite has been determined experimentally over the temperature range 300-725°C. The fractionation for each mineral pair is shown to vary as $T^{-2}$ so that three isotope geothermometers have been calibrated. Experimental results are applied to natural sulfide assemblages to determine the temperature of equilibration and extent to which isotopic equilibrium has been attained.
ACKNOWLEDGMENTS

The author wishes to thank Professor Henry P. Schwarcz for his supervision, advice and inspiration throughout the course of this work.

Deep appreciation is extended to all members of the Geology Department for their assistance, friendship and contribution to the author's education.

Assistance given by Mr. Jan Monster and the use of his mass spectrometer is gratefully acknowledged.
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CHAPTER 1

1. INTRODUCTION

1.1. Historical Background

The relative abundance of sulfur isotopes was first measured by Aston (1933) in 1927. Three stable isotopes $^{32}\text{S}$, $^{33}\text{S}$, and $^{34}\text{S}$ were identified in the approximate proportions 96:1:3. A fourth isotope $^{36}\text{S}$ of much lesser abundance was later detected by Nier (1938).

MacNamara and Thode (1950) measured the following relative percentage abundance for sulfur of meteoritic troilite:

$\text{S}^{32} = 95.081$, $\text{S}^{33} = 0.750$, $\text{S}^{34} = 4.215$ and $\text{S}^{35} = 0.017$. While most natural materials approximate closely to this composition, significant variations have been reported. Because of their high abundance relative to the other sulfur isotopes it is usual to measure only the abundances of $\text{S}^{32}$ and $\text{S}^{34}$. Variations in the $\text{S}^{32}/\text{S}^{34}$ ratio for natural materials may amount to a few percent.

A number of geochemical processes seem potentially capable of producing significant fractionation of sulfur isotopes. By far the most important of these is the fractionation associated with the bacterial reduction of sulfate to sulfide. Under optimum condi-
tions fractionations of 3% may result between hydrogen sulfide and the original sulfate and the effect can be cumulative. In comparison, other processes of fractionation appear more or less insignificant so that most workers in this field have either not detected or have ignored them. Mechanisms potentially capable of producing separation of the isotopes of sulfur in the geochemical cycle would include dynamic processes of precipitation, diffusion (as a function of temperature, osmotic pressure, or gravity), solution (during weathering) or equilibrium and disequilibrium exchange reactions.

Fractionation of sulfur isotopes has been observed for equilibrium exchange during oxidation-reduction reactions. Hydrogen sulfide and sulfur dioxide at fumarolic vents show differences in isotopic composition up to 2.5% (Sakai 1957). Similarly, barite-galena mineral pairs from Japan (Sakai 1957) and from Southeast Missouri (Ault and Kulp 1958) show fractionations of a few percent.

In contrast, it has long been held that similar fractionations between sulfide minerals pairs thought contemporaneous in their deposition, do not exist. Ault and Kulp (1958), considering possible processes of isotopic fractionation, conclude that if such effects are present they do not appear to exceed 0.2% of the $^{32}\text{S}/^{34}\text{S}$ ratio, the approximate precision of isotopic analysis at the time.
In recent years, the precision of isotopic measurement has been significantly improved and the occurrence of small but definite and systematic fractionations between co-existing sulfide minerals has been reported by a number of authors, among the more recent being Tatsumi (1967), Stanton and Rafter (1968) and Lusk and Crocket (1969). A survey of published results shows a consistent pattern of significant fractionations, especially between the sulfides pyrite, sphalerite and galena with the heavy isotope being enriched in the following order:

\[ \text{galena} < \text{sphalerite} < \text{pyrite} \]

The fractionation between given pairs of sulfide minerals furthermore shows a temperature dependence varying systematically as a function of the temperature of formation of the mineral assemblage or metamorphic grade.

While it would appear possible that several other processes of fractionation may contribute to these differences, or that they may result from changes in chemical or physical conditions of the depositional environment, their consistency and temperature dependence strongly suggest equilibrium exchange between the sulfide minerals at the time of formation. Such exchange may either take place between the minerals themselves or through a buffer phase such as a hydrothermal fluid.
The principles of isotopic fractionation during equilibrium exchange reactions are fairly well known and generally it is possible to calculate at least approximately, the equilibrium constant, which is directly related to the partition functions of the participating phases. The equilibrium constant is essentially a function of temperature only and it can be shown theoretically that the logarithm of the equilibrium constant varies approximately as the square of the inverse of the absolute temperature. The isotopic fractionation accompanying such a reaction would therefore be expected to decrease rapidly with increasing temperature.

Since the publication of Urey's (1947) theoretical paper on this subject, the fractionation of oxygen isotopes between equilibrium phases and its temperature dependence has received wide attention. Subsequent experimental calibration of oxygen isotope exchange reactions (Epstein et al., 1953, McCrea, 1950) have led to the development of the palaeotemperature scale where an accuracy of better than 1°C can be attained over the range 5-30°C. The mechanism has been extended to estimate the temperature of formation of high-temperature co-existing silicates, carbonates and oxides, e.g. Taylor and Epstein (1962a, b). The fractionation factor for most
oxygen isotope exchange reactions is large in comparison to experimental accuracy even at elevated temperatures.

The fractionation factors of different mineral pairs give good indication of the temperature of final equilibration for a variety of rock types and these oxygen isotope temperatures appear to be reasonable by most geologic criteria.

Similar effects of equilibrium exchange fractionation can, therefore, be expected for sulfur isotopes. The magnitude of the fractionation can be expected to be approximately proportional to the square root of the relative differences in isotope mass and hence the effect for $^{32}$S and $^{34}$S would be significantly smaller compared to $^{16}$O and $^{18}$O.

Fractionations for exchange between sulfides in which the exchanging isotopes are in the same valence state would probably be of the order of only a few permil or less at geologically reasonable temperatures.

Observed differences in isotopic composition of co-existing sulfides appear significantly greater than present day analytical accuracy of approximately 0.2 permil. This is especially true for the mineral pairs involving pyrite, galena and sphalerite where differences of a few permil are common. The isotopic fractionations correlate qualitatively with geologic temperature estimates and appear to have been 'frozen in' both phases at the time of their formation or recrystallization during the last period of metamorphism.
It therefore appears possible to use these fractionations to estimate the temperature of formation of ore-mineral assemblages, after experimental calibration of the fractionations accompanying exchange between synthetic sulfide pairs under laboratory conditions.

The isotopic fractionation factor can subsequently give a good indication of the temperature of final equilibration for a variety of sulfide occurrences. The accuracy of such temperature estimates depends on the temperature sensitivity of the fractionation factor for the mineral pair used. Through the use of more than one mineral pair it is possible to ascertain to what extent isotopic equilibrium was achieved in the mineral assemblage and frozen in.

1.2. Research Objectives

In order to assess the importance of equilibrium exchange reactions as a mechanism of producing fractionation of sulfur isotopes between co-existing sulfides, and its potential use as a geothermometer, measurement must be made of (1) the equilibrium fractionation between sulfides as a function of temperature, and (2) the rate of exchange reactions responsible for these fractionations. While similar effects for the exchange of oxygen isotopes between mineral species have been investigated in several studies (e.g. O’Niel and Clayton, 1964), only a single experimental investigation has as yet been reported.
for sulfur isotope exchange (Puchelt 1968). This was primarily concerned with the rate of exchange of sulfur isotopes rather than measuring equilibrium fractionations. While sulfur isotope fractionations can be expected to be significantly smaller, the results should be qualitatively similar to those obtained in the oxygen isotope work.

The objectives of the present research are (1) to establish the existence of consistent and significant fractionation of sulfur isotopes between natural mineral pairs and indicate the order of magnitude of such fractionations, (2) to show that these fractionations can reasonably be the result of equilibrium exchange reactions in that they are temperature dependent and comparable to theoretical estimates of the order of magnitude of the effect, (3) to determine experimentally the equilibrium fractionation as a function of temperature between several sulfides and thereby establish a calibrated isotopic geothermometer for geologic materials containing sulfide assemblages in isotopic equilibrium, (4) to investigate the kinetics of sulfur exchange between sulfides and other sulfur bearing phases, and (5) to test for isotopic equilibrium and "freezing in" of isotopic fractionation factors under suitable geological conditions.
1.3. Definition of Terms

1.3.1. Δl values

The isotopic composition of a substance X is reported in the permil (‰) notation. \( \delta_X \) is the relative difference in the \( \frac{S^{32}}{S^{34}} \) ratio between X and an arbitrary standard in parts per thousand.

\[
\delta S^{34} (\%) = \frac{(\frac{S^{34}}{S^{32}})_X - (\frac{S^{34}}{S^{32}})_{Std.}}{(\frac{S^{34}}{S^{32}})_{Std.}} \times 1000
\]

All \( \delta \)'s are reported relative to the Caimon Diablo troilite standard. The \( \frac{S^{32}}{S^{34}} \) ratio of this standard is taken as 22.225 (Thode et al. 1961).

1.3.2. Fractionation Factors and Isotopic Equilibrium Constants

For an isotopic exchange reaction such as

\[ aA + bB' \rightleftharpoons aA' + bB \]

where A and B are molecules having some one element as common constituent and the superscript denotes the heavy isotope, the equilibrium constant \( K \) is defined as,

\[ K = \left( \frac{A'}{A} \right)^a \left( \frac{B'}{B} \right)^b \]
The difference in isotopic composition of two species A and B is measured in terms of the fractionation factor $\alpha$ defined as

$$a_{A-B} = \frac{(S^{32}/S^{34})_A}{(S^{32}/S^{34})_B}$$

If A and B have come to isotopic exchange equilibrium and if the two isotopes are randomly distributed among the sulfur positions in the molecules, the fractionation factor can be related to the equilibrium constant to a very good approximation through the relationship

$$\alpha^{(E)}_{A-B} = K_{A-B}^{1/n}$$

where $n$ is the number of atoms involved in the exchange. In order to be able to express equilibrium constants in terms of quantities actually measured in the laboratory, it simplifies matters to write down the exchange reactions such that only one atom is exchanged, as:

$$\frac{1}{2}FeS^{32}_2 + ZnS^{34} \rightleftharpoons \frac{1}{2}FeS^{34}_2 + ZnS^{32}$$

The equilibrium constant for this reaction as written is equal to the fractionation factor (at equilibrium)
\[ K_{\text{Py-Sp}} = \alpha_{\text{Py-Sp}}^{(E)} = \frac{(S^{32}/S^{34})_{\text{Zns}}}{(S^{32}/S^{34})_{\text{FeS}_2}} \]

or in terms of $\delta$ values

\[ K_{\text{Py-Sp}} = \alpha_{\text{Py-Sp}}^{(E)} = \frac{1 + \frac{\delta(\text{ZnS})}{1000}}{1 + \frac{\delta(\text{FeS}_2)}{1000}} \]

A typical value of $\alpha$ encountered in sulfur isotope exchange is 1.00X and, therefore, to a very good approximation $1000 \ln \alpha = X$. This permits the useful approximation

\[ 1000 \ln \alpha_{A-B} \approx \delta_A - \delta_B \]

$\Delta_{A-B}$ (Delta) is defined as equal to $1000 \ln \alpha_{A-B}$ and frequently used for convenience of notation.
CHAPTER 2

2. Mechanisms of Isotopic Fractionation

The variation in isotopic composition of sulfur (and other light elements) from various sources in nature testifies to the existence of mechanisms of fractionation during the geochemical cycle. Geologic conditions are complex and these mechanisms generally will involve a combination of fundamental physical and chemical processes which may operate in competition. However, assuming geologic phenomena to be guided by physical laws of matter, these processes must nevertheless constitute the fundamentals of natural physico-chemical fractionation mechanisms.

Several physical and chemical processes may lead to isotopic fractionation. The former which depend exclusively upon the physical properties of the materials (often directly on the difference in isotopic mass) include processes of diffusion and adsorption. Slight variations in chemical properties of isotopic compounds arising from differences in thermodynamic functions may lead to isotope separations during unidirectional and exchange reactions.
Physiocochemical fractionation processes thought to be operative in the geochemical cycle of sulfur are discussed below. In the absence of sufficient information on geologic conditions, it is often difficult to make a quantitative assessment of their importance.

2.1. Chemical Fractionation Processes

The thermodynamic properties of isotopic substances depend largely on the vibrational frequencies of the molecules. These are directly dependent on the masses of the atoms constituting the molecule. There exists, therefore, a theoretical basis for the difference in chemical properties of isotopic substances and isotope separation during chemical reaction.

Fractionation due to differences in chemical properties may arise when two chemical systems containing an isotopic element coexist in chemical equilibrium (equilibrium isotope effect) or when one or more such systems change identity in the course of a chemical reaction (kinetic isotope effect).

2.1.1. Equilibrium Isotope Effect

The principles governing the distribution of stable isotopes among equilibrium components of a system are well understood. Fractionation arises directly from slight differences in the thermodynamic constants of isotopic molecules which affect the equilibrium
constant for an exchange reaction.

An exchange reaction of the type

\[ \text{H}_2\text{S}^{34} + \text{S}^{32} \text{O}_4 \rightleftharpoons \text{H}_2\text{S}^{32} + \text{S}^{34} \text{O}_4 \]

can be treated theoretically in terms of statistical mechanics as a system of particles in dynamic equilibrium. Such a theoretical treatment was first put forward by Urey (1947) and has subsequently been modified and expanded by numerous authors.

For the above reaction, using data obtained from molecular spectroscopy, the equilibrium constant can be calculated to have the value 1.071 at 25°C (Tudge & Thode, 1950).

Under conditions of isotopic equilibrium therefore, \( \text{S}^{34} \) will be favoured in the \( \text{S}_4^{32} \) by 71% over the associated \( \text{H}_2\text{S} \). The theoretical treatment does not consider the time required to attain equilibrium or whether mechanisms exist whereby equilibrium may be achieved.

Equilibrium exchange reactions constitute an important mechanism of fractionation in the geochemical cycle of sulfur. Exchange may take place between different sulfur species in the same state (solid, liquid, gaseous), between different sulfur species in different states, or between identical sulfur species in different states.
Because of the change in valency, oxidation-reduction reactions can be expected to produce larger isotope effects than exchange reactions between species in the same valence state.

Isotope effects arising from equilibrium exchange reactions are strongly temperature dependent, the fractionation often being related to temperature through an expression of the kind

\[ 10^3 \ln \alpha = \frac{A}{T^2} + B \]

(section 3.1) where A and B are constants and T is the absolute temperature.

2.1.2. Kinetic Isotope Effect

The large isotope effects involved in the biogeochemical sulfur cycle are for the most part non-equilibrium kinetic effects. Several other instances of unidirectional processes operative in the geochemical sulfur cycle would appear to exist, often potentially capable of producing significant isotope fractionation.

Fractionation arises directly from the fact that chemical reaction rates are mass dependent and that one isotopic species will react more rapidly than another. In general, the molecule containing the lighter isotope will have the faster reaction rate. Consequently,
the first products formed will be enriched in one isotope, the degree of enrichment (in a closed system) decreasing as the reaction goes to completion.

A reaction such as the chemical reduction of sulfate to sulfide can be considered as two separate reactions with different rate constants.

\[
S^{32}_4 \xrightarrow{k_1} H_2S^{32} \quad \text{and} \quad S^{34}_4 \xrightarrow{k_2} H_2S^{34}
\]

The ratio of the two rate constants \( k_1 / k_2 \) is equal to the kinetic isotope effect.

Bigeleisen (1949) has treated the problem of the kinetics of chemical reaction rates of different isotopic molecules theoretically in terms of statistical mechanics. Such theoretical treatment employs as model involving one or more 'activated complexes' along the coordinates of the reaction. Quantitative calculations of kinetic isotope effects are often limited by the lack of information on the structure of these activated complexes and recourse has to be taken to experimentation (Harrison and Thode, 1957). Experimentally
$^{32}\text{S}_{4}$ was found to react 2.2% faster than $^{34}\text{S}_{4}$ leading to an isotopic enrichment by 22% of the lighter isotope in the sulfide phase.

In nature the reduction of $\text{SO}_{4}^{2-}$ to $\text{H}_2\text{S}$ takes place extensively in the shallow muds at the bottom of lakes and seas in the presence of anaerobic bacteria. This reduction process is enzyme-catalyzed and more complicated than the direct inorganic reduction, apparently taking place in a series of steps each of which may control the overall reaction rate, depending on environmental conditions (Nakai 1964). Distinct kinetic isotope effects are associated with each of these reactions and consequently the isotope effect associated with the rate controlling reaction step will become dominant. Hence, it would appear that for a complex reaction the associated kinetic isotope effect may be strongly influenced by environmental conditions.

2.1.3. Others

Dynamic chemical processes of solution and precipitation may also be expected to affect isotopic ratios. The tendency for ions to dissolve or precipitate (in the absence of crystal boundary effects) should be determined largely by their chemical potential. It would, therefore, appear likely, inasmuch as the free energies of isotopic molecules are approximately proportional to the square roots of
their masses, that the heavier isotope could favour the undissolved
or precipitated phase and the lighter isotope the dissolved phase, al-
though in either case the preference is probably very slight. The
effect, however, is unidirectional and for a continued recycling such
as during repeated erosion and sedimentation would be cumulative.

It would appear conceivable that bonding forces within
lattice structures might depend upon quantities sensitive to the iso-
topic composition of the ions. Consequently, chemical fractionation
may take place during formation of a mineral. This fractionation
would show a dependence upon chemical and crystalline structure
and would be unaffected by the mode of origin of the mineral.

2.2. Rayleigh Processes

Through a process of recycling in a limited reservoir,
the simple isotopic fractionation factor (equilibrium or kinetic)
may be multiplied many times.

While the process applies to any type of reaction which
can undergo recycling, it is most readily visualised for the case
of crystallization from a solution.

Consider an isolated quantity of solution crystallizing at
constant temperature. Crystallization is accompanied by a simple
isotope fractionation of constant magnitude during the entire process.
It is assumed that no isotopic exchange takes place between the crystalline phase and the solution. The Rayleigh formula takes the form:

\[
\frac{R_F}{R_o} = f(1 - \alpha)
\]

Where

\(f = \text{Fractionation of the initial liquid remaining at any stage of the crystallization process.} \quad f = 1 \text{ at the start of the process and approaches 0 as crystallization proceeds.}\)

\(\alpha = \text{Simple fractionation factor accompanying crystallization.}\)

\(R_F = \text{Isotopic composition of the residual solution.}\)

\(R_o = \text{Isotopic composition of solution before crystallization is initiated.}\)

Also, for the solid phase,

\[
\frac{R_S}{R_o} = \frac{1 - f^\alpha}{1 - f}
\]

Where

\(R_S = \text{Isotopic composition of the solid.}\)
Quantitative applicability of the above formulae rests on the following requirements:

i) The fractionation factor remains constant throughout the entire process. For isotopic exchange reactions this would essentially imply that the temperature remains constant. Furthermore, the structure of the liquid and solid should not change nor their chemical composition.

ii) The solid phase should not exchange isotopically with the remaining fluid.

iii) The system must be closed.

It is obvious that these stringent requirements are never met under geologic conditions. Semi-quantitative results can, however, be obtained as is demonstrated by Dansgaard (1954) for oxygen isotope fractionation during water evaporation and by Taylor and Epstein (1963) for the solidification of the Skaergaard intrusion.

In sulfur isotope geochemistry the fractionation found accompanying the process of bacterial sulfate reduction, often is considerably larger than expected from theoretical and experimental information. This is thought to reflect the operation of Rayleigh-type recycling processes in limited reservoirs especially during diagenesis.
Measurements in the Uinta Basin of Utah (Harrison and Thode, 1958) where large scale sulfate reduction appears to have taken place, show a strong correlation between sulfur isotope ratios and stratigraphic level indicative of isotopic enrichment in a closed sedimentary basin.

2.3. Physical Fractionation Processes

Physical processes which are directly mass dependent can conceivably produce isotope separation. These are essentially processes of diffusion and in nature may be brought about by (i) temperature gradients, and (ii) gradients in osmotic pressure. It is often difficult to make quantitative deductions as to the importance of mechanisms of diffusion in isotope separation because of lack of theoretical treatment or experimental data. Arguments can be put forward, however, giving some idea of the time required to produce a certain minimum effect. The processes themselves cannot be ruled out, for given enough time, any amount of separation by diffusion is possible. The limiting factor in considering fluids is the time required to cool down to crystallization temperature, and in the case of solids, the age of the mineral.
2.3.1. Diffusion

Gradients in osmotic pressure between various phases of solutions or melts will invariably produce diffusion of one substance through another. A theoretical treatment for the one dimensional diffusion of isotopic ions from an infinite planar source in terms of concentrations of constituent isotopic phases is given by Grant (1954).

The diffusion coefficient \( D \) for a system of isotopic ions through a stable melt or solution should be given to the correct order of magnitude by the Stokes-Einstein formula.

\[
6 \pi \eta aD = kT
\]

which gives a value of about

- \( 5 \times 10^{-10} \text{ cm}^2/\text{Sec at 1000}^\circ\text{C} \) for magma of \( 10^3 \) poises
- \( 5 \times 10^{-3} \text{ cm}^2/\text{sec at 1000}^\circ\text{C} \) for solution of \( 10^{-4} \) poises
- \( 1.2 \times 10^{-3} \text{ cm}^2/\text{sec at 1000}^\circ\text{C} \) for solution of \( 10^{-4} \) poises

Now the diffusion coefficient is related to the mobility of the ions \( (\mu) \) by the Nernst-Einstein relation

\[
D = \mu kT
\]

and all other things being the same, the mobility of an ion is approximately proportional to the square root of its mass. If the concen-
t ration \( c_o \) of a given type of molecule throughout the fluid is initial-
ly uniform before migration begins, then its value at a distance \( x \)
from the plane \( x = 0 \) at a later time \( t \) may be found by an expression
of the form

\[
c(x, t) = c_o \text{ erfc} \left( \frac{X}{2\sqrt{Dt}} \right)
\]

Isotopic abundance ratios will therefore be represented by functions
of the type

\[
\varphi = \frac{c'}{c} = \frac{c'}{c_o} \text{ erfc} \xi'
\]

where

\[
\xi = \frac{x}{2\sqrt{Dt}}
\]

In general

\[
\frac{\xi'}{\xi} \approx \left( \frac{m'}{m} \right)^{1/4}
\]

writing

\[
\xi' = \xi + \Delta \xi
\]

\[
\frac{\Delta S}{S_o} = \frac{2}{\sqrt{\pi}} \cdot \frac{e^{-\xi^2}}{\text{erf} \xi} \cdot \Delta \xi
\]

where \( \Delta S \) is the change in original relative abundance \( (S_o) \) of sulfur
isotopes.
For the diffusion of isotopic HS⁻ ions \( \xi' = 1.015 \xi \)
(the highest ratio for a realistic sulfur species in hydrothermal solution). Highest accuracy of present mass spectrometers is about 0.01%. Thus, changes in relative abundance of sulfur isotopes due to diffusion becomes just perceptible when \( \xi \) is such that

\[
G(\xi) = \text{erfc} \xi - 30 \pi^{-\frac{1}{2}} \xi e^{-\xi^2} = 0
\]

This function has only one zero, at \( \xi = 2.2 \). Therefore, the relation that is implied between \( x \) and \( t \) is

\[
x = 4.4 \sqrt{Dt}
\]

Therefore, at a distance of only 1 cm. from the original boundary of the diffusing material, assuming no convection or flow, diffusion must proceed before producing a detectible effect in sulfur isotope ratios, for the following lengths of time:

(a) Magma 3 years  
(b) Hydrothermal solution at 1000°C 10 secs.  
(c) Hydrothermal solution at 100°C 40 secs.

This mechanism would appear, therefore, to be of considerable importance in producing separation of sulfur isotopes in the geologic environment. Movement of hydrothermal solutions will involve considerable
turbulence and convective mixing which will decrease or possibly obliterate the diffusion effect.

### 2.3.2. Thermal Diffusion (Soret Effect)

The existence of thermal gradients in fluids leads to a diffusion process in which the lighter molecules migrate towards the warmer and heavier molecules towards the cooler regions. For isotopic molecules this redistribution in molecular concentrations will produce isotopic fractionation.

Lovering (1950) has compared the temperature distribution adjacent to a vein with the diffusion fronts. Since the heat conductivities are so much larger than ionic or molecular diffusion coefficients, diffusion takes place under nearly isothermal conditions. Consequently, thermal diffusion is of no importance under hydrothermal conditions.

### 2.3.3. Solid Diffusion

Solid state diffusion constants are extremely small and consequently, rates of ionic diffusion will be very much slower than in fluids. On the other hand, time limitations are not nearly so severe since diffusion process will be operative during entire geological time subsequent to crystallization of the solid.
A detailed investigation of the effect (Senftle and Bracken 1955) indicates that the mechanism of solid diffusion cannot produce significant isotope separation.
CHAPTER 3

ISOTOPIC EQUILIBRIUM THEORY

The application of principles of statistical mechanics makes it possible to calculate equilibrium constants for isotope exchange reactions and hence predict the quantitative distribution of stable isotopes between component phases of a system. Under favourable conditions it is possible to calculate isotopic fractionation factors and their temperature dependence, and if this is not possible, theory can give qualitative information as to the nature of anticipated fractionations. Urey (1947) has outlined these calculations, initiating research into the field of stable isotope geochemistry. Since then many accounts have been published, among the more recent of which are Mayer (1958) and Vojta (1960). Calculations for exchange reactions involving sulfur isotopes have been published by Tudge and Thode (1950) and Sakai (1957 and 1968).
3.1. **Ideal Gases**

In a system composed of two phases in equilibrium whose molecules A and B have some element in common, the isotope exchange reaction may be written as,

\[ aA + bB \rightleftharpoons aA' + bB \]  

the superscript denoting the molecule containing the rarer (and usually heavier) isotope. A general expression for the equilibrium constant for this reaction can readily be derived (Urey 1949, Tudge and Thode 1950, and others) and takes the form,

\[
K = \left( \frac{Q_A^a}{Q_A} \right)^a \left( \frac{Q_B^b}{Q_B} \right)^b \cdot e^{\frac{a\Delta E^0_A - b\Delta E^0_B}{RT}} \cdot e^{\frac{(a\Delta V_A - b\Delta V_B)}{RT}}
\]  

(3.2)

where

- \( Q_A \) = partition function of molecule A
- \( \Delta E^0_A = E_A^{1^0} - E_A^0 \) = difference in "zero point energy" of the isotopic molecules of type A.
- \( \Delta V_A = \) difference in volume of isotopic molecules A in the ground state.

Instead of taking \( E_0^o \) as the zero point energy, it is convenient to take \( E_0^o \) as the bottom of the potential energy function for the molecule. Since the potential energy functions are to a very good approximation
identical for isotopic molecules, \( E^0_A \) equals \( E^0_A \) and \( E^0_B \) equals \( E^0_B \) so that the zero point energy term in equation 3.2 is eliminated.

Usually the change in volume due to isotopic substitution is neglected because it would appear to influence the equilibrium constant only to a minor extent. (This approximation is discussed further in the next section.) Therefore,

\[
K = \left( \frac{Q'_A / Q_A}{Q'_B / Q_B} \right)^a \left( \frac{Q'_B / Q_B}{Q'_A / Q_A} \right)^b
\]  

(3.3)

so that the calculation of the equilibrium constant involves only the evaluation of the ratios of the partition functions of the isotopic molecules.

The method that is usually adopted in calculating these ratios makes use of the assumption that the kinetic energy of each molecule can be separated completely into its various components, viz., translational, rotational, vibrational, electronic, nuclear, etc. and that there is no coupling or interaction between these. (Independence of degrees of freedom.) Furthermore, the internal degrees of freedom (electronic and nuclear) are neglected so that the partition function is approximated by,
\( Q = Q_{\text{tr}} \cdot Q_{\text{vib}} \cdot Q_{\text{rot}} \)  

where

- \( Q_{\text{tr}} \) = translational partition function
- \( Q_{\text{vib}} \) = vibrational partition function
- \( Q_{\text{rot}} \) = rotational partition function

Using the approximation of independent degrees of freedom the partition function for a system of non-interacting particles (molecules) can be expressed in terms of the symmetry numbers, moments of inertia and frequencies of the vibrational modes of the molecules. Through use of the Teller Redlich product rule, Urey (1947) eliminates the moments of inertia and arrives at an expression in terms of the fundamental eigen frequencies \( \nu_i \) of the internal vibrations of the molecule.

\[
\frac{''Q'}{''Q} = \frac{\sigma}{\sigma'} \left( \prod_{i} u_i^1 \frac{u_i'}{u_i} \frac{-u_i'\frac{1}{2}}{e^{-u_i'\frac{1}{2}}} \cdot \frac{1-e^{-u_i'}}{1-e^{-u_i'}} \right)^{3n-6} 
\]

(3.5)

Where "\( Q' \)" is the so-called reduced partition function related to \( Q \) through the relation

\[
\frac{''Q'}{''Q} = \frac{Q'}{Q} \left( \frac{m}{m'} \right)^{3n/2} 
\]
(In any chemical reaction the ratio of masses will cancel)

\[ \sigma = \text{symmetry number of the molecule} \]

\[ u_i = \frac{h \nu_i}{kT} \]

\( m = \text{atomic weight of the atom considered} \)

\( \nu_i = \text{vibrational frequency of the } i\text{'th mode} \)

\( h = \text{Planck's constant} \)

\( k = \text{Boltzmann's constant} \)

\( T = \text{absolute temperature} \)

The symmetry numbers \( \sigma \) are introduced into the expression because isotopic substitution may lower the symmetry of the molecule. This would cause a splitting of degenerate rotational energy levels and substantially alter the rotational contribution to the partition function.

The summation in equation (3.5) extends over \( 3n-6 \) modes of vibration (the other 6 degrees of freedom represent translation and rotation) for a nonlinear molecule or \( 3n-5 \) modes for a linear molecule.

A quantum mechanical treatment by Bigeleisen and Mayer (1947) yields an identical expression without invoking the Teller-Redlich rule. For the evaluation of equation (3.5) two simplifications are widely used.
Urey Approximation

\[ \ln \frac{Q'}{Q} = \ln \frac{\sigma}{\sigma'} + \sum_{i} \frac{3n-6}{u_i} \ln \frac{u_i'}{u_i} + \sum_{i} \delta_i \coth x_i \] (3.6)

where

\[ x_i = \frac{u_i + u_i'}{4} \quad \text{and} \quad \delta_i = \frac{u_i - u_i'}{2} \]

Bigeleisen Approximation

\[ \frac{\sigma'}{\sigma} \frac{Q'}{Q} = 1 + \sum_{i} G(u_i) \Delta u_i \] (3.7)

where

\[ G(u_i) = \frac{1}{2} - \frac{1}{u_i'} + \frac{1}{e^{-u_i'} - 1} \quad \text{and} \quad \Delta u_i = u_i - u_i' \]

(This notation differs slightly from that of Bigeleisen who denotes the lighter isotopic molecule as primed. Values for the function \( G(u_i) \) are calculated and tabulated by Biegeleisen and Mayer.)

If the \( \nu_i \) are known (usually from infrared and Raman spectra) then the isotopic shifts can generally be calculated. Force constants for the molecule can be calculated from a knowledge of the molecular structure and the known \( \nu_i \)'s. These force constants can
then be used to obtain the vibrational frequencies of the isotopic molecules.

In the calculation of the partition function ratios, Bigeleisen's expression is somewhat easier to use, because tabulated values of the function $G(u_i)$ are available. Theoretically, Urey's expression is the more accurate but for practical purposes the difference in results between the two approximations appears negligible.

Rees (1964) compares values obtained using the two approximations with those derived using the exact expression for the exchange of carbon between carbon dioxide and carbonate ion. These results are reproduced in Table 3.1.

Table 3.1

Calculations of Partition Function Ratios and the $^{13}$C exchange equilibrium constant for the $\text{CO}_2 - \text{CO}_3^{--}$ System at $25^\circ$C

<table>
<thead>
<tr>
<th>Equation</th>
<th>Exact</th>
<th>Urey Approximation</th>
<th>Bigeleisen Approximation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{Q(^{13}\text{C}_3)}{Q(^{12}\text{C}_3^-)}$</td>
<td>1.19263</td>
<td>1.1926</td>
<td>1.1750</td>
</tr>
<tr>
<td>$\frac{Q(^{13}\text{C}_2)}{Q(^{12}\text{C}_2)}$</td>
<td>1.18371</td>
<td>1.1837</td>
<td>1.1678</td>
</tr>
<tr>
<td>$K$</td>
<td>1.00754</td>
<td>1.0075</td>
<td>1.0062</td>
</tr>
</tbody>
</table>
3.1.1. **Temperature Dependence**

If the $u_i$'s are small, i.e. either the frequency low or the temperature high, equation (3.5) can be readily expanded to give,

$$
\frac{Q'}{Q} = \frac{\sigma}{\sigma'} \left( 1 - \frac{1}{24} \sum (u_2^2 - u_1^2) \right)
$$

Similarly, it is found for low $u_i$'s that the function $g(u_i)$ can be closely approximated by

$$
g(u_i) = u_i/12
$$

so that equation (3.7) under these conditions takes the form

$$
\frac{Q}{Q'} = \frac{\sigma}{\sigma'} \left( 1 - \sum \frac{\Delta u_i u_i}{12} \right)
$$

It should be noted that the only physical variable in these expressions is the temperature $T$. Since $u_i$ varies as $1/T$ it is immediately apparent that both the Urey and Bigeleisen equations predict that the contribution to the partition function from a single frequency at high temperatures (or for low frequencies) varies approximately as $1/T^2$. This may not necessarily be the case for the total vibrational partition function, which is the sum over all such frequencies. Calculations show the relationship to hold approximately for molecules such as $H_2S$ with vibrational frequencies of 2611, 1290 and 2684 cm$^{-1}$ respectively.
It can therefore be readily expected that for sulfides, where the frequencies are much smaller (Sakai 1968), this relationship will be observed even more closely.

### 3.1.2. Cross-over Temperature

It is fairly common that a phase which concentrates the light isotope at low temperatures, will concentrate the heavy isotope at high temperatures. This phenomenon is called "cross-over". Since the partition function ratio of any isotopic phase is a function of the frequency of vibration, the difference in the frequency of vibration of the isotopic species, and the number of degrees of vibrational freedom, a number of combinations of these factors can cause the equilibrium constant to change from less than unity to greater than unity as the temperature is varied.

### 3.1.3. Pressure Dependence

Returning to equation (3.2) and taking $E_o$ as the bottom of the potential energy curve, the equilibrium constant $K$ is given by the expression

$$K = \frac{Q_A^a}{Q_A^b} \cdot \frac{Q_B^b}{Q_B^a} \cdot e^{\frac{a\Delta V_A - b\Delta V_B}{RT}}$$  \hspace{1cm} (3.10)
where \( \Delta V_A \) is the difference in volume of isotopic molecules A

therefore

\[
\frac{\partial \ln K}{\partial P} = \frac{(a\Delta V_A - b\Delta V_B)}{RT} \quad (3.11)
\]

or since

\[
\frac{\partial \ln K}{\partial P} \ll 1
\]

\[
\frac{\partial K}{\partial P} \approx \frac{(a\Delta V_A - b\Delta V_B)}{RT} \quad (3.12)
\]

The fractional change in volume (\( \Delta V \)) can be estimated by assuming that it is approximately equal to the cube of the fractional change in distance between the centre of the molecule and the distance to the furthest position of any constituent atom. The latter factor can be evaluated in terms of the difference of the average squares of the amplitude of the stretching mode of vibration. The following expression is obtained (Joy & Libby, 1960, Libby 1961)

\[
\Delta V = 3 \left[ \sqrt{\omega} - \sqrt{\omega'} \right] \left( \frac{hc}{2k} \right) V^{2/3} \quad (3.13)
\]

where \( V \) is the average volume per molecule in the ground state at the temperature considered, \( \omega \) and \( \omega' \) (in cm\(^{-1}\)) are the frequencies of the isotopic molecules for the stretching mode of vibration, \( h \) is Planck's constant, \( c \) is the velocity of light, and \( k \) is the restoring force constant.
To estimate the effect of pressure on the equilibrium constant for equilibrium fractionation between sulfides, consider the reaction

\[ \text{ZnS}^{32} + \text{PbS}^{34} \rightleftharpoons \text{ZnS}^{34} + \text{PbS}^{32} \]

The fractional change in volume and the pressure dependence of the equilibrium constant have been calculated for this exchange reaction from values summarized in Table 3.2.

The frequencies of vibration of sphalerite and galena are not well known, but their order of magnitude can be estimated at 400 and 200 cm\(^{-1}\) respectively (Sakai 1968). The frequencies of the molecules enriched in the heavy isotopes can be calculated using the reduced masses of the respective isotopic molecules. In the absence of any information as to the magnitude of the force constants, these are assumed equal to \(5 \times 10^5\) dynes cm\(^{-1}\). Molecular volumes are obtained by dividing the volume of the unit cell (Robie 1966) by the number of formula units it contains.
Table 3.2
Lattice Properties of Sphalerite and Galena

<table>
<thead>
<tr>
<th>Mineral</th>
<th>( \omega ) (( \text{cm}^{-1} ))</th>
<th>( \omega' ) (( \text{cm}^{-1} ))</th>
<th>( k ) (( \text{dyne cm}^{-1} ))</th>
<th>Volume unit cell (( \text{cm}^3 ))</th>
<th>( V_3 ) (( \text{cm}^3 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphalerite</td>
<td>400</td>
<td>392.06</td>
<td>( 5 \times 10^5 )</td>
<td>( 158.28 \times 10^{-24} )</td>
<td>( 39.57 \times 10^{-24} )</td>
</tr>
<tr>
<td>Galena</td>
<td>200</td>
<td>194.62</td>
<td>( 5 \times 10^5 )</td>
<td>( 209.16 \times 10^{-24} )</td>
<td>( 52.29 \times 10^{-24} )</td>
</tr>
</tbody>
</table>

Hence,

\[
\Delta V_{\text{Sphalerite}} = 3 \left[ (200)^{1/2} - (194.62)^{1/2} \right] \left[ \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{2.5 \times 10^5} \right] \left( 39.57 \right)^{2/3} \times 10^{-16}
\]

\[= 6.98 \times 10^{-4} \text{ cm}^3 / \text{mole}\]

\[
\Delta V_{\text{Galena}} = 3 \left[ (400)^{1/2} - (392.06)^{1/2} \right] \left[ \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{2.5 \times 10^5} \right] \left( 52.29 \right)^{2/3} \times 10^{-16}
\]

\[= 6.07 \times 10^{-4} \text{ cm}^3 / \text{mole}\]

Therefore,

\[
\frac{\partial K}{\partial P} = (6.98 - 6.07) \times 10^{-4} / RT
\]

\[= 1.15 \times 10^{-8} \text{ atm}^{-1} \quad \text{(at room temperature)}\]
A pressure difference of $10^4$ atm. (10 kilobars) would therefore be needed to produce a detectable effect on the equilibrium constant.

3.2. Limitations of the Theoretical Treatment

3.2.1. Ideal gas assumption

Equation (3.5) is only valid in considering a system of non-interacting particles (ideal gas). Approximations involved in derivation of this expression are discussed in detail in Hill (1960) and the more important of these will be briefly outlined.

i) Molecular Non-interaction: Intermolecular forces are assumed negligible. Consequently the vibrational contributions to the partition function of an ideal gas are just those of $3n-6$ ($3n-5$) one-dimensional harmonic oscillators.

ii) Independence of Degrees of Freedom: It is assumed that the degrees of freedom of the molecule are rigorously separable and non-interacting. Translational motion is always separable to an excellent approximation. Separation of rotational and vibrational degrees of freedom is only possible on the assumption that the molecule has a fixed internuclear distance (rigid rotor model).
3.3.2. Anharmonicity

For the vibrational contribution to the partition function the harmonic oscillator model is used. The vibrations of real molecules are not harmonic but the approximation is adequate at moderate temperature. Anharmonicity effects can be of importance at high temperatures and need to be taken into consideration. Vojta (1961) has treated the anharmonic part and gives an expression of the form

$$\left(\frac{Q'}{Q}\right)_{\text{Anharmonic}} = \left(\frac{Q'}{Q}\right)_{\text{harmonic}}$$

+ (Anharmonic correction to zero point energy)

+ (Anharmonic correction for vibrational levels above the ground state).

For the majority of molecules only the observed fundamental frequencies are available, since it is only in a few cases that anharmonic constants have been studied. It is, however, found that the harmonic approximation is not greatly in error when considering the ratio of partition functions for isotopic molecules provided the observed fundamental frequencies are used for the purpose of calculation rather than zero order frequencies.
Anharmonic corrections for the isotope exchange between carbon dioxide and water vapor have been calculated by Bottinga (1968) and are listed in Table 3.3.

### Table 3.3

<table>
<thead>
<tr>
<th>Temp. °K</th>
<th>273.15</th>
<th>273.15</th>
<th>800</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>ln \left( \frac{\nu Q'}{\nu Q} \right)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.25382</td>
<td>0.20046</td>
<td>0.04739</td>
<td>0.04098</td>
</tr>
<tr>
<td>Carbon</td>
<td>-0.00331</td>
<td>-0.00327</td>
<td>-0.00113</td>
<td>-0.00112</td>
</tr>
<tr>
<td>Harmonic Terms</td>
<td>0.00010</td>
<td>0.00012</td>
<td>0.00025</td>
<td>0.00028</td>
</tr>
<tr>
<td>Zero-Point anharmonic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Excited-level anharmonic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.25061</td>
<td>0.19732</td>
<td>0.04651</td>
<td>0.04014</td>
</tr>
</tbody>
</table>

3.2.3. **Intramolecular Fractionation**

The fractionation constant for an isotope exchange reaction is equal to \( K \) when only one nucleus in each molecule is exchanged. When more than one atom of the isotopic element is contained in one or both of the molecules, it is generally assumed that the heavy isotope
is distributed randomly throughout the assemblage, or that (a priori) the probability of exchange of this isotope amongst molecules of species A, for example, is governed by the symmetry numbers alone of the various isotopic configurations of A.

This assumption, the rule of the geometric mean, has been discussed by Bigeleisen (1955). Formal justification requires knowledge of the vibrational frequencies of all the isotopically different molecules. Such information is seldom available and the effect can consequently not be evaluated. As Bigeleisen shows, however, it is reasonable to assume that the role of the geometric mean holds to the extent required for calculating fractionation factors for structurally equivalent atoms other than hydrogen.

3.3. Liquids

The equilibrium constant for an isotopic exchange reaction between a gas and a liquid phase is easily evaluated provided information is available about the vapour pressure of the normal and the isotopic liquid. Let $a_1$ be the fractionation factor for a reaction such as

$$\text{SO}_2^{32}(g) + \text{H}_2\text{S}^{34}(1) = \text{SO}_2^{34}(g) + \text{H}_2\text{S}^{32}(1)$$
and \( \alpha \) is the fractionation factor for the corresponding reaction

\[
\text{SO}_2^{32}(g) + \text{H}_2\text{S}^{34}(g) = \text{SO}_2^{34}(g) + \text{H}_2\text{S}^{32}(g)
\]

then

\[
\alpha_1 = \alpha \frac{P_{\text{H}_2\text{S}^{34}}}{P_{\text{H}_2\text{S}^{32}}}
\]

where \( P_{\text{H}_2\text{S}^{34}} \) = vapor pressure of \( \text{H}_2\text{S}^{34} \).

Theoretical calculations of vapor pressures of isotopic liquids are difficult and have been successfully undertaken only for argon, neon, etc. Occasionally experimental information is available which takes the form,

\[
\log \frac{P_{A'}}{P_{A}} = \text{constant} \cdot \frac{T}{T} - \text{constant}
\]

Theoretically the light isotope should always have the higher vapor pressure. Yet, numerous cases are known where the light isotope has the higher vapor pressure at the low temperature, but the heavy isotope has the higher vapor pressure at the high temperature (Bigeleisen 1960).
3.4. **Solids**

Calculations based on the Urey and Bigeleisen formulae for partition function ratios, show discrepancies when applied to solids, e.g. McCrea (1950). In the solid state the distance between neighbouring atoms or molecules is so small that the forces which they exert upon each other are considerable. The system can therefore no longer be treated as consisting of independent molecules or degrees of freedom and it is necessary to modify the theoretical treatment.

Translations in solids are insignificant and rotations are normally absent or of a restricted nature. The restricted nature of the vibrations makes it possible to treat them in this type of calculation as harmonic oscillators (Stockmayer 1957).

It is therefore sufficient to consider only the contribution of vibrational degrees of freedom to the partition function. In general, the free energy of a thermodynamic system is given by

\[ F = -kT \ln Q \]  \hspace{1cm} (3.14)

Treating only that part of the free energy due to vibrational degrees of freedom

\[ F_{\nu} = -kT \ln Q_{\nu} \]  \hspace{1cm} (3.15)
where
\[ Q_{v} = \prod_{i} Q(v_{i}) \]  \hspace{1cm} (3.16)

\[ \prod_{i} Q(v_{i}) \] is the product over all states of an independent harmonic oscillator of frequency \( v_{i} \). A crystal consisting of \( N \) strongly coupled atoms can be considered mechanically equivalent to a system of \( 3N \) independent oscillators, so that the product extends over \( 3N \) oscillators. 3 degrees of freedom each are required to describe the simple translation of the crystal as a whole and its rotation around the center of mass. It follows that 6 \( v_{i}'s \) vanish so that the product should be extended only over \( 3n-6 \) terms. However, since six is a very small number compared to \( 3n \), this difference may be neglected.

The energy of a state \( n \) of the total crystal (Mayer and Mayer, 1960, p. 239) is given by

\[ E_{n} = \sum_{1}^{3N} \frac{(n_{i}+1/2)}{h} v_{i} \]  \hspace{1cm} (3.17)

and the partition function of the system becomes a product of the partition functions for each individual oscillator,
\[ Q_v = \sum_n e^{-\frac{E_n}{kT}} \] (3.18)

\[ = \prod_{i=1}^{3N} \frac{\frac{-h\nu_i}{kT}}{e^{\frac{-h\nu_i}{kT}} - 1} \] (3.19)

or,

\[ \ln Q = -\prod_{i=1}^{3N} \frac{h\nu_i}{2kT} + \ln \left( 1 - e^{-\frac{h\nu_i}{kT}} \right) \] (3.20)

For a continuous spectrum of frequencies it is possible to replace the summation terms by integrals over the distribution function \( g(\nu) \) so that

\[ \ln Q(\nu) = \frac{1}{2kT} \int h\nu \cdot g(\nu) d\nu + \int \ln \left( 1 - e^{-\frac{h\nu}{kT}} \right) g(\nu) d\nu \] (3.21)

Exact theoretical calculation of the frequency spectrum may present great difficulties; in a periodic lattice this involves the evaluation of the eigenvalues of matrices, the dimensions of which are equal to the number of degrees of freedom. Elements of these matrices depend on the existence of satisfactory force constant models. In practice, even with the use of computers, such calculations can only take into account the effect of third order nearest neighbours in the most simple solids.
Instead of considering the total frequency distribution \( g(\nu) \) for all the vibrational degrees of freedom for a solid, it is common procedure when calculating partition function ratios to break down the vibrational modes into separate branches. Each of these can be approximated individually by a simple frequency distribution (Debye or Einstein). It is assumed that such branches are non-interacting and their individual contributions can be summed directly to give the total vibrational contribution to the partition function ratio.

A typical solid can be considered as consisting of vibrational units (cells) located at points in a periodic lattice. These cells are chosen arbitrarily and commonly correspond to the unit cell, multiples thereof, or individual "molecules".

The lattice modes of vibration of such a solid may be subdivided into acoustical, optical and librational modes. The optical branches are considered to contain only a narrow range of frequencies; these are approximated to a single average frequency and their contribution to the partition function ratio evaluated by means of Einstein functions. Librational modes are similarly approximated by Einstein functions while the contribution of the acoustical vibrational is evaluated by means of Debye functions. In molecular crystals containing strongly bonded groups such as, for instance, \( \text{CO}_3 \) an additional
"internal" mode is used to represent the modes of vibration of the molecular ion. Such strongly bonded molecular groups are not present in sulfides and strictly speaking, vibrations cannot be resolved into distinct lattice and internal modes.

In this type of approach it is necessary to calculate the frequencies for each mode of vibration from experimental information directly applicable to that mode. It is, for example, impossible to use the Debye temperature for calcite to calculate the contribution of the acoustical mode alone since the Debye temperature is a function of all the modes of vibration.

3.5. Partition Function Ratios for Sulfide Minerals

In the absence of sufficient spectroscopic data, it is impossible to calculate accurately the partition function ratios for sulfide minerals. The order of magnitude of the effect can, however, be readily estimated from crude models.

Values are reported by Sakai (1968) for the sulfides sphalerite, galena and pyrite (Table 3.4). Calculations are based on a subdivision of the vibrational modes into acoustical and optical branches each of which is assumed to represent 3N degrees of freedom. Experimentally determined frequencies are used to evaluate the
contribution of the optical modes for sphalerite and galena, while an approximate frequency is calculated for pyrite. Acoustical modes are evaluated from a knowledge of the Debye temperature.

Table 3.4

Calculated values of $10^3 \ln \alpha$ (in permil) (Sakai 1968)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS$_2$(1/2)</td>
<td>18.4</td>
<td>10.9</td>
<td>7.0</td>
<td>4.8</td>
<td>3.6</td>
<td>2.7</td>
</tr>
<tr>
<td>ZnS</td>
<td>13.4</td>
<td>8.0</td>
<td>5.2</td>
<td>3.6</td>
<td>2.6</td>
<td>2.0</td>
</tr>
<tr>
<td>PbS</td>
<td>3.6</td>
<td>2.0</td>
<td>1.3</td>
<td>0.9</td>
<td>0.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>
CHAPTER 4

FRACTIONATION IN NATURAL SULFIDE ASSEMBLAGES

4.1. Review of Observed Fractionations

Several recent investigations have indicated the possibility of systematic fractionation of sulfur isotopes between co-existing sulfide species in an assemblage. The available data is often difficult to interpret due to the small magnitude of the effect in relation to analytical accuracy. Only occasionally has evidence been presented which can serve as a guide to estimating the degree to which the co-existing minerals are in equilibrium. In a statistical survey of all available information, therefore, any systematic trends to emerge despite the sampling problems should be considered meaningful.

The earliest report of fractionations between sulfides is given by Sakai (1957) for assemblages from "Kuroko" and epithermal deposits. In the light of his experimental accuracy, however, these were not considered meaningful at the time.

Ault and Kulp (1960) described a specimen from the Northwestern Illinois lead-zinc district consisting of successive
concentric growths of sulfides around a dolomite core (Figure 4.1). A discontinuous layer of soft spheroidal marcasite occurs enclosed within concentric growth layers of sphalerite. Galena mineralization appears contemporaneous with the successive sphalerite zones, but persisted later than the sphalerite in growing crystals external to the outermost sphalerite layer. The marcasite and sphalerite layers have closely similar isotopic compositions, but the galena is consistently enriched in the lighter isotope. Variation in isotopic composition within this hand specimen has been ascribed to fluctuations in isotopic composition of the depositing solutions but equilibrium fractionation between sulfide species would appear to have exerted some influence on the fractionation pattern.

The first reliable data on fractionation of sulfur isotopes between sulfides was presented by Gavelin et al. (1960). A specimen of temperature colloform zinc ore (Schallenblende) from Diepenlinchen was analyzed to investigate the extent of isotopic variation within a single hand specimen. The specimen (Fig. 4.2) consisted mainly of sphalerite occurring as narrow layers of varying coloration from light yellow to dark brown. One band of galena and several bands or nodules of pyrite are also present. The individual sulfides display remarkable variation in isotopic composition with significant differences between
FIG. 4-1 $^{32}S / ^{34}S$ RATIO S IN CONCENTRIC SULFIDES FROM NORTHEASTERN ILLINOIS

FIG. 4-2 $S^{32}/S^{34}$ RATIOS OF SULFIDES IN SCHALENBLENDE FROM DIEPENLINGHEN

(after Gavelin et al., 1960)
the individual sulfide species. There is, however, no general trend of variation such as would be indicative of changing isotopic composition of the depositing solution. Pyrite is characterized by the heaviest sulfur, sphalerite by intermediate values and galena is invariably enriched in the lighter isotope.

The same study also describes a specimen of pyrite from the Laisvall mine in Northern Sweden. A kernel and margin of a concretionary nodule of pyrite in sandstone was found to give a surprisingly high difference in isotopic composition with the margin enriched in the lighter isotope by some 15 permil. While this could readily reflect variations in isotopic composition of the solutions from which the pyrite was deposited, it might equally well serve as an indication of equilibrium exchange fractionation between pyrite and sulfur species in solution under changing temperature conditions.

A study of the Heath Steele deposit (Dechow 1960) involved analysis of a large number of specimens from galena-sphalerite-pyrite-chalcopyrite-pyrrhotite assemblages. Unfortunately, galena and sphalerite were not separated. No significant fractionations between sulfide species were detected though a possible enrichment of $S^{34}$ in pyrrhotite relative to other sulfides is indicated. These results are in marked contrast to those obtained during a later study of the same
ore deposit (Lusk & Crocket 1969). This disagreement is thought to be primarily the result of analytical inaccuracy at the time of the first study.

v. Gehlen et al. (1962) reported on the isotopic composition of sulfides and sulfates from barite veins in the Black Forest (Germany). The range of sulfur isotope ratios is relatively narrow for each individual species and differs from one another in spite of subsequent generations of mineralization. The same pattern is observed for the individual sulfides from different localities as indicated in Table 4.1 and Figure 4.3.

The distribution of sulfur isotopes amongst sulfides of igneous rocks has been investigated in a few studies. Because of the relatively high temperatures of sulfide deposition, isotopic fractionations would be expected to be of very small magnitude. Coexisting chalcopyrite and pyrrhotite in disseminations and veins of the Noril'sk deposit as reported by Godlevskii and Grinenko (1963) show no systematic fractionation. Subsequent studies by Vinogradov and Grinenko (1964) on similar sulfides from the Talnakh and Mt. Chernaya deposits show a similar lack of consistent fractionation.

Smitheringale and Jensen (1963) in a study of Triassic igneous rocks of the Eastern United States, analyzed co-existing pyrite, chalcopyrite and pyrrhotite from a number of basic intrusives.
<table>
<thead>
<tr>
<th>Locality</th>
<th>Mineral</th>
<th>$\delta^{34}S$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schauinsland</td>
<td>PbS-I</td>
<td>-2.6</td>
</tr>
<tr>
<td></td>
<td>ZnS-Ia</td>
<td>+0.4</td>
</tr>
<tr>
<td></td>
<td>ZnS-Ib</td>
<td>+0.3</td>
</tr>
<tr>
<td></td>
<td>ZnS-IIa</td>
<td>+0.5</td>
</tr>
<tr>
<td>Schindler</td>
<td>PbS-Ib</td>
<td>-7.0</td>
</tr>
<tr>
<td></td>
<td>PbS-Ic</td>
<td>-7.2</td>
</tr>
<tr>
<td></td>
<td>PbS-II</td>
<td>-9.1</td>
</tr>
<tr>
<td></td>
<td>PbS-III</td>
<td>-3.2</td>
</tr>
<tr>
<td>Tannenboden</td>
<td>PbS-II</td>
<td>-3.4</td>
</tr>
<tr>
<td></td>
<td>ZnS-I</td>
<td>-1.2</td>
</tr>
<tr>
<td></td>
<td>FeS$_2$</td>
<td>-36.2</td>
</tr>
<tr>
<td>Spitzdobel</td>
<td>PbS-II</td>
<td>-4.6</td>
</tr>
<tr>
<td></td>
<td>PbS-II</td>
<td>-3.6</td>
</tr>
<tr>
<td>Brenden</td>
<td>PbS</td>
<td>-12.4</td>
</tr>
<tr>
<td>Wenzel Frohnbach</td>
<td>PbS</td>
<td>-3.5</td>
</tr>
<tr>
<td>Friedrich-Chr.</td>
<td>PbS</td>
<td>-9.8</td>
</tr>
<tr>
<td></td>
<td>PbS</td>
<td>-10.7</td>
</tr>
<tr>
<td>Weilersbach</td>
<td>ZnS</td>
<td>+2.3</td>
</tr>
<tr>
<td>Anton Wiede</td>
<td>FeS$_2$</td>
<td>-27.8</td>
</tr>
</tbody>
</table>
FIG. 4-3 ISOTOPIC COMPOSITION OF SULFIDES FROM BLACK FOREST BARITE VEINS
(v. Gehlen et al. 1962)
Sulfides from normal diabase showed no significant difference between co-existing minerals. For differentiated intrusives, however, pyrite was significantly enriched in the heavier isotope compared to chalcopyrite. The amount of fractionation appears to increase with progressive stages of crystallization (falling temperature) with the smallest fractionation being found in a fine chilled selvage of the Gettysbury sill. Pegmatites associated with the Belmont Stock, Va., show fractionations of up to 2 permil.

Buschendorf et al. (1963) in a general study of the sulfur isotope ratio in sulfides and sulfates from Meggen measured a limited number of co-existing sulfides and showed that there was a clear tendency for pyrite to be enriched in the heavier isotope with respect to sphalerite. Only five sphalerite-galena pairs were measured but in four of these sphalerite showed the higher $\delta S^{34}$. Comparable results were obtained in a detailed study of a large number of samples from three ore zones of the Sierra de Cartagena deposits in Spain (Friedrich et al. 1964). Small but consistent differences in sulfur isotopic ratios between sulfides exist with as a general rule,

$$\delta FeS > \delta FeS_2 > \delta ZnS > \delta PbS$$

and are summarized in table 5.2.
Table 4.2

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Isotopic Composition (${\delta S^{34}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Central Zone</td>
</tr>
<tr>
<td>Pyrite-marcasite</td>
<td>+ 5.5</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>+ 5.0</td>
</tr>
<tr>
<td>Galena</td>
<td>+ 4.0</td>
</tr>
</tbody>
</table>

Tatsumi (1965) investigated pairs of sulfides in some Japanese Tertiary deposits and found a regular trend of isotopic fractionation among co-existing sulfide minerals, the order of the $S^{34}$-enrichment being: pyrite $>$ sphalerite $>$ chalcopryite $>$ galena. It was furthermore suggested that there was a correlation between the magnitudes of mineralogical fractionations and the presumed temperature of formation of these ores, the larger fractionations being measured in deposits though to have formed at lower temperatures.

Recently Anger, Nielsen, Puchelt and Ricke (1966) have examined the isotopic composition of sulfide and sulfate sulfur at Rammelsberg and again have encountered systematic fractionation between sulfides. Pyrite shows comparatively low $S^{34}/S^{32}$ ratios,
which the authors suggest may be due to biogenic contributions. Of ten measurements of well concentrated sphalerite-galena pairs, all but one showed sphalerite with a significant enrichment of the heavier isotope.

An investigation of the isotopic composition of sulfur in co-existing sphalerites and galena from Broken Hill, New South Wales (Stanton and Rafter 1967) shows consistent relative concentration of the heavier isotope in sphalerite. The average fractionation of 16 pairs amounts to 0.83 permil with only a single pair showing sphalerite enriched in the light isotope relative to galena.

Probably the most detailed investigation of fractionation in co-existing sulfides was conducted by Lusk & Crockett (1969) for the Heath Steele B-1 Orebody, New Brunswick. Sulfur isotope ratios were determined in a large number of specimens from the B-1 orebody and five other stratiform deposits in the Bathurst Camp. Isotopic fractionations between given sulfide minerals are relatively constant and would indicate that sulfur isotopic equilibrium was closely approached at a fairly uniform temperature. It is suggested that the stratiform deposits in this camp have undergone low grade regional metamorphism which has generated the observed fractionations and caused isotopic homogenization with respect to given minerals.
Analytical results are represented in Table 4.3.

### Table 4.3

**Bathurst Camp - Mineralogical Isotopic Fractionation**

<table>
<thead>
<tr>
<th>Sample Group</th>
<th>$\Delta$FeS$_2$-ZnS</th>
<th>$\Delta$FeS$_2$-PbS</th>
<th>$\Delta$ZnS-PbS</th>
<th>$\Delta$FeS$_2$-FeS</th>
<th>$\Delta$FeS$_2$-CuFeS$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1 Known precision</td>
<td>1.04±0.12</td>
<td>2.90±0.25</td>
<td>1.96±0.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-1 Unknown precision</td>
<td>0.75±0.07</td>
<td>2.66±0.18</td>
<td>1.78±0.17</td>
<td>0.50±0.14</td>
<td>0.48±0.14</td>
</tr>
<tr>
<td>All B-1 data</td>
<td>0.87±0.07</td>
<td>2.72±0.15</td>
<td>1.82±0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other deposits</td>
<td>0.64±0.20</td>
<td>2.68±0.21</td>
<td>1.80±0.12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Several additional reports on systematic differences in isotopic composition of sulfide minerals have been published amongst the more recent of these are Jensen and Dessau (1966), Ryznar et al. (1967), Nielsen (1968), Runnell (1969) and Both et al. (1969).

#### 4.2. Compilation of Analyses

A compilation of all available data relating to isotope fractionation between some of the more common sulfides is presented in Figures 5-4, 5-5, 5-6, 5-7, 5-8 and 5-9. In such a statistical com-
pilation it can be assumed that if the effects of disequilibrium and analytical error are random, they will cancel out and any trends which do emerge may be regarded as significant.

The difference in isotopic composition of co-existing minerals from the same hand specimen is presented in the form of histograms. The interval of 0.5% was chosen as being representative of the overall experimental accuracy of the analyses. The information has further been grouped roughly as to the probable temperature of formation of the minerals concerned. Since most of the information is derived from ore deposits, the classification according to "class" of deposit (Lindgen 1933), i.e. hypothermal, mesothermal, and epithermal, has been adopted to this purpose. It must be emphasized that this is merely a rough classification for the purpose of observing any statistically significant temperature effect on the isotopic fractionation rather than a rigorous pigeonholing of these deposits into a particular "class" or even implying that the concept of "class" of ore deposits has any exact significance. Where deposits are thought to have undergone metamorphism, observed fractionations are plotted according to the temperature indicated by the metamorphic products in the country rock.
Data was obtained from the following sources:

1) Magmatic Deposits - Temperature above 500°C (includes pyrometasomatic deposits and pegmatites):

<table>
<thead>
<tr>
<th>Location</th>
<th>Source(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eastern U.S. Triassic</td>
<td>Smitheringale and Jensen (1963)</td>
</tr>
<tr>
<td>Igneous rocks</td>
<td></td>
</tr>
<tr>
<td>Noril'sk</td>
<td>Godlevskii and Grinenko (1963)</td>
</tr>
<tr>
<td>Chernaya</td>
<td>Vinogradov and Grinenko (1964)</td>
</tr>
<tr>
<td>Quemont</td>
<td>Ryznar (1967)</td>
</tr>
<tr>
<td>Broken Hill (metamorphosed)</td>
<td>Stanton and Rafter (1967)</td>
</tr>
<tr>
<td>Cornwall, Penna.</td>
<td>Ault (1957)</td>
</tr>
<tr>
<td>Vignus</td>
<td>Jensen (1957)</td>
</tr>
<tr>
<td>Frood</td>
<td>Jensen (1957)</td>
</tr>
<tr>
<td>Sterling Hill</td>
<td>Ault and Kulp (1960)</td>
</tr>
<tr>
<td>Magdalena</td>
<td>Ault and Kulp (1960)</td>
</tr>
<tr>
<td>Japanese Black Ores</td>
<td>Tatsumi (1965)</td>
</tr>
</tbody>
</table>
2) Hypothermal Deposits - Temperature 300-500°C

Heath Steele Dechow (1960)
(metamorphosed) Lusk and Crocket (1969)
Kearny Ault and Kulp (1960)
Gilman Ault and Kulp (1960)
Pine Cone Lake Ault and Kulp (1960)
Sierra de Cartagena Friedrich et al. (1964)

3) Mesothermal Deposits - Temperature 200-300°C

Sierra de Cartagena Friedrich et al. (1964)
(Middle and Outer Zones) Sawkins (1964)
(Metamorphosed ?) Zacatecas
Rammelsberg Anger et al. (1966)
(Metamorphosed ?) Zuker (1966)
Ruby Creek Runnell (1969)
Zeehan (pyritic zone) Both et al. (1969)
Taupo Steam Wells Steiner and Rafter (1966)
Yellowknife Wanless et al. (1960)
Japanese Black Ores Sakai (1957)
Tatsumi (1965)
4) Epithermal Deposits - Temperature 50-200°C

Japanese Black Ores  
Tatsumi (1965)

N.W. Illinois  
Ault and Kulp (1960)

Ivigtut

S. E. Missouri

Aachen (Diepenlinchen)  
Gavelin et al. (1960)

S. German Barite Veins  
v. Gehlen (1962)

Meggen  
Buschendorf et al. (1963)

S. W. Sardinia  
Jensen and Dessau (1966)

Zeehan (Sideritic zone)  
Both et al. (1963)

The number of analyses is indicated in brackets for each deposit. Where fractionations fall off the diagrams their values have been plotted on either side.

From this compilation it is apparent that the phenomena described for individual hand specimens and deposits apply in general and indeed become more apparent when a large number of deposits of different modes of origin are examined. Considering the mineral
MAGMATIC DEPOSITS (INCLUDING FARMATITES AND PYROMETAMORPHIC DEPOSITS)
TEMPERATURE 500-1200°C

HYPOTHERMAL DEPOSITS
TEMPERATURE 300-500°C

MESOTHERMAL DEPOSITS
TEMPERATURE 200-300°C

EPITHERMAL DEPOSITS
TEMPERATURE 0-200°C

TOTAL

FIG. 4-4 SPHALERITE-GALENA FRACTIONATION
(HISTOGRAMS FOR $\Delta g = 0$ SPHALERITE-GALENA FROM PUBLISHED ANALYSES)
MAGMATIC DEPOSITS
INCLUDING PEGMATITES AND
PYROMETASOMATIC DEPOSITS
TEMPERATURE 500-1200°C

HYPOTHERMAL DEPOSITS
TEMPERATURE 300-500°C

MESOTHERMAL DEPOSITS
TEMPERATURE 200-300°C

EPITHERMAL DEPOSITS
TEMPERATURE 0-200°C

TOTAL

FIG. 4-5 PYRITE-SPHALERITE FRACTIONATION
(HISTOGRAMS FOR \( \Delta \delta = \delta_{\text{pyrite}} - \delta_{\text{spalhlerite}} \) FROM PUBLISHED ANALYSES)
MAGMATIC DEPOSITS
(INCLUDING FENITITES AND PYROMETAMORPHIC DEPOSITS)
TEMPERATURE 500-1200°C

HYPOTHERMAL DEPOSITS
TEMPERATURE 300-500°C

MESOTHERMAL DEPOSITS
TEMPERATURE 200-300°C

EPITHERMAL DEPOSITS
TEMPERATURE 0-200°C

TOTAL

FIG. 4-6 PYRITE - GALENA FRACTIONATION
(HISTOGRAMS FOR $\Delta \delta^{6} = \delta^{6}_{\text{pyrite}} - \delta^{6}_{\text{galena}}$ FROM PUBLISHED ANALYSES
MAGMATIC DEPOSITS
(INCLUDING PEGMATITES AND PYROMETASOMATIC DEPOSITS)
TEMPERATURE 500-1200°C

HYPOTHERMAL DEPOSITS
TEMPERATURE 300-500°C

MESOTHERMAL DEPOSITS
TEMPERATURE 200-300°C

EPITHERMAL DEPOSITS
TEMPERATURE 0-200°C

TOTAL

FIG. 4-7 PYRITE-CHALCOPYRITE FRACTIONATION
(HISTOGRAMS FOR $\Delta$6 = 6PYRITE - 6CHALCOPYRITE FROM PUBLISHED ANALYSES)
MAGMATIC DEPOSITS
(INCLUDING PEGMATITES AND PYROMETASOMATIC DEPOSITS)
TEMPERATURE 500-1200°C

HYPOTHERMAL DEPOSITS
TEMPERATURE 300-500°C

MESOTHERMAL DEPOSITS
TEMPERATURE 200-300°C

EPITHERMAL DEPOSITS
TEMPERATURE 0-200°C

TOTAL

FIG. 478 CHALCOPYRITE - PYRRHOTITE FRACTIONATION
(HISTOGRAMS FOR $\Delta^6 = \delta_{\text{CHALCOPYRITE}} - \delta_{\text{PYRRHOTITE}}$ FROM PUBLISHED ANALYSES)
MAGMATIC DEPOSITS
(INCLUDING PEGMATITES AND PYROKETASOMATIC DEPOSITS)
TEMPERATURE 500-1200°C

HYPOTHERMAL DEPOSITS
TEMPERATURE 300-500°C

MESOTHERMAL DEPOSITS
TEMPERATURE 200-300°C

EPITHERMAL DEPOSITS
TEMPERATURE 0-200°C

TOTAL

FIG. 4-9. PYRITE - PYRRHOTITE FRACTIONATION
(HISTOGRAMS FOR $\Delta$g = $\delta_{\text{pyrite}} - \delta_{\text{pyrrhotite}}$ FROM PUBLISHED ANALYSES)
pairs in details:

1) **Sphalerite-Galena**

Fractionations are consistent, with sphalerite almost invariably enriched in the heavier isotope. The magnitude of the fractionation appears to range from approximately 2 permil in high temperature assemblages to 4 permil in the lower temperature assemblages.

2) **Pyrite-Sphalerite**

Pyrite is almost invariably enriched in the heavier isotope. While information is relatively scarce for the intermediate and lower temperature assemblages, fractionation would nevertheless appear to be larger in these, especially when compared with the high-temperature assemblages from Sterling Hill. Fractionations would appear to vary from 0 permil to 3 or 4 permil at the lower temperatures.

3) **Pyrite-Galena**

Again insufficient information is present to establish a definite temperature dependence. Fractionations appear relatively large averaging between 2 to 3 permil.

4) **Pyrite-Chalcopyrite**

Pyrite is enriched in the heavy isotope relative to chalcopyrite except for a few assemblages of igneous origin. Fractionations appear to range between 1 and 2 permil. Many of the analyses representing igneous assemblages are from early work, and the spread
obtained in these high temperature assemblages are thought to result from impure mineral concentrates and analytical inaccuracy. Later results (such as those from Heath Steele) show greater consistency.

5) Chalcopyrite-pyrrhotite

No consistent pattern of fractionation is apparent for chalcopyrite-pyrrhotite assemblages. Values are centered around zero fractionation and this is thought to reflect a small equilibrium fractionation effect, as well as the fact that this is typically a high temperature mineral assemblage. The spread in values and sign of the fractionation is thought to result from analytical inaccuracy. If any fractionation does exist, it would appear to be less than 0.5% at geologically reasonable temperatures.

6) Pyrite-pyrrhotite

Insufficient data is available but it would appear that there is a possibility that pyrite may be slightly enriched in the heavier isotope relative to pyrrhotite. Such fractionation appears less than 1 permil for mesothermal mineral assemblages.

In addition, it should be noted that a large number of obviously anomalous fractionations are associated with the pairs pyrite-sphalerite and pyrite-galena. This is thought to arise from an
anomalous isotopic composition of pyrite which may partially be of biogenic origin in several deposits.

Another contributing factor could be the ubiquity of pyrite which in hydrothermal deposits often persists throughout the whole of the paragenetic sequence. Pyrite in such deposits may have precipitated before and/or after the various other sulfides.

Crystallization commonly appears to have started before that of various other sulfides (sphalerite and galena in particular) and may persist after crystallization of these has ceased. Subsequently, a considerable proportion of the pyrite found in such deposits was not co-precipitated with these sulfides and cannot be expected to be in isotopic equilibrium with these.

4.3. Discussion

From the evidence presented there appear to exist systematic and definite differences in the isotopic composition of some co-existing sulfides. The consistency of the results for these widely separated deposits occurring under various geological conditions, would suggest the influence of a fractionation process solely affected by the mineral species. The larger fractionations for a given sulfide pair occur in mineral assemblages whose temperature of formation can be presumed to be relatively low as based on geological and
mineralogical observations. The largest fractionations such as for the pairs pyrite-galena and sphalerite galena, appear to be temperature sensitive to such an extent to serve as an indication of temperatures within approximately $25^\circ$C. at elevated temperatures. It appears, therefore, that the fractionation of sulfur isotopes between co-existing sulfides may have considerable value as an indicator of geological temperature.

Inconsistency of results in a single deposit can be readily anticipated because of the apparent general lack of equilibrium in mineral assemblages of hydrothermal origin. The more consistent fractionations have been measured in deposits which would appear to have undergone some degree of metamorphism (Heath Steele, Broken Hill, Sierra de Cartagena). It would appear that metamorphism leads to isotopic exchange in the solid state within a localized mineral assemblage. Isotopic equilibrium may, therefore, be approached closely during such an event, even though the original assemblage may have precipitated under conditions of disequilibrium.
CHAPTER 5

EXPERIMENTAL ISOTOPE FRACTIONATION

5.1. General Experimental Design

In order to use natural $^{34}S/^{32}S$ ratios to determine the temperature of equilibration of sulfide mineral assemblages, it is necessary to calibrate one or more sulfur-isotope geothermometers experimentally. This involves experimental determination of the isotopic equilibrium fractionation of sulfide pairs (A and B) as a function of temperature. This can be done by synthesis of these sulfide pairs at known temperatures and subsequent measurement of the difference in isotopic composition of the individual phases ($\alpha_{A-B}$).

Alternately it is possible to synthesize each sulfide individually with a third sulfur bearing phase (X) and subsequently obtain the fractionation between the sulfides as the ratio

$$\alpha_{A-B} = \frac{\alpha_{A-X}}{\alpha_{B-X}}$$

While co-existing sulfides can be readily synthesized from the native metals and sulfur, the products typically have a grain size
of 10-100 Microns on quenching. Separation of such sulfide inter-growths would present great difficulties. It was therefore decided to synthesize the sulfides individually from mixtures of native metal and sulfur in the presence of an excess of sulfur liquid, serving as an isotopic exchange medium. Separation of the sulfide and sulfur phases is readily achieved by dissolving the sulfur in an organic solvent.

From a survey of published analyses for natural assemblages and from theoretical calculations, it would appear that the largest fractionations amongst the common sulfides are associated with the pairs pyrite-galena and sphalerite-galena. The isotopic fractionation between the sulfides galena, pyrite and sphalerite was, therefore, investigated over the temperature range 300-700°C. The upper temperature limit was largely determined by the magnitude of the fractionation effect, which at this temperature was expected to be only a factor of 2 or 3 times larger than analytical accuracy. Temperatures above 700°C would also appear geologically unrealistic for assemblages involving galena, pyrite and sphalerite. The lower temperature limit was fixed by the slow rate of formation of sphalerite from zinc metal and sulfur at low temperatures.

Sulfides were synthesized by mixing finely ground metal with sulfur, in excess of the amount required to form the sulfide phase, in evacuated silica glass tubes. Reaction between the metal and sulfur
produced the desired sulfide which subsequently would exchange isotopically with the remaining sulfur until an equilibrium distribution of isotopes was reached. A kinetic isotope effect was expected to take place during the initial reaction, proceeding at approximately the same rate as the chemical reaction and producing an initial isotopic fractionation which would subsequently be modified by the approach to equilibrium exchange. In order to approach close to the equilibrium value for the exchange reaction it is necessary that the system be allowed to equilibrate for a period of time considerably longer than that over which the chemical reaction goes to completion.

Chemical reactions between lead metal and sulfur, and iron metal and sulfur, proceed very rapidly and go to completion within a few hours depending upon the temperature at which the reaction takes place (Kullerud, 1969, Kullerud & Yoder, 1959). In contrast, the reaction between zinc metal and sulfur at low temperatures may take several months (Kullerud, 1953). Because of the complete lack of information on the kinetics of isotopic exchange of sulfur between sulfides and a sulfur liquid, a preliminary set of galena-sulfur samples was run to obtain some idea of the time required for isotopic equilibration at various temperatures. These runs lasted from 1 to 240 hours. Subsequently, charges for all three sulfides were run at 350°C, 450°C and 710°C for lengths of time varying from 36 hours to ten days.
5.2. **Theory of Unilateral and Bilateral Approach to Equilibrium**

In the case of relatively fast exchange reactions it is possible to prove isotopic equilibrium by reaching a single value for the fractionation factor $a_{A-B}$ from starting materials that have either a larger or smaller value of $a_{A-B}$.

If such equilibrium cannot be achieved, the results of incomplete exchange can be used to determine the equilibrium fractionation (Northrop and Clayton 1966). The rate of isotopic exchange between two phases of a heterogeneous system depends on such properties as temperature, surface area, extent of solution and recrystallization etc., and is assumed to be independent of the relative number of $^{32}$S and $^{34}$S present. The rate of exchange at any stage of the reaction is directly proportional to the distance that the system is from isotopic equilibrium.

Northrop and Clayton (1966) consider the kinetics of isotope exchange between phases in heterogeneous systems. Modifications from the well known treatment of isotopic tracer exchange in homogeneous systems (e.g. Friedlander, Kennedy and Miller 1964), are necessitated by the fact that the rate of exchange of isotopes often may not be constant during the course of the reaction as is the case for homogeneous exchange, but varies with time.
The exchange of sulfur isotopes between two phases can be considered in terms of two simultaneous reactions, one in the forward direction with reaction rate $K_r$ (mole/sec.) and the other in the reverse direction with reaction rate $r$, giving the equilibrium constant for the reaction as $K$.

$$M(32) + S(34) \xrightleftharpoons{Kr}{r} M(34)++ S(32) \quad (5-1)$$

(where $M$ denotes the metal sulfide and $S$, the sulfur phase)

in which the equilibrium constant is,

$$K = (S^{34}/S^{32})M / (S^{34}/S^{32})S \quad (5-2)$$

The reaction rates in the most general case are functions of temperature, pressure, solution concentration, and surface areas.

If the system contains $m$ moles of $M$ with $S^{34}/S^{32}$ ratio $x$, and $s$ moles of $S$ with ratio $y$, then $M$ contains $mx$ moles of $S^{34}$ (since $x \ll 1$) and $S$ contains $sy$ moles of $S^{34}$. The total number of moles of $S^{34}$ in the system is

$$T = mx + sy \quad (5-3)$$

The rate of increase of $S^{34}$ in phase $M$ with time is given by the rate of its formation minus the rate of destruction. The rate of formation of $S^{32}_M$ is given by $Kr$ times the factor $y/m$ (fractional
content of \( S^{32} \) in reactants) whereas the rate of destruction is given by the
rate of the reverse reaction times \( x/m \) (fractional content of \( S^{32} \) in pro-
ducts). Therefore,

\[
\frac{dx}{dt} = \frac{1}{m} (rK_y - rx)
\]

(5-4)

Defining \( \alpha = x/y \) at any time \( t \) then

\[
\frac{dx}{dt} = \frac{rx}{m} \left( \frac{K}{\alpha} - 1 \right)
\]

(5-5)

In terms of the rate of change of \( \alpha \), using the conserva-
tion relationship (5-3)

\[
\frac{d\alpha}{dt} = r \left( \frac{Ma + S}{MS} \right) (K - \alpha)
\]

(5-6)

In all of the exchange experiments \( \alpha \) is very near unity
and \((Ma + S)\) can be taken as \((M + S)\). Integrating between the limits
\( t = t_1 \) and \( t = t_2 \) with \( \alpha = \alpha_1 \) and \( \alpha = \alpha_2 \)

\[-\ln \frac{K - \alpha_2}{K - \alpha_1} = \frac{M + S}{MS} r(t_2 - t_1)\]

(5-7)

if \( r \) is assumed to be independent of \( t \) for exchange between sulfides and
a sulfur liquid.

6.2.1. Constant Reaction Time

For a series of experiments with starting materials with
different \( \alpha \)'s at time \( t_1 = 0 \), the expression for isotopic exchange at a
time \( t \) can be written as

\[-\ln \frac{K - \alpha_t}{K - \alpha_0} = \frac{M + S}{MS} rt.\]

(5-8)
The right hand side is a constant for a given time \( t \) so that

the ratio

\[
\frac{K - \alpha_t}{K - \alpha_o}
\]

is constant.

This, in turn, implies constancy of the ratio

\[
\frac{\alpha_t - \alpha_o}{K - \alpha_o}
\]

Since all the \( \alpha \)'s and \( K \) are very near unity, we can write

\[
\ln a = 1 + a,
\]

giving,

\[
\frac{\ln \alpha_t - \ln \alpha_o}{\ln K - \ln \alpha_o} = -\frac{1}{B}
\]

where \( B = \text{constant} \)

and

\[
\ln \alpha_o = \ln K + B(\ln \alpha_t - \ln \alpha_o)
\]

Hence, a plot of \( (\ln \alpha_t - \ln \alpha_o) \) against \( \ln \alpha_o \) will give a

straight line of slope \( B \) and an intercept \( \ln K \). Hence by allowing a set

of samples with different \( \alpha_o \)'s to equilibrate for a time \( t \) under identical

conditions, the equilibrium constant can be determined without the re-

actions approaching equilibrium. If equilibrium is attained in all

samples of a set, \( \ln \alpha_t = \ln K \) and \( B = -1 \). For samples not yet at

equilibrium, \( B \) will lie between \(-1\) and \(-\infty\).
Verification of the assumptions involved relies on obtaining linear plots for experimental data. In the case of oxygen isotopic exchange in heterogeneous systems many different sets of samples run under widely varying conditions yield linear plots (O'Neil 1963; Northrop and Clayton 1966), Any difference in the experimental conditions within a set of samples would cause deviations from the predicted and observed linear behavior.

The accuracy of the fractionation determined by the intercept method increases with increasing percentage of exchange. For a minor amount of exchange, the linear plot has a steep negative slope and consequently, the equilibrium value cannot be read off with any great accuracy.

Greatest accuracy can be achieved by choosing samples with initial fractionations very close to the expected equilibrium value, both larger and smaller, and observing the change in isotopic composition in these.

5.2.2. Constant Initial Fractionation

Consider a series of experiments for which $\alpha_0$ is identical but where the samples are allowed to undergo exchange for varying lengths of time. Since $\alpha_0$ is a constant
\[-\ln(K-\alpha) = A_t \frac{M+S}{MS} r(t_2 - t_1) \quad (5-11)\]

or since $K$ and $\alpha$ have values very close to unity

\[-\ln (\ln K - \ln \alpha) = A_t \frac{M+S}{MS} r(t_2 - t_1) \quad (5-12)\]

or,

\[-\ln \left[ \Delta_{M-S}^{(E)} - \Delta_{M-S}^{(t)} \right] = A_t \frac{M+S}{MS} r(t_2 - t_1) \quad (5-13)\]

This equation is valid only if $r$ remains constant with time. This is verified by the experimental results obtained which yield straight line plots of $\ln \left( \Delta_{M-S}^{(E)} - \Delta_{M-S}^{(t)} \right)$ versus $t_2 - t_1$. The only variable which could cause $r$ to vary with time is the surface area of the sulfide phase.

It would, therefore, seem that variations in surface areas persist only for a short length of time and that a stable surface area is reached early in the reaction, remaining constant thereafter. O'Neill (1963) also found that the kinetics of inhomogeneous isotope exchange reactions is affected by grain size to a much smaller extent than expected from variations in the amount of surface area.

A kinetic isotope effect accompanies sulfide synthesis when the starting materials consist of native metal and sulfur. Clearly this phase of the exchange reaction cannot be treated in terms of the above theory. It is, therefore, necessary to restrict the application to that
portion of the exchange reaction where the kinetic effect has gone to completion and equilibrium exchange is being established. Only information from this portion of the fractionation curve can be used for the purpose of calculating the equilibrium fractionation. The kinetic isotope effect during sulfide synthesis was observed in all instances to be of short duration (less than 8 hours) and in practice it is not even necessary to correct for the difference in \( t_0 \) (between the start of the experiment and the approximate start of the exchange reaction), the error introduced in calculating the equilibrium fractionation being insignificant.

The initial value of \( a_0 \) arises from the kinetic isotope effect and for a set of experiments at the same temperature can be assumed to be constant. The actual value of \( a_0 \) does not enter into the calculation of the equilibrium fractionation.

In practice it was found most convenient to estimate the equilibrium fractionation \( \Delta^{(E)}_{M-S} = 10^3 \ln K \) from the fractionation curve (plot of fractionation versus time). To refine this estimate \( \Delta^{(E)}_{M-S} - \Delta^{(t)}_{M-S} \) was then plotted on semilog paper and the value of \( \Delta^{(E)}_{M-S} \) producing the best straight line plot accepted as the equilibrium fractionation.

It should be noted that the "equilibrium" value arrived at by an approach from one side is only an estimate and may in fact represent a metastable equilibrium state. Equilibrium fractionation
can only be conclusively demonstrated if the same fractionation is arrived at starting on opposite sides of the equilibrium isotope distribution. O'Neil (1963) has shown that the equilibrium fractionation could be determined with greatest accuracy if one of the initial systems was close to the supposed equilibrium value.

In the absence of any data on equilibrium fractionation between sulfide minerals, a bilateral approach to equilibrium was not possible in the present investigation.

5.2.3. Reaction Kinetics

From the well known Arrhenius rate law it is expected that the reaction rate \( r \) is of the form,

\[
r = A e^{(E^*/RT)}
\]

(5-14)

where \( E^* \) represents an activation energy.

During unilateral approach to equilibrium, \( r \) is most readily obtained by considering the half life \( t_{1/2} \) at which the fractional exchange

\[
\frac{(\ln K - \ln \alpha_t)}{(\ln K - \ln \alpha_o)} = 1/2
\]

\( t_{1/2} \) can best be read from a plot on semilog paper.
Subsequently,

\[ r \cdot t^{1/2} \frac{M+S}{MS} = 0.693 \]

or

\[ r = \frac{0.693}{t^{1/2}} \frac{MS}{M+S} \]  \hspace{1cm} (5-15)

For bilateral approach to equilibrium it can be shown in similar fashion that in terms of the slope of the straight-line plot,

\[ r = \frac{MS(1 + B)}{tB(M + S)} \]  \hspace{1cm} (5-16)

The molecular species may contain more than one lattice site at which isotopic atoms may be located. So long as the several isotopic atoms are entirely equivalent (or at least indistinguishable in exchange experiments) in each of these molecules, the equations derived may be applied without modification.

If in a molecule the two atoms are not equivalent and if they exchange through two different reactions with rates \( r_1 \) and \( r_2 \), it may be seen that the resultant approach to equilibrium will not be logarithmic but a complex curve. The different equations for the exchange involving the several positions may be set up and solved simultaneously but it becomes very difficult to resolve the curve for more than two rates.
5.3. Phases and Phase Relations

5.3.1. Molecular Sulfur Species

The number and variety of allotropic forms of elementary sulfur in the solid, liquid and vapor phases, form a subject of great complexity. The literature is marked by a variety of confusing and often contradictory results. These difficulties stem from several causes (i) most sulfur allotropes are often of very limited stability, (ii) small amounts of impurities have great effects on the physical properties of sulfur.

a) Liquid Sulfur

Most physical properties of liquid sulfur can be adequately explained in terms of a model postulating the existence of an equilibrium between distinct \( S_8 \) molecules and a long-chain sulfur polymer \( S_x \) \((\text{Gee, 1955})\). It is assumed that below the temperature at \( 160^\circ\text{C} \) (at which many physical properties show anomalous behaviour) the liquid consists of ring shaped \( S_8 \) molecules and that at \( 160^\circ\text{C} \) polymerization starts. Both the weight fraction of polymer and the average number of sulfur atoms belonging to any one chain are temperature dependent. In addition to these two species, it would seem that molecular forms representing \( S_6 \) and \( S_2 \) are present to a minor extent. Because of the very low heat conduction of liquid sulfur some time is required for equilibrium among the various species to be reached.
This generally takes of the order of a few minutes at elevated temperatures but in the vicinity of the melting point (135°C) several hours may be necessary (West, 1959).

While the polymer model is commonly accepted and provides a satisfactory explanation for the anomalous physical behaviour of liquid sulfur, nevertheless, little direct physical evidence for the existence of the polymer is available.

Quantitative information on the distribution of molecular species in the sulfur liquid is limited. The extremely poor heat conduction of liquid sulfur prevents quenching of the equilibrium assemblage present at elevated temperature. Data listed by Aten (1914) for the equilibrium distribution of $S_\lambda$ (corresponds to $S_8$), $S_\mu$ (corresponds to polymer) and a third phase $S_\pi$ (probably corresponding to $S_6$) appear of doubtful validity (Figure 5-1). A theoretical distribution of molecular species as calculated by Gee (1955) is shown in Figure 5-2.

Since it can be expected that the equilibrium distribution of molecular species of pure sulfur in experimental runs at the same temperature will be identical, the fractionation factors associated with these individual species will produce an identical "overall sulfur liquid" fractionation factor with respect to the co-existing sulfide. Such effects will cancel out when sulfide-sulfide fractionation factors are subsequently calculated.
The presence of impurities could, however, be of importance since the chain length of the polymer appears to depend critically on any small amount of impurity present. Fractionation effects between chains of varying lengths can be expected to be extremely small since only those contributions to the partition function arising from the atoms at the end of the chains could be expected to differ. In view of chain lengths of $10^6$ atoms this effect would appear to be totally insignificant.

b) The Saturated Vapor

It has been shown (Kelley 1949) that the species $S_8$, $S_6$, $S_2$, and $S_1$ are present in sulfur vapor, although the latter does not appear until very high temperatures are reached. As is to be expected, equilibrium among the various species is attained quite rapidly in the vapor state. Figure 5-3 indicates the equilibrium molecular composition of saturated sulfur vapor at various temperatures and indicates the average number of atoms in the molecule as calculated by Tuller (1954). It is evident that the mole fraction of $S_8$ decreases with increasing temperature while that of $S_6$ and $S_2$ increases.

Because of variations in the volume of free space in individual capsules, the fraction of these molecular species of the vapor phase will not be constant with respect to the liquid and solid phases.
g. 5-1

ALLOTROPIC EQUILIBRIUM IN THE SULFUR LIQUID

(Aten 1914)
FIG. 5-2  CALCULATED COMPOSITION OF LIQUID SULFUR

(After Gee, 1955)
for a series of experiments performed at the same temperature. Sulfur representing the vapor and liquid phases are extracted simultaneously and analyzed, and this effect can therefore be expected to influence the fractionation factors measured. Because of the close similarity in force constants and since the fractional mass difference is identical for all the species, intermolecular fractionation effects would appear insignificant as is borne out by calculation (section 5.3.2.). Any such effects would, furthermore, largely cancel out in calculating sulfide-sulfide fractionation factors.

c) Crystalline Allotropes

The only molecular form thermodynamically stable in solid sulfur is the eight member ring $S_8$, so that different solid allotropes are either crystal modifications (rhombic or monoclinic) or metastable. Of importance to the present study are,

$S_\alpha$ Orthorhombic or 'rhombic' sulfur. Only thermodynamically stable form at S. T. P. Starting material for all experiments. Soluble in organic solvents.

$S_\beta$ Monoclinic sulfur. Stable above 95.5°C and is commonly prepared by crystallization from a hot solution of sulfur in an organic solvent. During mineral separation $S$ crystallized out from benzene solution in the form of long needles.
Fig. 5-3. MOLECULAR COMPOSITION OF SATURATED SULFUR VAPOR

(Tuller 1954)
Polymeric sulfur. Insoluble in organic solvents. Liquid sulfur quenched from above 160°C first forms a plastic mass which rapidly hardens. This consists of a mixture of \( S_\alpha \) and \( S_\omega \). Quenching of sulfur vapor produces a similar mixture of \( S_\alpha \) and \( S_\omega \), encountered in all experimental syntheses.

5.3.2. Fractionation between Sulfur Species

Vibrational frequencies have been measured for the species \( S_2 \), \( S_6 \) and \( S_8 \) in the vapor or dissolved state (Herzberg 1962, Scott et al. 1964, Nimon et al. 1967). Force constants are available so that it is possible to calculate accurately the isotopic fractionation between these species in the vapor phase. Anharmonicity constants are available only for the \( S_2 \) molecule, so that no anharmonic correction can be made for the other two species.
Table 5-1

Vibrational frequencies for Molecular Sulfur Species (in cm$^{-1}$)

<table>
<thead>
<tr>
<th>$S_2$ (Vapor)</th>
<th>$S_6$ (Solution) $^3$2</th>
<th>$S_6$ (Solution) $^3$4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_6^{32}$</td>
<td>$S_6^{34}$</td>
</tr>
<tr>
<td>725.68</td>
<td>266</td>
<td>258.06</td>
</tr>
<tr>
<td>$\omega_{v_{\Sigma_2}}$</td>
<td>312</td>
<td>302.68</td>
</tr>
<tr>
<td>2.852</td>
<td>394$^a$</td>
<td>382.23</td>
</tr>
<tr>
<td>182(2)</td>
<td>476</td>
<td>461.79</td>
</tr>
<tr>
<td>197.91</td>
<td>435.53</td>
<td>475(2)</td>
</tr>
<tr>
<td>451(2)</td>
<td>448.20</td>
<td>152(2)</td>
</tr>
<tr>
<td>462(2)</td>
<td>86(2)</td>
<td>83.43</td>
</tr>
<tr>
<td></td>
<td>437(2)</td>
<td>123.95</td>
</tr>
<tr>
<td></td>
<td>248(2)</td>
<td>240.59</td>
</tr>
</tbody>
</table>
Table 5-2
Partition Function Ratios for S₂, S₆ and S₈

<table>
<thead>
<tr>
<th>Molecular Species</th>
<th>10⁻³ ln Ω'/Ω</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2S₂(gas)</td>
<td>(Harmonic)</td>
<td>3.91</td>
<td>2.88</td>
<td>2.21</td>
<td>1.74</td>
<td>1.41</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>(Anharmonic)</td>
<td>3.86</td>
<td>2.84</td>
<td>2.17</td>
<td>1.71</td>
<td>1.38</td>
<td>1.14</td>
</tr>
<tr>
<td>1/6S₆(aq.)</td>
<td></td>
<td>3.89</td>
<td>2.83</td>
<td>2.14</td>
<td>1.68</td>
<td>1.35</td>
<td>1.11</td>
</tr>
<tr>
<td>1/8S₈(aq.)</td>
<td></td>
<td>3.88</td>
<td>2.81</td>
<td>2.11</td>
<td>1.67</td>
<td>1.34</td>
<td>1.11</td>
</tr>
</tbody>
</table>

From these results it is apparent that fractionation between the various sulfur species in the vapor phase is small. The close similarity in partition function ratios arises from the similarity in bonding in all the molecular sulfur species (always S-S bonds) and the fact that the fractional mass difference of the isotopic molecules is identical. The polymer can be expected to show partition function ratios close to that of the other molecular species.
Vibrational frequencies for $S_2$, $S_6$ and $S_8$ in the solid state are almost identical to those listed above and isotopic fractionation between these species would again appear small. It is also reasonable to expect that the same holds for the sulfur liquid.

5.3.3. The System Pb-S

The only compound PbS (galena), is cubic; it melts congruently at 1127°C (Fig. 5-4) (Kullerud 1969). In the sulfur rich portion of the system a liquid immiscibility field exists above $799°C ± 2°C$. The solubility of PbS in liquid S is less than 7 weight percent at $799°C$ and decreases rapidly with decreasing temperature. Phase assemblages encountered in the present investigation will, therefore, consist of galena and essentially pure sulfur liquid.

5.3.4. The System Zn-S (Fig. 5-5)

ZnS, the only known compound, is trimorphic. A cubic modification (sphalerite) is stable below approximately 600°C. A rhombohedral form, which is almost indistinguishable from cubic Zns, is stable between 600 and 1020°C (Buck and Strock, 1955). Wurtzite (hexagonal) with several polytypes (Frondel and Palache, 1950) is stable above 1020°C. There is no evidence to indicate that any appreciable amount of zinc is soluble in liquid sulfur (Barton and Toulmin 1966). Reaction products will, therefore, consist of sphalerite and sulfur (with the rhombohedral form of ZnS present in runs above 600°C).
5.3.5. The System Fe-S

In addition to the compounds FeS (troilite), Fe₁₋ₓSₓ (pyrrhotite) and FeS₂ shown in Fig. 5-6 (Kullerud & Yoder 1959), a third compound Fe₃S₄ (smythite), is probably stable at low temperature (≤70°C). FeS₂, which has a "low-temperature" orthorhombic (marcasite) form, and a high-temperature cubic form (pyrite), melts incongruently at 743°C. The field of stability of pyrite appears to extend to temperatures at least as low as 400°C and presumably lower. During experimental synthesis, marcasite has never been reported above 300°C. The solubility of Fe would appear to be less than 0.1 weight percent at all temperatures encountered (Arnold 1958).

The reaction of iron metal and excess sulfur would be expected to yield pyrite and sulfur product phases when synthesized between 300 and 743°C. In practice, however, it is found that the reaction may not go to completion. A pyrrhotite phase is formed readily and subsequently reacts with some of the remaining sulfur to form pyrite. Grains of pyrrhotite are covered by a rim of pyrite. Diffusion of sulfur through this pyrite rim appears so slow as to effectively bring the reaction to a halt. In order to reach equilibrium it is, therefore, necessary to either regrind the reactants after pyrrhotite formation or to start of with extremely fine grained metal.
FIG. 5-4. PHASE RELATIONS IN THE Pb-S SYSTEM. (All phases and phase assemblages co-exist with vapor. After Kullerud, 1969)
FIG. 5-5. APPROXIMATE PHASE RELATIONS IN THE SYSTEM Zn-S
(After Barton and Toulmin, 1966).
FIG. 5-6. PHASE RELATIONS IN THE Fe-S SYSTEM. (Vapor is present in all assemblages and the pressure of the system is not constant. The solubility of iron in sulfur has been exaggerated and polymorphic changes neglected. After Kullerud and Yoder, 1959.)
5.4. Sulfide Synthesis

5.4.1. Experimental Procedure

Three sets of experiments were performed in which native metal (Pb, Zn and Fe) and sulfur were heated in evacuated silica glass capsules at controlled temperatures for varying lengths of time. A sulfide phase is formed through reaction of the metal and sulfur, and this sulfide phase subsequently undergoes isotopic exchange with the excess sulfur remaining until an equilibrium distribution of isotopes is attained.

Because of the complete lack of information on the kinetics of isotopic exchange between sulfides and sulfur, a preliminary set of charges for galena-sulfur exchange (Series A) were run for lengths of time varying from 1 to 240 hrs. at temperatures ranging from 310°C to 725°C. This preliminary set of runs furthermore served to test and develop methods of separating the two resultant phases.

A second series of experiments (Series B) was performed for the mineral pairs sphalerite-sulfur, pyrite-sulfur and galena-sulfur at temperatures of 350°C, 450°C and 710°C, the lengths of the runs being 36, 96 and 240 hrs. Samples were run simultaneously in the same furnace so as to approximate identical conditions (especially with respect to temperature) for all the exchange reactions. It was found
that reaction rates for the synthesis of sphalerite were slow in comparison to the length of these runs and that often the reaction had not gone to completion.

5.4.2. Starting Materials

Because the presence of a third component in the system may cause a large unknown fractionation effect, starting materials of high purity were used throughout the experiments.

**Sulfur:** Sulfur powder in the form of rhombic crystals approximately 2-5 mm. in size were obtained from United Minerals and Chemical Corp., New York. Purity is 99.9999%.

**Iron:** Fine grained iron sponge, Batch S 5332 was obtained from Johnson, Matthey & Co., London. Grade 1, purity is 99.999%. Grain size was measured as ranging from 0-50 micron and averaging 10 micron.

**Lead:** Lead shot, Lot 4397 obtained from United Mineral and Chemical Corp., New York. Purity 99.999%.

**Zinc:** Zinc rods, Lot 5906, obtained from United Mineral and Chemical Corp. Purity 99.999%.
Immediately before preparation of the charges, the iron sponge was reduced over a period of 6 hrs. at 700°C in a hydrogen reduction furnace. Lead shot was melted into a bar under vacuum. Lead and zinc metal were both freshly filed from bars immediately before weighing of the charges. A hand magnet was used to remove any contaminant steel derived from the file. Zinc metal was sieved and only the -100 mesh fraction used so as to speed up reaction rates.

5.4.3. Preparation of Charges

All experiments were carried out in evacuated silica glass capsules as described by Kullerud (1953). The glass tubes are rigid and of fixed volume so that the pressure inside the capsule is determined by the composition of the charge. The free space within the tube, usually half filled with starting materials, is further reduced by placing closely fitting silica glass rods over the charge.

Capsules were prepared initially from silica glass tubing of 3 mm. internal diameter and a wall thickness of 1 mm. In subsequent experiments tubing of 5 mm. internal diameter and 1 mm. wall thickness was used allowing the size of the charge to be increased. Silica glass rod of 3 and 5 mm. diameter, respectively, was placed in the capsule above the reactants to reduce the vapor space. It was
found that the dimensions of the commercially obtained glass fluctuated up to approximately 10% and tubes and rods were matched individually to provide the closest possible fit. Typical dimensions for such silica glass capsules are shown in Figure 5-7.

Capsules were prepared as follows. Silica glass tubing of approximately 15 cm. length was cleaned in benzene and subsequently dried in a heating oven. The tube was closed at one end with an oxygen-acetylene flame. These tubes were subsequently again cleaned in benzene and dried in a heating oven, care being taken not to rub the glass, avoiding the build-up of electrostatic charges. Silica glass rods approximately 2-3 cm. in length were cut and cleaned in benzene.

The amounts of starting material for all the charges was such as to allow for 50 mg. of sulfur in both the sulfide and excess sulfur phases. Difficulties were occasionally encountered in transferring the sulfur from the scale pan to the silica glass tube with fine grained sulfur adhering to the sides of the tube due to electrostatic attraction. Often it was possible to dislodge this material by tapping of the tube walls. If this was not possible, the capsule was discarded. A closely fitting silica glass rod was placed inside the tube and pressed down on the reactants. The tube was then connected to a Welch Duo-Seal Pump and evacuated to a pressure of approximately $10^{-5}$ mm. Hg.
FIG. 5-7. SILICA GLASS CAPSULES
The air in the system has to be pumped away slowly to avoid pumping the glass rod from the capsule and subsequent pumping away of the reactants. This was done by controlling the rate of air flow with a partially closed stopcock. After a suitable vacuum was obtained, the capsule was heated in an oxygen-acetylene flame immediately above the top of the glass rod and the capsule sealed off. It is possible to control closely the amount of free space above the silica glass rod during the sealing off procedure. After some practice it was possible to prepare capsules with a minimum of vapor space in excess of that necessary to accommodate thermal expansion of the reactants and products. During this procedure the remainder of the capsule was held in a wet piece of cloth to avoid heating of the reactants and explosion of the capsule. Subsequent to sealing-off the capsule, it was numbered with a diamond scribe and weighed.

5.4.4. **Temperature Control**

Capsules were heated in electrical resistance furnaces of similar design to those described by Kullerud (1953) and used in the horizontal position. This design is aimed at minimizing temperature gradients along the length of the furnace and producing a centrally located "hot spot" several inches long over which the temperature does not vary by more than a few degrees. A diagrammatic presentation of the furnace design is shown in Figure 5-8.
The core, located along the long axis of the furnace consists of two concentric alundum tubes approximately 18" long with a copper plate measuring about 6 inches in length centrally located between them. This plate helps to distribute the heat to produce a zone of even temperature. The inner tube in which the silica glass capsules are placed has an internal diameter of 1 inch. The outer alundum tube is wound with No. 18 nichrome resistance wire according to the following scheme starting from one end; one inch blank, 1 inch with 12 turns per inch, 3 inches with 10 turns per inch, 6 inches with 8 turns per inch, 3 inches with 10 turns per inch, one inch with 12 turns, and another 1 inch blank. The increasing number of turns towards the ends of the furnace helps to offset heat losses at both ends. The total resistance of each furnace was approximately 20 ohm.

The core is enclosed in a cylindrical shell of stainless steel of 10" diameter with asbestos end plates. Vermiculite serves as an insulator. The inner alundum tube is provided with two firebrick plugs to minimize heat loss from the ends of the core. A controlling chromel-alumel thermocouple is located on the outside of the larger alundum tube while a recording chromel-alumel thermocouple is centrally located at the "hot spot" amongst the charges.
FIG. 6-8. DIAGRAMMATIC SECTION THROUGH ELECTRICAL RESISTANCE FURNACE
At various temperatures, each furnace was thoroughly investigated with a thermocouple to locate the "hot spot" and measure the temperature gradients in its vicinity. Typical temperature profiles at both ends of the temperature range encountered during sulfide synthesis are shown in Figure 5-9. The individual furnaces were found to exhibit slightly different characteristics, each furnace producing optimum temperature profiles over different temperature ranges. For runs at a particular temperature, therefore, only the furnace producing minimum temperature gradients at that temperature was used. In all cases it was possible to achieve a zone of 3 inches length over which the furnace temperature varied by less than 2°C. Charges representing different sulfides and different reaction times could always be readily placed together within this zone so that the temperature variation between these is less than 2°C in every instance.

The furnace temperature was controlled through Fisher (Mercury switch) and Bach-Simpson (photo cell) regulators, a variable voltage transformer and a relay across a resistance of approximately 4 ohms. This had the effect of regulating the power supplied to the furnace at between 80 and 100 percent of the transformer output. With a suitable transformer setting, therefore, the furnace temperature could be controlled considerably more accurately than with an "ON-OFF" type regulator.
FIG. 5-9. TEMPERATURE GRADIENTS ALONG LENGTH OF FURNACE
The furnace temperature was monitored with calibrated chromel-alumel thermocouples centrally located in the "hot spot". Initially this was done manually several times per day, but later temperature was recorded automatically. Temperature control depended on the type of regulator used. With the mercury-switch type it was possible to control to within ±2°C while the photocell regulators generally controlled to within ±10°C. Temperature fluctuations were recorded for each individual run over its entire length and the maximum fluctuation is quoted in Tables 5-4, 5.

5.4.5. Sulfur Vapor Pressure

The pressure inside the capsule is not known but is always less than that of pure sulfur at the same temperature (Allen & Lombard, 1917). Because of the presence of sulfur liquid in all the capsules, the pressure can be expected to approximate closely to that of the pure phase. The maximum pressure can be estimated from the vapor pressure curve as given by Kullerud and Yoder (1959) (see Figure 5.10) and would appear to be less than 30 bars in all cases. Pressure effects can, therefore, be regarded as insignificant as far as affecting the experimentally determined isotope fractionation factors.
FIG. 5-10. VAPOR PRESSURE CURVE FOR PURE SULFUR
(after Kullerud and Yoder, 1959)
5.4.6. Quenching

After completion of a run, the capsule was removed from the furnace with metal tongs and dropped into a beaker of water. It is believed that room temperature is reached within seconds, at least in the sulfide phase which is invariably found in close contact with the walls of the capsule where it has settled during the run owing to its larger density. Heat conduction in the sulfur phase is slow and a length of time of the order of 1 minute was required to completely crystallize the sulfur liquid. Isotopic exchange may therefore take place between the molecular sulfur species in the liquid phase during quenching, but since the whole phase is extracted and isotopically analyzed, this should not affect the results obtained. Samples were weighed to check for leakage.

5.5. Composition of Charges

5.5.1. Sulfur Vapor Phase

A certain amount of sulfur will exist in the vapor phase and can be expected to show a small fractionation with respect to the liquid sulfur and sulfide phases. Since this vapor phase will be extracted simultaneously with the liquid phase during analysis of the charges and varies from capsule to capsule, it could affect the results obtained. In order to eliminate this effect, capsules were constructed so
as to allow minimum of free space. The actual amount of free space in
a capsule was determined for each capsule through specific gravity
measurements and the amount of sulfur in the vapor phase calculated
from the ideal gas law.

The volume of free space in individual capsules was deter-
mined from a knowledge of the total weight and volume of the capsule,
the weights of the individual constituents, and the densities of these
constituents. The volume of the capsule was measured by weighing
the capsule while suspended in water and comparing with the weight in
air. Information on the densities of the constituents at various tempera-
tures was calculated from a knowledge of the densities at room tempera-
ture and the thermal expansion of the materials (Clark, 1966, Handbook
of Physics and Chemistry, V. 40). Information on the density of sulfur
at various temperatures was taken from Tuller (1954). This informa-
tion is represented in Figs. 5.11, 12. The density of silica glass was
determined experimentally. Three measurements yielded an average
value of $2.208 \pm 0.002 \text{ gm/cm}^3$. It was assumed that the volume
expansion of silica glass is negligible over the range of temperatures
considered and this density was used at all temperatures. The effect of
compressibility was neglected as insignificant.
FIG. 5-11. DENSITY OF PYRITE, SPHALERITE, AND SULFUR AT ELEVATED TEMPERATURES
FIG. 5-12  DENSITY OF LEAD, IRON, ZINC, AND GALENA AT ELEVATED TEMPERATURES
At any temperature the volume of free space within a capsule was calculated as,

\[ V_{\text{Free Space}} = V_{\text{Total}} - V_{\text{Sulfide}} - V_{\text{Sulfur}} - V_{\text{Silica}} \]

Where,

\[ V_{\text{Sulfide}} = \frac{\text{Mass Sulfide}}{\text{Density}} \]
\[ V_{\text{Sulfur}} = \frac{\text{Mass Sulfur}}{\text{Density}} \]
\[ V_{\text{Silica}} = \frac{(\text{Mass Total} - \text{Mass Sulfide} - \text{Mass Sulfur})}{\text{Density}} \]

Example: Consider Run G720-A; Consists of a mixture of zinc and sulfur, run at 689°C for 36 hrs. The volume of free space in the capsule is calculated both before and after the sulfide has been formed.

Before Reaction:

Total Weight \(= 2.8327 \text{ gm.}\)
Weight Zinc \(= 0.1019 \text{ gm.}\)
Weight Sulfur \(= 0.1000 \text{ gm.}\)
Therefore, Weight Silica \(= 2.6308 \text{ gm.}\)

Total volume is \(1.350 \text{ cm}^3\) (measured)
Volume silica \(= 1.191 \text{ cm}^3\)
Volume zinc \(= 0.016 \text{ cm}^3\)
Volume sulfur \(= 0.069 \text{ cm}^3\)

Therefore, Volume free space \(= 0.074 \text{ cm}^3\)
After Reaction

Total Weight = 2.8327 gm.
Weight ZnS = 0.1519 gm.
Weight S = 0.0500 gm.

Therefore, Weight Silica = 2.6308 gm.

Total volume is $1.350 \text{ cm}^3$
Volume silica = $1.191 \text{ cm}^3$
Volume ZnS = $0.038 \text{ cm}^3$
Volume S = $0.035 \text{ cm}^3$

Therefore, Volume free space = $0.086 \text{ cm}^3$

Information for all the capsules comprising the "Series B" experiments is presented in Table 5-3. No measurements were performed for the capsules of Series A. In practice, however, it was found that a large proportion of the capsules of Series A would explode when heated in the furnace. This indicates that the amount of free space in these capsules was insufficient to allow for the thermal expansion of the materials. In preparing the samples of Series B, therefore, slightly more free space was allowed in the capsules during preparation of the charges. There is thus every reason to believe that the volume of free space in the capsules comprising "series A" in all cases is considerably less than the measured volumes.
### Table 5-3

**Volume of Free Space in Silica Capsules**

*a) Galena*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Weight (gm.)</th>
<th>Weight Quartz (gm.)</th>
<th>Volume (cm³)</th>
<th>Total</th>
<th>Silica</th>
<th>Lead</th>
<th>Sulfur</th>
<th>Vapour Space (Original)</th>
<th>Galena</th>
<th>Sulfur</th>
<th>Vapour Space (Final)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N690A</td>
<td>2.7176</td>
<td>2.2943</td>
<td>1.21</td>
<td>1.039</td>
<td>0.032</td>
<td>0.069</td>
<td>0.07</td>
<td>0.053</td>
<td>0.035</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>N690B</td>
<td>2.7092</td>
<td>2.2860</td>
<td>1.39</td>
<td>1.035</td>
<td>0.032</td>
<td>0.069</td>
<td>0.25</td>
<td>0.053</td>
<td>0.035</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>N690C</td>
<td>2.5957</td>
<td>2.1725</td>
<td>1.23</td>
<td>0.984</td>
<td>0.032</td>
<td>0.070</td>
<td>0.13</td>
<td>0.053</td>
<td>0.035</td>
<td>0.16</td>
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<tr>
<td>N447A</td>
<td>2.6228</td>
<td>2.1995</td>
<td>1.23</td>
<td>0.996</td>
<td>0.031</td>
<td>0.063</td>
<td>0.14</td>
<td>0.051</td>
<td>0.031</td>
<td>0.15</td>
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</tr>
<tr>
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<td>3.0214</td>
<td>1.53</td>
<td>1.368</td>
<td>0.031</td>
<td>0.062</td>
<td>0.08</td>
<td>0.051</td>
<td>0.031</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
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<td>2.5270</td>
<td>2.1041</td>
<td>1.12</td>
<td>0.953</td>
<td>0.031</td>
<td>0.062</td>
<td>0.07</td>
<td>0.051</td>
<td>0.031</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>N340A</td>
<td>2.5956</td>
<td>2.1726</td>
<td>1.19</td>
<td>0.984</td>
<td>0.030</td>
<td>0.060</td>
<td>0.12</td>
<td>0.051</td>
<td>0.030</td>
<td>0.13</td>
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<tr>
<td>N340B</td>
<td>2.9328</td>
<td>2.5098</td>
<td>1.30</td>
<td>1.137</td>
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<td>0.060</td>
<td>0.07</td>
<td>0.051</td>
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</tr>
<tr>
<td>N340C</td>
<td>2.9234</td>
<td>2.5006</td>
<td>1.33</td>
<td>1.133</td>
<td>0.030</td>
<td>0.060</td>
<td>0.11</td>
<td>0.051</td>
<td>0.030</td>
<td>0.12</td>
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</tbody>
</table>
Table 5-3 (continued)

b) Sphalerite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Weight (gm.)</th>
<th>Weight Quartz (gm.)</th>
<th>Total Silica</th>
<th>Zinc</th>
<th>Sulfur</th>
<th>Vapour Space</th>
<th>Sphal. Sulfur Vapour Space</th>
</tr>
</thead>
<tbody>
<tr>
<td>G690A</td>
<td>2.8327</td>
<td>2.6308</td>
<td>1.35</td>
<td>1.191</td>
<td>0.016</td>
<td>0.07</td>
<td>0.038</td>
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<td>2.4227</td>
<td>2.2208</td>
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<td>0.016</td>
<td>0.13</td>
<td>0.038</td>
</tr>
<tr>
<td>G690C</td>
<td>2.5225</td>
<td>2.3206</td>
<td>1.24</td>
<td>1.051</td>
<td>0.016</td>
<td>0.10</td>
<td>0.038</td>
</tr>
<tr>
<td>G447A</td>
<td>2.4536</td>
<td>2.2517</td>
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<td>1.090</td>
<td>0.016</td>
<td>0.08</td>
<td>0.038</td>
</tr>
<tr>
<td>G447B</td>
<td>2.5904</td>
<td>2.3885</td>
<td>1.25</td>
<td>1.082</td>
<td>0.016</td>
<td>0.09</td>
<td>0.038</td>
</tr>
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<td>2.9341</td>
<td>2.7322</td>
<td>1.39</td>
<td>1.237</td>
<td>0.016</td>
<td>0.08</td>
<td>0.038</td>
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<td>G340A</td>
<td>2.6913</td>
<td>2.4894</td>
<td>1.32</td>
<td>1.127</td>
<td>0.016</td>
<td>0.12</td>
<td>0.038</td>
</tr>
<tr>
<td>G340B</td>
<td>2.1671</td>
<td>2.9652</td>
<td>1.06</td>
<td>0.890</td>
<td>0.016</td>
<td>0.09</td>
<td>0.038</td>
</tr>
<tr>
<td>G340C</td>
<td>2.1273</td>
<td>1.9254</td>
<td>1.14</td>
<td>0.872</td>
<td>0.016</td>
<td>0.19</td>
<td>0.038</td>
</tr>
</tbody>
</table>
Table 5-3 (continued)

c) Pyrite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Weight (gm.)</th>
<th>Weight Silica (gm.)</th>
<th>Total Silica</th>
<th>Iron</th>
<th>Sulfur</th>
<th>Vapour Space</th>
<th>Pyrite</th>
<th>Sulfur</th>
<th>Vapour Space</th>
</tr>
</thead>
<tbody>
<tr>
<td>P690A</td>
<td>2.7274</td>
<td>2.5840</td>
<td>1.32</td>
<td>1.170</td>
<td>0.006</td>
<td>0.07</td>
<td>0.019</td>
<td>0.035</td>
<td>0.10</td>
</tr>
<tr>
<td>P690B</td>
<td>2.9312</td>
<td>2.7875</td>
<td>1.47</td>
<td>1.262</td>
<td>0.006</td>
<td>0.13</td>
<td>0.019</td>
<td>0.035</td>
<td>0.15</td>
</tr>
<tr>
<td>P690C</td>
<td>2.8165</td>
<td>2.6729</td>
<td>1.32</td>
<td>1.211</td>
<td>0.006</td>
<td>0.03</td>
<td>0.019</td>
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<td>0.06</td>
</tr>
<tr>
<td>P447A</td>
<td>3.3442</td>
<td>3.2006</td>
<td>1.53</td>
<td>1.450</td>
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<td>0.019</td>
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</tr>
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<td>P447B</td>
<td>2.4997</td>
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<td>0.006</td>
<td>0.08</td>
<td>0.019</td>
<td>0.031</td>
<td>0.10</td>
</tr>
<tr>
<td>P447C</td>
<td>2.7441</td>
<td>2.6006</td>
<td>1.29</td>
<td>1.178</td>
<td>0.006</td>
<td>0.04</td>
<td>0.019</td>
<td>0.031</td>
<td>0.06</td>
</tr>
<tr>
<td>P340A</td>
<td>2.5885</td>
<td>2.4449</td>
<td>1.23</td>
<td>1.107</td>
<td>0.006</td>
<td>0.06</td>
<td>0.019</td>
<td>0.030</td>
<td>0.02</td>
</tr>
<tr>
<td>P340B</td>
<td>2.5904</td>
<td>2.4470</td>
<td>1.21</td>
<td>1.108</td>
<td>0.006</td>
<td>0.04</td>
<td>0.019</td>
<td>0.030</td>
<td>0.05</td>
</tr>
<tr>
<td>P340C</td>
<td>2.8062</td>
<td>2.6626</td>
<td>1.35</td>
<td>1.206</td>
<td>0.006</td>
<td>0.08</td>
<td>0.019</td>
<td>0.030</td>
<td>0.10</td>
</tr>
</tbody>
</table>
of subsequent samples.

The amount of sulfur in the vapor phase can now be calculated using the ideal gas law,

\[ PV = nRT \]

where,

- \( P \) is the pressure of the system, estimated from the sulfur vapor pressure curve
- \( V \) = volume of free space in the capsule (calculated)
- \( R \) = gas constant \( (82.06 \text{ cm}^3 \text{ atm deg}^{-1} \text{mol}) \)
- \( n \) = no. of moles of sulfur
- \( T \) = absolute temperature

For G690A we have,

\[ P = 16.4 \text{ atm. (Fig. 6-10)} \]
\[ V = 0.086 \text{ cm}^3 \]

consequently,

\[ n = \frac{PV}{RT} = \frac{16.4 \times 0.086}{82.06 \times 973} \text{ moles} \]
\[ = 1.765 \times 10^{-5} \text{ moles} \]

Number of atoms per molecule at \( 690^\circ \text{C} = 4.9 \) (Fig. 5.3), i.e. molecular weight of sulfur vapor = \( 4.9 \times 32.06 \)
\[ = 157 \]
Therefore, weight of sulfur in vapor phase = 1.57 \times 1.765 \times 10^{-5} \text{ gm.}

= 0.00287 \text{ gms.}

The total amount of sulfur in the charge = 0.05000 \text{ gms.}

Therefore, approximately 6\% of the total amount of free sulfur occurs in the vapor phase.

5.5.2. Composition of Charges

Details as to the composition of individual charges and the experimental condition under which they were run are presented in Tables 5-4, 5.

The amount of sulfur present in the vapor phase in capsules of "Series B" has been calculated. No information is available for Series A, but the amount of sulfur in the vapor phase is invariably believed to be considerably less than indicated for the second series of experiments.

In Series B, the vapor phase never amounted to more than 3\% of the liquid phase, except in the highest temperature runs, where it constituted a maximum of 10\%.

Fractionation between the vapor and liquid phase can be expected to be small (Section 5.3.2.) and probably less than 1 permil at 700°C so that the presence of a sulfur vapor phase and its influence
on fractionation factors between sulfide and liquid sulfur can be neglected. Furthermore, the effect would always be in the same direction and of approximately the same magnitude for exchange between the various sulfides and sulfur liquid, so that it would largely cancel out when sulfide-sulfide fractionation is considered.

5.6. Reaction Products

5.6.1. Sulfur

Quenching of sulfur produced a yellow plastic mass which rapidly hardened. This is a mixture of \( S_\alpha \) and the amorphous polymeric phase \( S_{w} \). The latter phase is metastable and spontaneously inverts to \( S_\alpha \). At room temperature, however, this transition requires years. All experiments, therefore, yielded a mixture of rhombic and polymeric sulfur.

5.6.2. Galena

Galena is readily recognized macroscopically by its metallic lustre and well developed crystals. It occurred typically as small single or intergrown cubes, dispersed in the sulfur matrix. The largest crystals were formed in the high temperature runs and measured up to 1 mm. in diameter.
Table 5-4

Series A - Composition of Charges

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. oC</th>
<th>Time hrs</th>
<th>Lead Weight (mg.)</th>
<th>Weight Sulfur (mg.)</th>
<th>Total Weight (mg.)</th>
<th>Weight Galena (mg.)</th>
<th>Weight Sulfur Liquid (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A15-2</td>
<td>390±4</td>
<td>2</td>
<td>129.90</td>
<td>170.20</td>
<td>300.10</td>
<td>150.00</td>
<td>150.10</td>
</tr>
<tr>
<td>A15-3</td>
<td>4</td>
<td>139.93</td>
<td>170.29</td>
<td>300.22</td>
<td>150.04</td>
<td>150.18</td>
<td></td>
</tr>
<tr>
<td>A15-4</td>
<td>8</td>
<td>129.94</td>
<td>170.18</td>
<td>300.12</td>
<td>150.05</td>
<td>150.07</td>
<td></td>
</tr>
<tr>
<td>A15-5</td>
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<td>170.08</td>
<td>299.98</td>
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<tr>
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<td>170.10</td>
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<td>170.10</td>
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<td>300.02</td>
<td>150.03</td>
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<td>129.93</td>
<td>170.10</td>
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<td>170.14</td>
<td>300.05</td>
<td>150.02</td>
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<td>300.06</td>
<td>150.02</td>
<td>149.94</td>
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<tr>
<td>A25-4</td>
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<td>129.93</td>
<td>170.29</td>
<td>300.02</td>
<td>150.04</td>
<td>150.18</td>
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</tr>
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<td>299.92</td>
<td>149.95</td>
<td>149.97</td>
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<td>129.88</td>
<td>170.12</td>
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a) Galena
### Table 5-5

**Series B - Composition of Charges**

#### a) Galena

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<thead>
<tr>
<th>Sample</th>
<th>Temp. (°C)</th>
<th>Time (hours)</th>
<th>Lead (mg.)</th>
<th>Sulfur (mg.)</th>
<th>Total (mg.)</th>
<th>Galena (mg.)</th>
<th>Sulfur liquid (mg.)</th>
<th>Sulfur vapour (mg.)</th>
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<td>422.8</td>
<td>372.9</td>
<td>49.8</td>
<td>0.1</td>
</tr>
</tbody>
</table>
The synthesis of galena appeared to have been completed at all temperatures within one hour. (Puchelt, 1968, indicates that the chemical reaction may reach completion in as little as 5 minutes at 300°C.) No lead metal could be observed macroscopically in any of the charges.

5.6.3. Sphalerite

The formation of sphalerite did not take place as readily as that of galena. The reaction had not gone to completion at 340°C after 240 hours, while after 36 hours at 445°C some zinc metal was still present. Sphalerite was, however, found in all the charges though the amounts present in the shorter runs at 340°C proved insufficient to be analyzed. Similar slow rates of formation of sphalerite have been reported by various other workers. Kullerud (1953) attributes some of this effect to the formation of ZnO films on the zinc metal due to reaction with oxygen present in capsules where a sufficiently high vacuum was not obtained during preparation of the charges.

The sphalerite formed was of an almost pure white colour and occurred as cubic crystals the size of which was approximately 1/25 mm. Such crystals appeared on the surface of dull grey filings of zinc when the reaction had not gone to completion or otherwise, as intergrown clusters up to 1 mm. in size and approximating to the form
of the original zinc filings. All the phases were identified only under the binocular microscope.

5. 6. 4. **Pyrite**

Kullerud and Yoder (1959) describe the reaction of iron metal with excess sulfur. Reaction took place readily yielding grains of pyrrhotite which reacted with some of the remaining sulfur to form pyrite. The grains of pyrrhotite were, therefore, covered by a rim of pyrite retarding further reaction. It was found necessary to increase the surface area by regrinding before the reaction could go to completion.

The iron sponge used in the present series of experiments has a grain size varying between 10 and 50 Microns. Since the reaction rims described by Kullerud and Yoder appeared of the order of 20 microns in thickness it was believed that the formation of pyrite would reach completion in a single step.

All the runs yielded a brassy yellow metallic product in the form of cubic crystals reaching a maximum grain size of 1 mm. at the higher temperatures. X-ray analysis of the products, however, show the presence of pyrrhotite in the sulfide phase of all the runs. Native metal was also found to be present in the 36 hour run at 340°C but not in the longer runs.
The amount of pyrrhotite in the sulfide phase was measured semi-quantitatively from the intensity of X-ray diffraction patterns on these samples in comparison to those obtained for standards of known composition (Appendix A). Results are presented in Table 5-6.

The amount of pyrrhotite in the runs at 445 and 690°C does not appear to exceed 10% by weight in any of the reaction products. Because pyrrhotite contains half as much sulfur in the molecule as does pyrite, this contributes a maximum of 5% sulfur contaminant relative to a pure pyrite phase.

On the other hand, assemblages synthesized at 350°C would appear to consist almost exclusively of pyrrhotite. Since the relative amounts of pyrrhotite and pyrite are known approximately for three sets of runs, and if the fractionation factor between pyrite and pyrrhotite is relatively small, it is possible to calculate pyrite-sulfur and pyrrhotite-sulfur fractionation factors to well within experimental accuracy (section 5.9.4.). The fractionation between the two sulfides, however, would appear to be so small as to be almost negligible.
**TABLE 5-6**

**COMPOSITION OF PYRITE-PYRRHOTITE MIXTURES**

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<th>Reaction Temperature</th>
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<td>447°C</td>
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<tr>
<td>690°C</td>
<td>89</td>
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</table>
5.7. Mineral Separation

After quenching, the following mineral phases are present in a synthetic charge:

a) Sulfide. Excess metal may be present if the sulfide-producing reaction has not gone to completion.

b) Sulfur. This phase consists of a mixture of rhombic and polymeric allotropes. The metastable polymer is insoluble in any organic solvent and has to be inverted to the rhombic form.

Separation of the sulfide and sulfur phases is therefore accomplished by inverting the sulfur to the readily soluble crystalline state by grinding and dissolving the sulfur through use of a suitable organic solvent. After filtering, the sulfur can be precipitated through evaporation of the solvent, while the sulfide may be separated from any silica glass fragments derived from the capsule, through the use of heavy liquids.

Step 1. Silica glass capsule is broken. Care is taken that no material is lost. The larger glass fragments are scraped clear of adhering material and removed individually.

Step 2. Material is ground under acetone for 2-3 minutes. The amorphous sulfur phase is converted to rhombic sulfur.
Step 3. Material is transferred to a small glass beaker and about 20 ml. benzene is added. The mixture is heated at 40°C and stirred until all sulfur is dissolved.

Step 4. After all sulfur appears to have been dissolved, liquid is carefully poured off into 50 ml. beaker. Step 3 is repeated for the remaining material and benzene again poured off. Remaining solids are washed in benzene. (Liquid is poured off because it was found that too much fine-grained sulfide was lost if separated through filtering.)

Step 5. A small amount of water is added to the benzene solution to form a thin immiscible layer at the bottom of the beaker. Benzene is slowly evaporated at 40°C. Sulfur needles crystallize on top of water layer and can readily be removed with a spatula or separated through filtering depending on the nature of the crystal mass.

Step 6. Solids (mixture of sulfides and glass) are dried in a heating oven and separated in tetra-bromoethane in a centrifuge. This separation is repeated several times if necessary.

Step 7. If on subsequent examination under the microscope sulfur is still present in the sulfide phase, the separation procedure is repeated.
Separation of the galena and sulfur phase involved several difficulties resulting in a low yield. The separation of the benzene solution and galena crystals originally was attempted through filtering. Owing to the fine grain-size of the galena a considerable portion of the sample was lost in the filter paper. Great difficulty was also encountered in precipitating the sulfur from the solution until the technique of adding a layer of water to the benzene solution was devised. Initial yields are, therefore, low but increase for subsequent samples. Recovery of products is reported in Tables 5-7, 8.

The low percentage recovery does not affect the analytical results except that not enough material for analysis was recovered for a few samples and no results are available for these. In other cases samples of small size were analysed and the possibility of errors being introduced during the preparation of $S_0^2$ cannot be discounted. Such samples are marked with a question mark in the tabulation of results.
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**Table 5-7**

Sample Recovery, Series A - Galena
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<td>96</td>
<td></td>
<td>79.2</td>
<td>58.2</td>
</tr>
</tbody>
</table>
For every sample, sulfur of high purity was readily separated and it was never found necessary to repeat any stage of the separation process for the sulfur phase. Sulfide impurities as estimated under the microscope never amounted to more than 1%.

Pyrite and sphalerite were readily recovered containing less than 1% sulfur impurity. For a few samples a greater amount of impurity was estimated and these were reground and the separation procedure was repeated. None of the samples burned contained more than 1% sulfur impurity (by volume).

Galena concentrations, upon examination, frequently showed the presence of relatively large amounts of sulfur. Virtually all the samples had to undergo mineral separation a second time or even a third time. A product of 98% purity is believed to have been obtained in all cases.

The effect of sulfur impurities is especially important in the case of galena because of the low sulfur content of the sulfide (13% by weight). 2% sulfur impurity by volume approximates to 1% by weight or 13% in terms of relative amounts of sulfur in the sulfide and sulfur phase. For a maximum observed fractionation of 2% the error arising directly as a result of sample impurity would amount to 0.15%, approximately equal to experimental accuracy.
In order to estimate the magnitude of fractionation (if any) during the separation process a sample of sulfur was repeatedly dissolved in benzene and precipitated under conditions identical to those of routine separation. During the recycling process any fractionation would have a cumulative effect. Results are summarized in Table 5-9 and Figure 5-11.

Table 5-9
Fractionation Effects During Mineral Separation

<table>
<thead>
<tr>
<th>No. of extraction cycles</th>
<th>Isotopic Composition</th>
<th>( \delta S^{34}(%_o) ) ( \text{mean} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.44 8.30</td>
<td>8.37</td>
</tr>
<tr>
<td>3</td>
<td>8.27 8.44 8.44</td>
<td>8.38</td>
</tr>
<tr>
<td>8</td>
<td>8.24</td>
<td>8.24</td>
</tr>
<tr>
<td>14</td>
<td>7.71 7.95 7.88 7.85</td>
<td>7.85</td>
</tr>
</tbody>
</table>

The fractionation during a single phase separation can be calculated to amount to approximately 0.02\%\(_o\). This error is negligible.
FIG. 5-13 FRACTIONATION DURING CYCLIC SEPARATION PROCESS.
5.8. Isotopic Analysis

After phases had been separated their isotopic composition was measured by mass spectrometric analysis of sulfur dioxide.

5.8.1. \( \text{SO}_2 \)-Preparation

\( \text{SO}_2 \) was prepared by burning samples in a purified oxygen stream at 1350°C. The gas was purified by freezing out \( \text{CO}_2 \), \( \text{H}_2\text{O} \) and pumping away excess oxygen (Thode et al. 1961).

The apparatus and procedure used in preparing \( \text{SO}_2 \) gas has been described in detail by Lusk (1968). Approximately 12 samples were burned per working day. A sample of Park City pyrite (\( \delta^{34}\text{S} = 2.34\% \)) was used as a line standard and burned each day.

5.8.2. Mass-Spectrometric Analysis

The \( \text{SO}_2 \) samples were analyzed on a 6 inch, 90 degree sector mass spectrometer employing simultaneous collection and sample switching techniques as described by Wanless and Thode (1953).

5.8.3. Precision of Analysis

For samples of sufficient purity, analytical errors are thought to result from various small fractionation effects encountered during \( \text{SO}_2 \) preparation and during introduction of the sample into the mass spectrometer, as well as from fluctuations in the operating
conditions of the mass spectrometer. The total analytical error can be represented approximately as

\[ E_{\text{Total}} = \sqrt{(E_A)^2 + (E_B)^2} \]

Where,  
- \( E_A \) is the analytical error associated with \( S0_2 \) preparation;
- \( E_B \) is the error associated with mass spectrometer analysis.

Both \( E_A \) and \( E_B \) can be expected to show fluctuations from day to day and during a single day so that for samples burned and analyzed on different days,

\[ E_{\text{Total}} = \sqrt{(E_A^o)^2 + (E_A^t)^2 + (E_B^o)^2 + (E_B^t)^2} \]

where the superscripts "o" and "t" refer to single day and day-to-day fluctuations.

If such fluctuations are random, \( E_A^t \) and \( E_B^t \) can be eliminated for fractionation measurements between pairs of samples by burning and analyzing pairs of samples on the same day. If such fluctuations are not random and result from mixing and memory effects, this procedure will systematically lower the magnitude of the fractionation measured between such pairs.
In the present series of experiments a procedure was adopted whereby pairs of samples were analyzed consecutively on the mass spectrometer, though the SO$_2$ preparation was randomized. $E_A^t$ was corrected for by running a standard sample (Park City pyrite) each day in conjunction with the synthetic sulfides. All analytical results were expressed relative to this standard.

The effect of sample mixing in mass spectrometer analysis appears to be small (Monster, 1963). For the so-called identical sample test in which line standard SO$_2$ ($\delta S^{34} = 1.7$) is admitted to both reservoirs and the two samples run against each other, it was found that the two samples rarely differed by more than 0.2% (i.e. $\sqrt{(E_B^0)^2 + (E_B^t)^2}$. During this period an S$^{34}$ enriched reservoir standard ($\delta S^{34} = \pm 29.3$) was also run against the line standard and the standard deviation found to be 0.35 (i.e. $\sqrt{(E_B^0)^2 + (E_B^t)^2 + (E_B^{\text{mixing}})^2}$). Hence, the effect of mixing two samples of approximately 28% difference in isotopic composition corresponds approximately to an error of 0.15%.

Since it is reasonable to assume that the mixing error is linearly related to the difference in isotopic composition between the two samples, the mixing error between samples of less than 5% isotopic difference would appear negligible. Consecutive mass spectrometric analysis of pairs of coexisting phases, therefore, appears readily justifiable.
No such information is available for mixing effects during sample burning.

Information regarding the probable average magnitude of various analytical errors can be deduced from the analytical results of the present study. These results can be used to estimate errors for samples where only single analyses are available. If multiple analyses are available, errors can best be calculated directly from the analytical results.

1) Repeat burning of Park City Pyrite standard on one day and same day mass spectrometer analysis.

\[
\text{Error} = \sqrt{\left(\epsilon_A^0\right)^2 + \left(\epsilon_B^0\right)^2}
\]

Results are tabulated below,

<table>
<thead>
<tr>
<th>Std.</th>
<th>$\delta^{34}%_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.11</td>
</tr>
<tr>
<td>2</td>
<td>2.32</td>
</tr>
<tr>
<td>3</td>
<td>2.19</td>
</tr>
<tr>
<td>4</td>
<td>2.06</td>
</tr>
<tr>
<td>5</td>
<td>2.13</td>
</tr>
<tr>
<td>6</td>
<td>2.18</td>
</tr>
<tr>
<td>7</td>
<td>2.09</td>
</tr>
<tr>
<td></td>
<td>2.14 Std. Dev. = 0.08.</td>
</tr>
</tbody>
</table>
2) Repeat burning of Standard on different days and same-day mass spectrometer analysis.

\[
\text{Error} = \sqrt{(E_A^0)^2 + (E_A^t)^2 + (E_B^0)^2}
\]

Results are tabulated below,

**Analyses of P.C.P.**

<table>
<thead>
<tr>
<th>Date of burning</th>
<th>$\delta S^{34}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.1.67</td>
<td>2.09</td>
</tr>
<tr>
<td>1.2.67</td>
<td>2.58</td>
</tr>
<tr>
<td>2.2.67</td>
<td>2.19</td>
</tr>
<tr>
<td>4.2.67</td>
<td>2.60</td>
</tr>
<tr>
<td>5.2.67</td>
<td>2.51</td>
</tr>
<tr>
<td>6.2.67</td>
<td>2.10</td>
</tr>
<tr>
<td>7.2.67</td>
<td>2.20</td>
</tr>
</tbody>
</table>

2.33 Std. Dev. = 0.22

3) Repeat burning of Standard on different days and mass spectrometer analysis on different days.

\[
\text{Error} = \sqrt{(E_A^0)^2 + (E_A^t)^2 + (E_B^0)^2}
\]
<table>
<thead>
<tr>
<th>Date of burning</th>
<th>$\delta S^{34}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.6.67</td>
<td>1.67</td>
</tr>
<tr>
<td>26.6.67</td>
<td>2.40</td>
</tr>
<tr>
<td>27.6.67</td>
<td>2.46</td>
</tr>
<tr>
<td>28.6.67</td>
<td>2.36</td>
</tr>
<tr>
<td>30.6.67</td>
<td>2.23</td>
</tr>
<tr>
<td>1.7.67</td>
<td>2.31</td>
</tr>
<tr>
<td>2.7.67</td>
<td>2.10</td>
</tr>
<tr>
<td>3.7.67</td>
<td>1.88</td>
</tr>
<tr>
<td>4.7.67</td>
<td>2.48</td>
</tr>
<tr>
<td>7.7.67</td>
<td>3.04</td>
</tr>
<tr>
<td>13.8.67</td>
<td>2.98</td>
</tr>
<tr>
<td>14.8.67</td>
<td>2.35</td>
</tr>
<tr>
<td>15.8.67</td>
<td>2.45</td>
</tr>
<tr>
<td>16.8.67</td>
<td>2.38</td>
</tr>
<tr>
<td>17.8.67</td>
<td>2.26</td>
</tr>
<tr>
<td>19.8.67</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td>$2.34 \text{ Std. Dev.} = 0.33$</td>
</tr>
</tbody>
</table>

4) Repeat mass spectrometric analysis on different days

$$\text{Error} = \sqrt{\left(E_B^t\right)^2 + \left(E_B^o\right)^2}$$

A large number of samples were thus repeatedly run on the mass spectrometer on different days. Results are tabulated below.
## Repeat Mass Spectrometer Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{34}$ S</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Series A. Galena-Sulfur</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.90 5.82</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>5.92 6.04</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>5.53 5.49</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>5.79 5.62</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>5.95 6.00</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>6.44 6.22</td>
<td>0.15 mean = 0.08</td>
<td></td>
</tr>
<tr>
<td><strong>Series B. Galena-Sulfur</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.86 5.90</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>5.02 5.15</td>
<td>0.09 mean = 0.06</td>
<td></td>
</tr>
<tr>
<td><strong>Sphal. -Sulfur</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.61 5.73</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>5.92 6.07 5.81</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>5.93 5.96 5.76</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>6.14 6.09 6.28</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>5.01 5.09</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>5.36 5.32</td>
<td>0.03 mean = 0.08</td>
<td></td>
</tr>
<tr>
<td><strong>Pyrite-Sulfur</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.64 6.52</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>4.94 4.95</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>5.73 5.75</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>5.93 6.10</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>6.10 6.10</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>4.63 4.85</td>
<td>0.15 mean = 0.05</td>
<td></td>
</tr>
</tbody>
</table>

Average standard deviation = 0.07
5) Repeated burning of a single sample and same-day mass spectrometer analysis. After correction for burning standard the error is,

\[
\text{Error} = \sqrt{2(E_A^o)^2 + 2(E_B^o)^2}
\]

(since the error in the burning standard amounts in \(E_A^o + E_B^o\)).

### Analyses for repeated sample burning

<table>
<thead>
<tr>
<th>(\delta S^{34} )</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Series A. Galena-Sulfur</strong></td>
<td></td>
</tr>
<tr>
<td>6.53 6.69</td>
<td>0.03</td>
</tr>
<tr>
<td>5.53 5.79</td>
<td>0.18</td>
</tr>
<tr>
<td>5.49 5.62</td>
<td>0.09</td>
</tr>
<tr>
<td>5.91 5.95</td>
<td>0.03</td>
</tr>
<tr>
<td>6.42 6.44</td>
<td>0.01 Mean = 0.07</td>
</tr>
<tr>
<td><strong>Series B. Galena-Sulfur</strong></td>
<td></td>
</tr>
<tr>
<td>5.30 5.28</td>
<td>0.01</td>
</tr>
<tr>
<td>5.39 5.28</td>
<td>0.08</td>
</tr>
<tr>
<td>4.98 5.05</td>
<td>0.05</td>
</tr>
<tr>
<td>4.74 4.95</td>
<td>0.15</td>
</tr>
<tr>
<td>6.17 6.22</td>
<td>0.03</td>
</tr>
<tr>
<td>5.97 5.89</td>
<td>0.06</td>
</tr>
<tr>
<td>6.62 6.88</td>
<td>0.18</td>
</tr>
<tr>
<td>4.97 5.00</td>
<td>0.02</td>
</tr>
<tr>
<td>5.40 5.22</td>
<td>0.13 Mean = 0.08</td>
</tr>
<tr>
<td><strong>Sphal. -Sulfur</strong></td>
<td></td>
</tr>
<tr>
<td>5.11 5.03</td>
<td>0.06</td>
</tr>
<tr>
<td>5.94 5.91</td>
<td>0.02</td>
</tr>
<tr>
<td>5.37 5.20</td>
<td>0.12</td>
</tr>
<tr>
<td>5.64 5.59 5.59</td>
<td>0.03</td>
</tr>
<tr>
<td>5.63 5.45</td>
<td>0.13 Mean = 0.07</td>
</tr>
<tr>
<td>Pyrite-Sulfur</td>
<td>6.18</td>
</tr>
<tr>
<td>--------------</td>
<td>------</td>
</tr>
<tr>
<td></td>
<td>6.18</td>
</tr>
<tr>
<td></td>
<td>5.49</td>
</tr>
<tr>
<td></td>
<td>4.85</td>
</tr>
<tr>
<td></td>
<td>5.39</td>
</tr>
<tr>
<td></td>
<td>5.56</td>
</tr>
<tr>
<td></td>
<td>5.87</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.94</td>
</tr>
<tr>
<td></td>
<td>5.86</td>
</tr>
<tr>
<td></td>
<td>4.93</td>
</tr>
<tr>
<td></td>
<td>4.50</td>
</tr>
</tbody>
</table>

Mean = 0.12
Average standard deviation = 0.09 permil.

Summary of Results:

1) \[ \sqrt{(E_A^0)^2 + (E_B^0)^2} = 0.08\% \]

2) \[ \sqrt{(E_A^0)^2 + (E_A^t)^2 + (E_B^0)^2} = 0.22\% \]

3) \[ \sqrt{(E_A^0)^2 + (E_A^t)^2 + (E_B^0)^2 + (E_B^t)^2} = 0.33\% \]

4) \[ \sqrt{(E_B^t)^2 + (E_B^0)^2} = 0.07\% \]

5) \[ \sqrt{2(E_A^0)^2 + 2(E_B^0)^2} = 0.09\% \]
These results appear consistent with the following approximate values for the individual analytical errors,

\[ E_A^o \sim 0.07\% \]

\[ E_A^t \sim 0.21\% \]

\[ E_B^o \sim 0.00\% \]

\[ E_B^t \sim 0.25\% \]

It would appear, therefore, that the largest error is represented by the day-to-day fluctuation in SO\(_2\) preparation and day-to-day fluctuation in mass spectrometer analysis. There would appear to be no fluctuation in mass spectrometer performance during a single day.

The error associated with a single analysis, i.e. a single SO\(_2\) preparation and mass spectrometer analysis, after correction w.r.t. the burning standard amounts to:

\[
\text{Error} = \sqrt{2 (E_A^o)^2 + 2 (E_B^o)^2} \approx 0.10\%
\]
The error in the measured fractionation between a pair of such samples amounts to

\[
\text{Error} = \sqrt{4(E_A^0)^2 + 4(E_B^0)^2}
\]

\[\approx 0.14\%\]

if the mass spectrometer analysis is performed on the same day.

These error estimates were used for those samples where only single analyses were available.

(Note: If paired samples are burned consecutively on the same day instead of randomly as in this study, the error associated with a single analysis is given by,

\[
\text{Error} = \sqrt{2(E_A^0)^2 + 2(E_B^0)^2 + (E_A^{\text{mixing}})^2}
\]

The magnitude of \(E_A^{\text{mixing}}\) cannot be estimated at the present time but if it is less than 0.15% greater analytical accuracy can be achieved by this alternative procedure.)

5.9. Analytical Results

5.9.1. Series A. Galena-Sulfur Exchange

Analytical results obtained for the exchange of sulfur isotopes between synthetic galena and sulfur phases are summarized in Table
5-10. Exchange reactions were investigated at temperatures of 725±2°C, 451±2°C, 390±4°C, 348±2°C, and 307±3°C. Reaction times varied from 1 to 144 hours.

Analyses obtained for the individual phases at all temperatures and reaction times are shown in Figs. 5-14, 15, 16, 17, 18 while values for the fractionation between the galena and sulfur phases are presented in Figs. 5-19, 20, 21, 22, 23.

All the samples analyzed show measurable fractionation with the sulfur phase invariably enriched in the heavier isotope. The magnitude of the fractionation effect may amount to approximately 5 permil for the lower temperature exchange reactions. Furthermore, it appears that two distinct fractionation processes are operative. An initial kinetic isotope effect accompanies the formation of galena from native lead and sulfur, leading to an enrichment of $^{32}$S in the galena so that the initial fractionation between galena and sulfur may amount to as much as -6 permil in the lowest temperature runs. This kinetic isotope effect does not appear to take place at the same rate as the sulfide-forming reaction, but would seem to be significantly slower. In some of the runs the effect is operative as much as 8 hours after initiation of the reaction.
### Table 5-10

**Series A. Experimental Galena-Sulfur Fractionation**

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C.)</th>
<th>Reaction Time (hours)</th>
<th>Isotopic Composition $\Delta S^{34}$</th>
<th>$\Delta Gn - S$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sulfur(S)</td>
<td>Galena(Gn)</td>
</tr>
<tr>
<td>725</td>
<td>1</td>
<td>5.44</td>
<td>5.04</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.41?</td>
<td>2.42</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6.13</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>5.42</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>72</td>
<td>6.29</td>
<td>5.84</td>
</tr>
<tr>
<td>451</td>
<td>2</td>
<td>6.31</td>
<td>5.15</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5.83</td>
<td>4.34</td>
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<td></td>
<td>8</td>
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<td>4.77</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>5.85</td>
<td>4.85</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>6.14</td>
<td>5.27</td>
</tr>
<tr>
<td></td>
<td>72</td>
<td>6.11</td>
<td>5.28</td>
</tr>
<tr>
<td></td>
<td>108</td>
<td>5.54</td>
<td>-</td>
</tr>
<tr>
<td>390</td>
<td>8</td>
<td>6.00</td>
<td>4.51</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>5.98</td>
<td>4.94</td>
</tr>
<tr>
<td></td>
<td>36</td>
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<td>4.91</td>
</tr>
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<td>80</td>
<td>5.71</td>
<td>4.80</td>
</tr>
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<td>345</td>
<td>1</td>
<td>6.16</td>
<td>5.54</td>
</tr>
<tr>
<td></td>
<td>2</td>
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<td>5.52</td>
</tr>
<tr>
<td></td>
<td>4-1/2</td>
<td>6.12</td>
<td>4.99</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>-</td>
<td>5.18</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>6.29</td>
<td>5.02</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>6.40</td>
<td>5.23</td>
</tr>
<tr>
<td></td>
<td>108</td>
<td>5.89</td>
<td>4.78</td>
</tr>
</tbody>
</table>
Table 5-10 (continued)

<table>
<thead>
<tr>
<th></th>
<th>Sulfur</th>
<th>Galena</th>
<th>ΔGN-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>307</td>
<td>5.90</td>
<td>6.69</td>
<td>-5.29</td>
</tr>
<tr>
<td></td>
<td>5.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.53</td>
<td>6.99</td>
<td>1.32</td>
</tr>
<tr>
<td>4</td>
<td>5.92</td>
<td>6.04</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>6.34</td>
<td>1.71</td>
<td>-4.63</td>
</tr>
<tr>
<td>36-1/2</td>
<td>5.53</td>
<td>5.79</td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td>5.49</td>
<td>5.62</td>
<td>-3.16</td>
</tr>
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<td>5.95</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td>6.00</td>
<td></td>
<td>-3.38</td>
</tr>
<tr>
<td>110</td>
<td>6.23</td>
<td>3.31</td>
<td>-2.92</td>
</tr>
<tr>
<td>144</td>
<td>6.42</td>
<td>6.44</td>
<td>3.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.22</td>
<td>-2.58</td>
</tr>
</tbody>
</table>

(All values relative to Park City Pyrite.)

(Values in different columns represent duplicate burnings.

Values in different rows represent duplicate mass spectrometer analyses.)
Temperature $= 725 \pm 2^\circ C$

**FIG. 5-14** SERIES A  ISOTOPIC COMPOSITION OF GALENA-SULFUR PAIRS AT 725$^\circ$C
Temperature = 451 ±2°C

FIG. 5-14  SERIES A  ISOTOPIC COMPOSITION OF GALENA-SULFUR PAIRS AT 451°C
Temperature = 390 ±4°C

FIG. 5-16. SERIES A ISOTOPIC COMPOSITION OF GALENA-SULFUR PAIRS AT 390°C
Fig. 5-17 Series A isotopic composition of galena-sulfur pairs at 348°C.

Temperature = 348 ±2°C
Temperature = $307 \pm 3^\circ C$

Fig. 5-18. Series A isotopic composition of galena-sulfur pairs at $307^\circ C$
FIG. 5-19  SERIES A  GALENA-SULFUR FRACTIONATION VERSUS REACTION TIME AT 725°C
FIG. 5-20. SERIES A  GALENA -SULFUR FRACTIONATION VERSUS REACTION TIME AT 451°C
FIG. 5-21. SERIES A GALENA-SULFUR FRACTIONATION AT 390°C VERSUS REACTION TIME
FIG. 5-22. SERIES A  GALENA-SULFUR FRACTIONATION VERSUS REACTION TIME AT 348°C
FIG. 6-23. SERIES A GALENA-SULFUR FRACTIONATION VERSUS REACTION TIME AT 307°C
Approach to equilibrium exchange between galena and sulfur starts immediately after the formation of the first galena but does not become the dominant fractionation-producing process until the kinetic effect has gone to completion. Since the kinetic isotope effect in the Pb-S system produces a fractionation greater than the equilibrium exchange fractionation, this process produces an exponential decrease in the difference in isotopic composition of sulfur and galena phases with time.

With the exception of the run at 307°C, equilibrium appears to have been approached closely in all experiments within the allowed reaction time. Isotopic equilibrium was attained within 1 hour for the exchange reaction at 725°C. Accurate values for the equilibrium fractionation factor can be obtained by plotting

\[ \Delta_{\text{Gn-S}}^{(t)} - \Delta_{\text{Gn-S}}^{(E)} \]

Where \( \Delta_{\text{Gn-S}}^{(t)} \) = fractionation at reaction time \( t \)
\( \Delta_{\text{Gn-S}}^{(E)} \) = fractionation at equilibrium = \( 10^3 \ln K_{\text{Gn-S}} \)

versus reaction time \( t \) on semilog paper for various values of \( \Delta_{\text{Gn-S}}^{(E)} \).
The value producing the closest approximation to a straight-line plot represents the equilibrium fractionation. Such semilogarithmic plots are shown in Figs. 5-24, 25, 26, 27.

It is apparent that where more than 3 points are available and these are plotted in this fashion, they do fall on a straight line, thus justifying this procedure of calculating equilibrium fractionation factors (see Section 5.2).

The following equilibrium fractionations are obtained: (errors are assumed identical to those in longest run at a particular temperature. Since no duplicates are available, the error in a single fractionation is taken as ±0.2 permil (Section 5.8.3.)).

1) At 725°C \[ \Delta_{\text{Gn-S}}^{(E)} = 0.45 \pm 0.20 \]

Value chosen as measured in longest run. Equilibrium appears to have been established within one hour.

2) At 450°C \[ \Delta_{\text{Gn-S}}^{(E)} = 0.85 \pm 0.20 \]

Value obtained from semilog plot. Appears to lie between 0.80 and 0.85 permil.
FIG. 5-24.

SERIES A  GALENA-SULFUR EQUILIBRIUM FRACTIONATION AT 450°C

Semilogarithmic plot of $\Delta(t)_{Gn-S} - \Delta(E)_{Gn-S}$ versus reaction time for selected values of $\Delta(E)_{Gn-S} = 10^3 \ln K_{Gn-S}$
FIG. 5-25.

SERIES A  GALENA-SULFUR EQUILIBRIUM FRACTIONATION AT 390°C

Semilogarithmic plot of $\Delta^{(E)}_{\text{Gn-S}} - \Delta^{(t)}_{\text{Gn-S}}$ versus reaction time for selected values of $\Delta^{(E)}_{\text{Gn-S}} 10^3 \ln K_{\text{Gn-S}}$
FIG. 5-26.

SERIES A  GALENA-SULFUR EQUILIBRIUM FRACTIONATION AT 348°C

Semilogarithmic plot of $\Delta^{(E)}_{\text{Gn-S}} - \Delta^{(t)}_{\text{Gn-S}}$ versus reaction time for selected values of $\Delta^{(E)}_{\text{Gn-S}} = 10^3 \ln K_{\text{Gn-S}}$
SERIES A  GALENA-SULFUR EQUILIBRIUM FRACTIONATION AT 307°C

Semilogarithmic plot of $\Delta_{Gn-S}^{(t)} - \Delta_{Gn-S}^{(E)}$ versus reaction time for selected values of $\Delta_{Gn-S}^{(E)} = 10^3 \ln K_{Gn-S}$
3) At $390^\circ$C, $\Delta_{\text{Gn-S}}^{(E)} = 0.95 (\pm0.20)$

Value obtained from semilog plot. Lies between 0.90 and 0.95 permil.

4) At $348^\circ$C, $\Delta_{\text{Gn-S}}^{(E)} = 1.10 (\pm0.20)$

Value obtained from semilog plot. Value slightly larger than 1.105 permil.

5) At $307^\circ$C, $\Delta_{\text{Gn-S}}^{(E)} = 1.2-1.6$

Reaction is still a considerable distance from equilibrium and no accurate value for the equilibrium fractionation can be obtained. From the semilog plot, however, this value would appear to lie between the above limits. Except in the run at $307^\circ$C, therefore, the fractionation as measured in the longest runs, does not differ from the calculated equilibrium value by more than the analytical precision.

The equilibrium fractionation to a very good approximation appears to vary linearly with $T^{-2}$ as predicted theoretically (Fig. 5.27). This linear behaviour furthermore implies that fractionation effects between the various molecular species are negligible and that we are essentially dealing with a single exchange fractionation between galena and a sulfur phase.
A least squares fit of the data (including the origin) indicates that the galena-sulfur fractionation can be represented by the equation

$$10^3 \ln \alpha_{\text{Gn-S}} = -0.43(\pm0.07) \times 10^6 T^{-2}$$

5.9.2. Series B. Galena-Sulfur Exchange

Exchange reactions between galena and sulfur were investigated at temperatures of 689±10, 445±9, and 340±7°C. Reaction times were 36, 96, and 240 hours. Analytical results are presented in Table 5-11.

The isotopic composition of the individual phases in all the runs is shown in Figs. 5-29, 31, while the variation of the fractionation as a function of reaction time at the various temperatures is represented in Fig. 5-32. From the previous series of experiments it is known that the kinetic isotope effect has gone to completion at all temperatures within 36 hours, so that the results of the Series B experiments reflect approach to equilibrium fractionation between the galena and sulfur phases.
FIG. 5-28. SERIES A EQUILIBRIUM GALENA-SULFUR FRACTIONATION VERSUS $1/T^2$
Table 5-11
Series B. Experimental Galena-Sulfur Fractionation

<table>
<thead>
<tr>
<th>Temp. (°C.)</th>
<th>Reaction time (hours)</th>
<th>Isotopic Composition ($\delta^{34}S$)</th>
<th>ΔGn - S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sulfur(S)</td>
<td>Galena(Gn)</td>
</tr>
<tr>
<td>690</td>
<td>36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>5.52</td>
<td>5.39</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>5.30</td>
<td>5.28</td>
</tr>
<tr>
<td>447</td>
<td>36</td>
<td>6.17</td>
<td>6.22</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>5.97</td>
<td>5.89</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>5.86</td>
<td>5.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.90</td>
<td>4.98</td>
</tr>
<tr>
<td>340</td>
<td>36</td>
<td>6.62</td>
<td>6.88</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>6.85</td>
<td>5.40</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>5.99</td>
<td>4.71</td>
</tr>
</tbody>
</table>
FIG. 5-29. SERIES B ISOTOPIC COMPOSITION OF GALENA-SULFUR PAIRS AT 690°C
FIG. 5-30. SERIES B ISOTOPIC COMPOSITION OF GALENA-SULFUR PAIRS AT 447°C
FIG. 5-31. SERIES B ISOTOPIC COMPOSITION OF GALENA-SULFUR PAIRS AT 340°C
FIG. 5-32. SERIES B  GALENA - SULFUR FRACTIONATION VERSUS REACTION TIME
SERIES B  GALENA-SULFUR EQUILIBRIUM FRACTIONATION AT 340°C

Semilogarithmic plot of $\Delta_{\text{Gn-S}}^{(E)} - \Delta_{\text{Gn-S}}^{(t)}$ versus reaction time for selected values of $\Delta_{\text{Gn-S}}^{(E)} = 10^3 \ln K_{\text{Gn-S}}$. 

[Graph showing reaction time in hours on the x-axis and values on the y-axis, with lines for different reaction times marked with 'x'.]
Series B  
GALENA-SULFUR EQUILIBRIUM FRACTIONATION AT 447°C

Semilogarithmic plot of $\Delta_{Gn-S}^{(E)} - \Delta_{Gn-S}^{(t)}$ versus reaction time for selected values of $\Delta_{Gn-S}^{(E)} = 10^3 \ln K_{Gn-S}$
Equilibrium fractionation factors can be calculated for the exchange reactions at $447^\circ C$ and $340^\circ C$ through the use of semilogarithmic plots. These are shown in Figs. 5-33, 34. The following equilibrium values are obtained:

1) At $690^\circ C$ $\Delta_{\text{Gn-S}}^{(E)} = -0.30 (\pm 0.11)$

Value chosen as measured in longest run. Reaction appears to have established equilibrium within 96 hours.

2) At $447^\circ C$ $\Delta_{\text{Gn-S}}^{(E)} = -0.80 (\pm 0.12)$

Value obtained from semi-log plot. Lies between 0.75 and 0.80.

3) At $340^\circ C$ $\Delta_{\text{Gn-S}}^{(E)} = -1.15 (\pm 0.20)$

Value obtained from semi-log plot. Lies between 1.10 and 1.15.

The run at $340^\circ C$ appears to be the only one in which the equilibrium value has not been approached within experimental accuracy in the longest run. Within experimental accuracy the equilibrium fractionation between galena and sulfur as measured from the present series of experiments again varies linearly with $T^{-2}$ (Fig. 5-48). A least squares fit through the origin yields the following equation for galena-sulfur fractionation,
$10^3 \ln \alpha_{\text{Gn-S}} = -0.41(\pm 0.05) \times 10^6 \ T^{-2}$

These results are in good agreement with those obtained in Series A.

Combining results from Series A and B yields

$10^3 \ln \alpha_{\text{Gn-S}} = -0.42(\pm 0.05) \times 10^6 \ T^{-2}$

Puchelt (1968) describes the fractionation effect during synthesis of galena from native lead and sulfur at 300°C. Results are summarized in Table 5-12 and plotted in Fig. 5-35.

**Table 5-12**

Fractionation between Galena and Sulfur at T 300°C
(from Puchelt, 1968)

<table>
<thead>
<tr>
<th>$\delta S^{34}$ (Galena) - $\delta S^{34}$ (Sulfur) (%)</th>
<th>Reaction Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-4.8</td>
<td>0.083</td>
</tr>
<tr>
<td>-7.6</td>
<td>0.25</td>
</tr>
<tr>
<td>-10.8</td>
<td>0.42</td>
</tr>
<tr>
<td>-7.5</td>
<td>1</td>
</tr>
<tr>
<td>-6.1</td>
<td>5</td>
</tr>
<tr>
<td>-4.6</td>
<td>16</td>
</tr>
<tr>
<td>-3.9</td>
<td>96</td>
</tr>
<tr>
<td>-2.8</td>
<td>240</td>
</tr>
</tbody>
</table>
FIG. 5-35.  PUCHELT (1968) - GALENA-SULFUR FRACTIONATION AT 300°C
Insufficient information is available to determine to what extent experimental condition for the various runs were similar. Consequently, it is not possible to calculate an equilibrium value. From the available data, however, it is clear that

\[ \Delta_{\text{Gn-S}}^{(E)} \geq -2.8 \text{ at } 300^\circ C \]

Further experiments are described in which galena and sulfur of different isotopic composition are allowed to exchange. An initial difference in \( S^{34} \) content of -18\%\(^{o}\) (\( \delta_{\text{galena}} - \delta_{\text{sulfur}} \)) increased to -4.1\%\(^{o}\) in 96 hours at 400\(^\circ\)C and to -0.8\%\(^{o}\) in 24 hours at 500\(^\circ\)C (Fig. 5-36). It is therefore apparent that

\[ \Delta_{\text{Gn-S}}^{(E)} \geq -4.1 \text{ at } 400^\circ C \]

\[ \Delta_{\text{Gn-S}}^{(E)} \geq -0.8 \text{ at } 500^\circ C \]

These results are in agreement with the present study.

5.9.3. Series B, Sphalerite-Sulfur Exchange

The isotopic exchange of sulfur between sphalerite and sulfur was investigated at temperatures of 689±10\(^\circ\)C, 445±9\(^\circ\)C and 340±7\(^\circ\)C. Reaction times were 36, 96 and 240 hrs. These experimental conditions are identical for the galena-sulfur and pyrite-sulfur exchange experi-
FIG. 5-36. PUCHELT (1968) SULFUR ISOTOPE EXCHANGE BETWEEN GALENA AND SULFUR AT 400 AND 500°C.
m ents of Series B. Analytical results are presented in Table 5-13. Insufficient sphalerite for isotopic analysis was present in the shorter runs at 340°C so that no fractionation data is available.

Analyses of the individual phases are presented in Figs. 5-37, 38, 39, and the measured isotopic fractionation between the sphalerite and sulfur phases is shown in Fig. 5-40 as a function of reaction time.

In all cases the isotopic fractionation is of small magnitude (less than 0.5 permil) and in contrast to the galena runs, the sphalerite phase is enriched in $^{34}$S relative to sulfur. The fractionation shows a slight increase with time. The results suggest that the kinetic isotope effect has gone to completion within 36 hours or that it is very small or both. Alternatively it could be possible that these runs all represent only that part of the exchange reaction where the kinetic isotope effect is still dominant and perhaps increasing. The regular shape of the fractionation curves, however, suggest that only a single isotopic exchange process is operative and it would appear extremely unlikely that the kinetic isotope effect would still be dominant after 240 hours at 690°C. Fractionation factors obtained from these results show a good linear relationship when plotted against $T^{-2}$ (Fig. 5-48) again indicative of equilibrium exchange rather than a kinetic effect.
The apparent absence of a kinetic isotope effect in these samples where the chemical sulfide-forming reaction has not always gone to completion is not necessarily contradictory. As long as the rate of isotopic exchange between sphalerite and sulfur liquid is rapid compared to the rate at which the kinetic effect proceeds, any fractionation produced in the freshly formed sphalerite will be rapidly eliminated through equilibration within the sulfide phase and subsequently, with the liquid phase. At no stage of the reaction, therefore, will it be possible for a significant kinetic fractionation to be built up.

If isotopic exchange takes place while a slow chemical reaction is still in progress, it cannot be expected that the physical conditions of the system remain constant. The surface area between the sphalerite and sulfur phases changes continuously throughout the reaction, while the concentration of the components is also altered. The theory for isotopic exchange in heterogeneous systems discussed earlier is therefore not strictly applicable. Analytical results would, however, appear to indicate that the total fractionation effects are small and furthermore, all exchange reactions may well have reached equilibrium in the longest runs, or otherwise, the distance from equilibrium is of the order of 0.05 permil. Values for the equilibrium fractionation factor at various temperatures can, therefore, be readily calculated or estimated.
Table 5-13

Series B. Experimental Sphalerite-Sulfur Fractionations

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Reaction Time (hours)</th>
<th>Sulfur(S)</th>
<th>Sphalerite(Sp)</th>
<th>ΔSp-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>690</td>
<td>36</td>
<td>5.75</td>
<td>5.61</td>
<td>5.89</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>5.11</td>
<td>5.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>5.92</td>
<td>5.93</td>
<td>6.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.07</td>
<td>5.96</td>
<td>6.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.81</td>
<td>5.76</td>
<td>6.28</td>
</tr>
<tr>
<td>447</td>
<td>36</td>
<td>5.37</td>
<td>5.20</td>
<td>5.61</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>5.56</td>
<td>5.82</td>
<td>5.99</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>5.01</td>
<td>5.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>36</td>
<td>5.39</td>
<td>5.36</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>5.64</td>
<td>5.59</td>
<td>5.59</td>
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<td></td>
<td>240</td>
<td>5.63</td>
<td>5.35</td>
<td>6.02</td>
</tr>
</tbody>
</table>
FIG. 5-37. SERIES B ISOTOPIC COMPOSITION OF SPHALERITE-SULFUR PAIRS AT 690° C
FIG. 5-38. SERIES B  ISOTOPIC COMPOSITION OF SPHALERITE-SULFUR PAIRS AT 447°C
FIG. 5-39. SERIES B ISOTOPIC COMPOSITION OF SPHALERITE-SULFUR PAIRS AT 340 °C
FIG. 5-40. SERIES B  SPHALERITE-SULFUR FRACTIONATION VERSUS REACTION TIME
FIG. 5-41.

SERIES B SPHALERITE-SULFUR EQUILIBRIUM FRACTIONATION AT 447°C

Semilogarithmic plot of $\Delta^{(E)}_{\text{Sp-S}} - \Delta^{(t)}_{\text{Sp-S}}$ versus reaction time for selected values of $\Delta^{(E)}_{\text{Sp-S}} = 10^3 \ln K_{\text{Sp-S}}$
The following equilibrium values were obtained for sphalerite-sulfur isotopic exchange:

1) At 689°C, $\Delta_{\text{Sp-S}}^{(E)} = 0.25 \pm 0.21$

Value chosen as measured in longest run and rounded off to nearest 0.05%. Equilibrium appears to have been established within 36 hours.

2) At 445°C, $\Delta_{\text{Sp-S}}^{(E)} = 0.40 \pm 0.16$

Value obtained from semi-log plot. Equilibrium appears to have been established within 96 hours.

3) At 340°C, $\Delta_{\text{Sp-S}}^{(E)} = 0.55 \pm 0.23$

Value chosen slightly larger than measured in single run at 240 hours. In comparison to runs at other temperatures, it would appear likely that this value represents very close approach to equilibrium.

The equilibrium fractionation as estimated above, to a very good approximation varies linearly with $T^{-2}$ (Fig. 5-48). A least squares fit to a line through the origin indicates that the fractionation of sulfur isotopes between sphalerite and sulfur phases can be represented by the equation

$$10^3 \ln a_{\text{Sp-S}} = 0.21(\pm 0.07) \times 10^6 T^{-2}$$
5.9.4. Series B. Pyrite-Sulfur Exchange

Analytical results obtained for the exchange of sulfur isotopes between pyrite and sulfur phases are summarized in Table 5-14.

Experimental conditions were identical to those under which the galena and sphalerite runs were performed. Analyses of the individual phases are presented in Fig. 5-42, 43, 44 and the measured isotopic fractionation between the pyrite and sulfur phases is plotted in Fig. 5-45 as a function of reaction time.

Table 5-14

Series B. Experimental Pyrite-Sulfur Fractionations

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Reaction Time (hours)</th>
<th>Sulfur(S)</th>
<th>Pyrite(Py)</th>
<th>Isotopic Composition ($^{34}S$)</th>
<th>$\Delta_{Py-S}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>690</td>
<td>36</td>
<td>4.85</td>
<td>4.66</td>
<td>6.64</td>
<td>6.53</td>
</tr>
<tr>
<td>96</td>
<td>4.62</td>
<td>5.39</td>
<td>5.51</td>
<td></td>
<td>0.83</td>
</tr>
<tr>
<td>240</td>
<td>5.87</td>
<td>5.56</td>
<td>4.98</td>
<td></td>
<td>0.50</td>
</tr>
<tr>
<td>447</td>
<td>36</td>
<td>4.84</td>
<td>5.21</td>
<td>5.94</td>
<td>5.96</td>
</tr>
<tr>
<td>96</td>
<td>4.93</td>
<td>4.87</td>
<td>5.86</td>
<td>5.59</td>
<td>5.64</td>
</tr>
<tr>
<td>240</td>
<td>4.84</td>
<td>5.73</td>
<td>5.75</td>
<td></td>
<td>0.95</td>
</tr>
<tr>
<td>340</td>
<td>36</td>
<td>5.49</td>
<td>5.69</td>
<td>5.93</td>
<td>6.10</td>
</tr>
<tr>
<td>96</td>
<td>4.63</td>
<td>5.04</td>
<td>6.18</td>
<td>6.07</td>
<td>6.04</td>
</tr>
<tr>
<td>240</td>
<td>4.50</td>
<td>4.92</td>
<td>6.18</td>
<td>6.38</td>
<td>1.36</td>
</tr>
</tbody>
</table>
As has been mentioned previously, the lowest temperature run was found to contain pyrrhotite rather than pyrite, while the higher temperature runs consisted of pyrite with a small amount of pyrrhotite impurity. From the analytical results it would appear, therefore, that the kinetic isotope effect during pyrrhotite and pyrite formation is in opposite directions. The first formed pyrrhotite phase would appear highly enriched in the light isotope while on the other hand the pyrite is initially enriched in $^{34}S$. Subsequent approach to equilibrium exchange produces a decrease in the pyrite-sulfur fractionation and an increase in the pyrrhotite-sulfur fractionation. Equilibrium values can be calculated from semi-log plots for pyrite-sulfur exchange at 690°C and pyrrhotite-sulfur exchange at 340°C. The pyrite-sulfur exchange reaction at 447°C appears to have approached equilibrium closely after 96 hours and the equilibrium value can be estimated accurately from the value obtained for the longest run at this temperature. Semi-log plots are shown in Figs. 5-46, 5-47. The following equilibrium fractionations for the impure phases are obtained.
FIG. 5-42. SERIES B  ISOTOPIC COMPOSITION OF PYRITE-SULFUR PAIRS AT 699°C
FIG. 5-43. SERIES B  ISOTOPIC COMPOSITION OF PYRITE-SULFUR PAIRS AT 447°C
FIG. 5-44. SERIES B  ISOTOPIC COMPOSITION OF PYRITE-SULFUR PAIRS AT $340^\circ\text{C}$
FIG. 5-45 SERIES B - PYRITE - SULFUR FRACTIONATION VERSUS REACTION TIME
FIG. 5-46.

SERIES B  PYRITE-SULFUR EQUILIBRIUM FRACTIONATION AT 690°C

Semilogarithmic plot of $\Delta_{Py-S}^{(t)} - \Delta_{Py-S}^{(E)}$ versus reaction time for selected values of $\Delta_{Py-S}^{(E)} = 10^3 \ln K_{Sp-S}$
FIG. 5-47

SERIES B  PYRITE-SULFUR EQUILIBRIUM FRACTIONATION AT 340°C.

Semilogarithmic plot of $\Delta^{(E)}_{\text{Py-S}} - \Delta^{(t)}_{\text{Py-S}}$ versus reaction time for selected values of $\Delta^{(E)}_{\text{Py-S}} = 10^3 \ln K_{\text{Py-S}}$
1) At $690^\circ C$, $\Delta_{Py-S}^{(E)} = 0.50 (\pm 0.35)$
   Calculated from semilog plot. Reaction appears to have reached equilibrium after 240 hours.

2) At $447^\circ C$, $\Delta_{Py-S}^{(E)} = 0.95 (\pm 0.05)$
   Value estimated from fractionation observed in longest run.
   Equilibrium appears to have been attained in 96 hours.

3) At $340^\circ C$, $\Delta_{Py-S}^{(E)} = 1.35 (\pm 0.24)$
   Calculated from semilog plot. Reaction has reached equilibrium after 240 hours.

In all cases, therefore, the fractionation as measured in the longest runs is identical with the equilibrium fractionation. Values obtained for the equilibrium fractionation at various temperatures are plotted against $T^{-2}$ in Fig. 5-48. The two results for exchange between impure pyrite and sulfur indicate that the equilibrium fractionation factor varies linearly with $T^{-2}$ over the temperature range investigated. It is reasonable to assume that a linear extrapolation of these results to a temperature of $340^\circ C$ will yield a value for the impure pyrite-sulfur fractionation at this temperature accurate to within experimental precision. From Fig. 5-48 this value can be measured at 1.30 permil.
Therefore, the pyrrhotite-pyrite fractionation at this temperature amounts to approximately 0.05 permil which is insignificant in view of a standard deviation of 0.24 permil in the measured fractionation between impure pyrrhotite and sulfur at this temperature. The maximum amount of pyrrhotite in the pyrite phase at 690°C and 447°C is less than 15% by weight (Appendix A) while the amount of pyrite impurity in the pyrrhotite phase at 340°C can be estimated from measurement of x-ray intensities to amount to less than 20%. In view of the extremely small fractionation between the impure pyrite and pyrrhotite phases, the effect of these amounts of impurities is negligible. The values of 1.35 and 1.30 permil can, therefore, be taken as representative of fractionation between pure pyrrhotite and sulfur, and pure pyrite and sulfur respectively at 340°C. A least squares fit to the measured and extrapolated values for pure pyrite yields the equation,

\[ 10^3 \ln a_{Py-S} = 0.49 (\pm 0.07) \times 10^6 T^{-2} \]

While the influence of contaminant phases, therefore, does not affect the measured fractionation factors, the slow diffusion of sulfur through the pyrite phase causing the incomplete reaction may be of considerable importance. While the present study does not seem to indicate this, it would generally be expected that such apparent slow diffusion
could lead to disequilibrium effects within a pyrite phase, producing significant differences in isotopic composition within single crystals. This would be particularly true in natural pyrite crystals which frequently have dimensions of the order of several millimeters or even centimeters as opposed to grainsizes of the order of tens of microns which were studied experimentally. Slow rates of isotopic exchange between pyrites of different isotopic composition at elevated temperatures have been described by Puchelt (1968). These results refer to physical mixtures of pyrite grains and surface effects could be of considerable importance. Some of the analyses of pyrite presented here show variations greater than expected to result from analytical error (e.g. P690-240 hrs). There does not seem to be an obvious explanation for these fluctuations and they may represent real differences in isotopic composition of the pyrite phase. While the results obtained show general agreement with theoretical predictions and results obtained from natural specimens, more experimentation would appear warranted to ascertain whether these pyrite phases are indeed completely homogeneous. The kinetic isotope effect appears of a much more complex character than encountered for sphalerite and galena.
An explanation could lie in the possible inequivalence of the two sulfur atoms in the FeS$_2$ molecule. Thode (1963) for instance mentions that "certain samples of pyrite, perhaps with a particular history of mode of formation, decompose to pyrrhotite and sulfur with a large intramolecular sulfur isotope effect". Such effects could be interpreted as suggesting that the two sulfur atoms are not equivalent and that two different fractionation factors may be associated with exchange between each of these and another sulfur bearing phase.

5.9.5. Sulfide-Sulfide Fractionation

Fractionation factors between various sulfide pairs can readily be obtained from results for the fractionation between sulfide and sulfur phases. Fractionation factors have been calculated from the measured values at 340, 447 and 690°C and also from least squares fits to these values. The latter are bracketed.
FIG. 5-48 SERIES B EQUILIBRIUM SULFIDE-SULFUR FRACTIONATION VERSUS 1/T^2

(Series A Galena-sulfur Fractionation shown as dashed line)
Table 5-15
Sulfur Isotope Fractionation between Pyrite, Sphalerite and Galena

<table>
<thead>
<tr>
<th>Sulfide Pair</th>
<th>$10^3 \ln \alpha$ at 690°C</th>
<th>$10^3 \ln \alpha$ at 447°C</th>
<th>$10^3 \ln \alpha$ at 340°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite-Galena</td>
<td>-0.80 (-0.98)</td>
<td>-1.75 (-1.75)</td>
<td>-2.45 (-2.42)</td>
</tr>
<tr>
<td>Sphalerite-Galena</td>
<td>0.55 (0.68)</td>
<td>1.20 (1.22)</td>
<td>1.70 (1.68)</td>
</tr>
<tr>
<td>Pyrite-Sphalerite</td>
<td>0.25 (0.30)</td>
<td>0.55 (0.54)</td>
<td>0.75 (0.74)</td>
</tr>
</tbody>
</table>

Since all the sulfide-sulfur fractionation factors vary as $1/T^2$ in accordance with theory, it is obvious that the sulfide-sulfide fractionations will show the same behaviour. Equations representing the equilibrium fractionation between sulfide pairs can be readily obtained from those previously calculated for exchange between sulfide and sulfur phases (least squares fits through the origin).

Therefore,

\[
10^3 \ln \alpha_{Py-Gn} = 0.90(\pm0.09) \times 10^6 T^{-2}
\]

\[
10^3 \ln \alpha_{Sp-Gn} = 0.62(\pm0.10) \times 10^6 T^{-2}
\]

\[
10^3 \ln \alpha_{Py-邵} = 0.28(\pm0.09) \times 10^6 T^{-2}
\]
FIG. 5-49. EQUILIBRIUM FRACTIONATION BETWEEN PYRITE, SPHALERITE AND GALENA VERSUS $1/T^2$
CHAPTER 6

EQUILIBRIUM EXCHANGE FRACTIONATION AND GEOTHERMOMETRY

6.1. $\frac{\text{S}^{32}}{\text{S}^{34}}$ Ratio in Co-existing Minerals

The isotopic composition of a sulfide mineral crystallizing during a hydrothermal or other geologic process in local equilibrium from a fluid will depend on (a) the overall isotopic composition of the entire system, (b) the chemical nature of the fluid and solid phases, and (c) the temperature of the system. Parameters such as pH or pressure may influence the distribution of ionic sulfur species in the fluid (Barnes and Kullerud, 1961), thus exerting an indirect influence on the isotopic composition of the solid phase (Sakai 1968).

If two sulfides are crystallized in equilibrium with each other, the isotopic fractionation between them will be determined only by the temperature of crystallization and the nature of the sulfide phases, it will be independent of the presence of any other minerals or solutions or changes in the chemical nature of these solutions. Therefore, if in a hydrothermal environment two sulfides (pyrite and sphalerite)
crystallize simultaneously the isotopic fractionation between them will depend exclusively on the partition function ratios of sphalerite and pyrite in the solid state at the temperature of crystallization. The presence of other phases such as sulfur species in the fluid (HS\textsuperscript{−}, S\textsubscript{0}\textsuperscript{−}, etc.) will have no influence on this fractionation nor will any other sulfate or sulfide minerals which may be crystallizing simultaneously.

If the necessary isotopic exchange equilibrium constants have been determined experimentally as a function of temperature, the measured fractionation between two co-existing sulfides in isotopic equilibrium can be used to determine (a) the temperature of last equilibration and (b) the isotopic composition of the other phases in equilibrium with the sulfides at the time of their crystallization.

Many of the common sulfide geothermometers do not depend exclusively on temperature alone, but are influenced by additional physical parameters such as total pressure or partial pressure of S\textsubscript{2} (Kullerud 1959). The iron content of sphalerite in a pyrite-sphalerite assemblage, for instance, is a function of both temperature and partial pressure of S\textsubscript{2} (Barton and Toulmin, 1966, Boorman 1957). In such an assemblage it would, therefore, be possible to obtain information on P\textsubscript{S\textsubscript{2}} from an isotopic temperature estimate.
If fractionation factors are measured in an assemblage of \( N \) phases, \( N-1 \) independent "temperatures of formation" can be obtained. If these temperatures are consistent within the limits of analytical error, it can be assumed (barring coincidence) that isotopic equilibrium with respect to sulfur had been obtained at the time of crystallization (or recrystallization during a metamorphic event) and frozen in at the same temperature in every mineral in the assemblage. If one mineral forms aberrant pairs, e.g. pyrite at Rammelsberg (Anger et al. 1966) it is likely that either it had not equilibrated with the rest of the assemblage at the time of crystallization, or otherwise, it had undergone sulfur isotope exchange subsequent to crystallization of the original assemblage.

6.2. Sulfur Isotope Geothermometry

Successful application of an isotopic geothermometer depends on (1) sensitivity of the isotopic fractionation to temperature variations, (2) sufficient analytical precision such that small changes in the fractionation factor can be measured accurately, (3) accurate calibration of the fractionation between two minerals as a function of temperature, and (4) isotopic equilibrium being achieved and frozen in the mineral assemblage under consideration.
Inaccuracy in the experimentally determined fractionation factors are large (Fig. 5-49) and it is apparent that at this stage it is not possible to determine temperatures to within $50^\circ$C in the intermediate range of geologic temperatures between $300$ and $400^\circ$C. At higher temperatures accuracy decreases even further, but at lower temperatures it should be possible to measure temperatures well within these limits. Of the three mineral pairs studied, the pair pyrite-galena has the strongest temperature dependence and should give the most accurate results. The inaccuracy and temperature dependence of the pyrite-sphalerite fractionation is such that it is doubtful whether any meaningful results can be obtained using this assemblage.

No accurate information is available as to the temperature of formation of those mineral assemblages in which sulfur isotope fractionations have been reported for co-existing pyrite, sphalerite and galena. It is therefore impossible to test the experimentally determined geothermometers with any accuracy in natural assemblages. It is possible to determine to some extent whether isotopic temperatures appear reasonable in comparison with temperature estimates based upon other geologic criteria.
The sulfur isotopic geothermometers have therefore been applied to a few orebodies for which analyses have been reported, to determine their practical applicability. Deposits have been selected on the basis of a reasonable amount of good analytical data being available and some indication that isotopic equilibrium may have been approached.

6.2.1. Heath Steele

Sulfur isotope fractionations have been reported for mineral assemblages from the Heath Steele B-1 orebody and other deposits in the Bathurst-Newcastle area of New Brunswick.

These deposits are of the stratiform type and consist of large conformable massive sulfide bodies in a folded metasedimentary complex. The massive sulfides of the B-1 orebody are composed dominantly of pyrite which in places contains economic concentrations of sphalerite and galena or chalcopyrite. Structural features in the ores suggest deformation and recrystallization accompanying regional metamorphism. Relatively constant fractionation of sulfur isotopes between given sulfide minerals has been observed throughout the B-1 orebody (Lusk and Crocket, 1969). Fractionation in other deposits from this camp and in sulfides from the country rock show close similarity.
This consistency of sulfur isotopic fractionation has been interpreted as equilibrium or near-equilibrium partitioning established during an episode of regional metamorphism. Silicate mineralogy indicates that the country rock has been metamorphosed to lower quartz-albite-epidote-biotite rank, and presumably the ores have also recrystallized under this rank of metamorphism.

Isotopic fractionation of sulfur isotopes in co-existing sulfides in the B-1 orebody has been measured in 26 pyrite-sphalerite, 13 sphalerite-galena and 13 pyrite-galena pairs. The averages for all $\Delta S^{34}$ values for these pairs are 0.87±0.07, 1.82±0.15 and 2.27±0.15% respectively. These average fractionations have been fitted to the experimental fractionation curves in Fig. 6-1. Owing to analytical error a range of temperatures is indicated for each mineral pair. These areas have been shaded and can be seen to overlap. The three isotope geothermometers, therefore, appear to yield concordant temperatures of 300-320°C. These temperatures would appear low in relation to the rank of metamorphism which suggests temperatures in the range 350°C - 450°C. In view of the uncertainty in the experimentally calibrated isotope geothermometers, the discrepancy appears small and it is not possible to come to any definite conclusion as to whether
the fractionation was frozen in at the temperature of metamorphism or at some lower temperature (if indeed isotopic homogenization resulted from the metamorphic event indicated in the country rock).

The agreement between all three isotope geothermometers would apparently suggest that sulfur isotopic equilibrium was indeed attained within the whole deposit at one temperature and frozen in. This is not necessarily the case since, if disequilibrium fractionations are randomly distributed with respect to the equilibrium fractionation (i.e. both larger and smaller), then disequilibrium effects would largely cancel out if a sufficiently large number of samples is considered. A true test of equilibrium involves obtaining consistent temperatures in individual specimens of three or more sulfides rather than in average values of a large number of specimens.

Measured isotopic fractionations as reported by Lusk and Crocket (1969) between 15 pyrite-sphalerite, 10 pyrite-galena and 10 sphalerite-galena pairs from the Heath Steele B-1 deposit have been fitted to the experimentally determined fractionation curves in Fig. 6-2. These results represent single analyses for each mineral so that analytical error cannot be estimated. Where 3 minerals co-exist in the same specimen, the data have been fitted to the fractionation curves for all three sulfide pairs so that three temperatures are ob-
FIG. 6-1 AVERAGE SULFUR ISOTOPE FRACTIONATIONS AND ISOTOPIC TEMPERATURES FOR HEATH STEELE B-1 OREBODY. (After Lusk and Crocket 1969).
Temperatures corresponding to the measured fractionations are plotted in Fig. 6-3 for the individual mineral pairs. Tie-lines connect values obtained for different mineral pairs from the same sample. Results indicate a very wide range of temperatures varying from 205–605°C, and it is immediately apparent that these individual analyses do not show the same consistency that the averaged values did. Nor do the different isotopic thermometers yield concordant temperatures within a single specimen. Pyrite-sphalerite pairs show the largest range in values (205–605°C) while the variation decreases for sphalerite-galena (220–560°C) and pyrite-galena pairs (240–480°C). This would suggest that a large amount of the scatter arises directly from analytical errors. These would have a much greater effect on the pyrite-sphalerite temperatures than on the pyrite-galena temperatures as a direct result of the small variation with temperature of the former fractionation effect. This also accounts for the large discordance in temperatures observed between pyrite-sphalerite pairs and the other two sulfide pairs.

The uncertainty in temperature estimates for a single sample arising directly from analytical error is illustrated in Fig. 6-4 where results have been plotted for a specimen for which multiple analyses are available so that it is possible to estimate the analytical
FIG. 6-2 SULFIDE-SULFIDE FRACTIONATION IN THE HEATH STEELE B-1 OREBODY.

(Data represents single analyses of unknown precision)
3. 6-3 ISOTOPIC TEMPERATURES FOR HEATH STEELE B-1 OREBODY FROM SINGLE ANALYSES (Analytical Precision unknown)
precision for each fractionation. The mean fractionation for each mineral pair is indicated and an area corresponding to one standard deviation on either side of this value is shaded. It is apparent that the temperature ranges are centered approximately on the same values, but the range indicated by the pyrite-sphalerite fractionation (210-410°C) is much greater than that for the pyrite-galena fractionation (260-290°C). Temperatures for all three thermometers are concordant over the temperature range 260-290°C and the specimen would appear to show isotopic equilibrium within experimental accuracy. Similar results are observed in a specimen representing mineralization in the country rock adjacent to the B-1 orebody as shown in Fig. 6-5. This specimen does not show the same degree of concordance as the previous specimen and the ranges of temperatures indicated by the various isotope thermometers are not centered. The sphalerite-galena and the pyrite-sphalerite pairs give respective ranges of lower and higher temperatures with respect to the pyrite-galena pair. This would suggest that sphalerite is out of isotopic equilibrium with respect to the other two sulfides. No definite conclusion can be reached since all three temperature ranges do overlap and concordant temperatures are indicated over the range 300-380°C.

It is apparent that a large amount of scattering arises from analytical inaccuracy and that often this is such as to prevent definite
FIG. 6-4  HEATH STEELE B-1 OREBODY - UNCERTAINTY IN FRACTIONATION MEASUREMENTS

FOR SAMPLE 10 (Mean fractionation and one standard deviation indicated for all three isotope geothermometers)
FIG. 6-5 HEATH STEELE B-1 OREBODY - UNCERTAINTY IN FRACTIONATION MEASUREMENTS

FOR SAMPLE 39 (Represents sulfide mineralization in hanging wall country rock.)
conclusions to be drawn as to the temperature of equilibration of a sulfide assemblage or whether or not isotopic equilibrium was attained. Results obtained from pyrite-sphalerite pairs particularly would appear of very limited value.

Fractionations as measured in 13 specimens from the Heath Steele B-1 orebody for which replicate analyses are available are fitted to the experimentally determined fractionation curves in Fig. 6-6. The analytical error can be estimated in these fractionations and is indicated. Where 3 sulfides coexist the three isotopic fractionations have been plotted to give an identical temperature (within experimental accuracy) for all three sulfide pairs. The mean temperature as well as the range for each of these mineral pairs is shown in Fig. 6-7. Pyrite-sphalerite pairs again indicate the largest range of temperatures (100-900°C) while results are available for only 3 pyrite-galena and 3 sphalerite-galena pairs indicating temperatures of 200-410°C and 230-390°C respectively. While it is clear that a large amount of the variation in temperatures may arise directly from analytical inaccuracy (especially in the higher temperature range), the overall variation appears to be too large to be accounted for solely by this effect. A large number of pyrite-sphalerite pairs give concordant temperatures of approximately 220-260°C but several analyses definitely fall outside these limits.
FIG. 6-6 HEATH STEELE B-1 OREBODY - ISOTOPIC FRACTIONATION FOR SAMPLES OF KNOWN PRECISION (Vertical bars correspond to one standard deviation.)
FIG. 6-7 ISOTOPIC TEMPERATURES FOR SAMPLES OF KNOWN PRECISION
FROM HEATH STEELE B-1 OREBODY (Mean value and temperature range corresponding to one standard deviation is indicated.)
The three sphalerite-galena pairs show a small range of concordant temperatures at 300°C, but the pyrite-galena pairs, which would be expected to give the most accurate results since the fractionation between these two sulfides is strongly temperature dependent, again shows discordant results.

Analytical precision is such that no definite conclusions can be drawn, but it would appear that while isotopic equilibrium may have been established in individual hand specimens (Fig. 6-3) and frozen in, the Heath Steele B-1 orebody as a whole has not equilibrated at the same temperature.

When analyses are available for three co-existing sulfides the degree to which they have equilibrated isotopically, as well as the temperature of equilibration can be most readily determined from a plot such as Fig. 6-8. In any assemblage of 3 sulfides two independent fractionations between sulfide pairs exist (the third fractionation is directly dependent on these and is equal to either their sum or difference).

Since the fractionations between all three sulfide pairs vary linearly with $T^{-2}$

$$\Delta_{x-y} = A_{x-y} T^{-2}$$

$$\Delta_{x-z} = A_{x-z} T^{-2}$$
Therefore,

$$\Delta_{x-y} = \frac{\Delta_{x-y}}{\Delta_{x-z}} \cdot \Delta_{x-z}$$

Therefore, a plot of any one fractionation factor against any of the other two will produce a straight-line relationship for equilibrium assemblages such as shown in Figs. 6-8, 9, 10.

Because only two fractionation factors are independent it is immaterial which two are plotted against each other. For the sake of completeness all three possible plots are presented here but each contains identical information and selection of any particular plot in preference to another becomes a matter of personal taste or convenience.

In Figs. 6-8, 9, 10, the straight line indicates the experimentally measured relationship between the sulfide-sulfide fractionation factors at all temperatures. Any equilibrium sulfide assemblage should plot on this line and the temperature of equilibration can be read off directly. If such assemblages do not plot on this line (within experimental accuracy) isotopic disequilibrium is indicated.

In these figures, data have been plotted representing sulfide assemblages from the Heath Steele B-1 and other orebodies in the Bathurst camp. Sample numbers correspond to those of Lusk and
FIG. 6-8 $\Delta_{\text{Py-Gn}}$ versus $\Delta_{\text{Sp-Gn}}$ FOR BATHURST-NEWCASTLE DEPOSITS

(Sample numbers refer to Lusk and Crocket, 1969)
FIG. 6-9 $\Delta_{Sp-Gn}$ versus $\Delta_{Py-Sp}$ FOR BATHURST-NEWCASTLE DEPOSITS
FIG. 6-10 $\Delta_{Py-Gn}$ versus $\Delta_{Py-\text{Sp}}$ FOR BATHURST-NEWCASTLE DEPOSITS
Crocket (1969). An estimate of the analytical error is indicated for those sulfide pairs where replicate analyses are available. The analyses for the Heath Steele B-1 deposit as well as other deposits in the area cluster around the equilibrium line. A few points would appear to plot more than one standard deviation of analytical inaccuracy away from the equilibrium line but in view of the small number of replicate analyses (seldom more than 3) it is impossible to determine whether these are definite disequilibrium assemblages. It would therefore appear that isotopic equilibrium has been attained in these specimens or, alternately, that it has been approached and that deviations from equilibrium are random with no particular sulfide showing preferential enrichment of either the light or heavy isotope.

The temperature at which equilibrium has been frozen in would, however, appear to vary for these sulfide assemblages. The isotopic temperatures cover a range from approximately 400 to 250°C and it would appear unlikely that all assemblages crystallized at the same temperature. No distinction can be drawn between specimens from B-1 and the other deposits since each group shows approximately the same distribution. While the general mode of origin of these deposits would, therefore, seem similar, indications are that crystallization took place over a range of temperatures rather than at any one particular temperature. It should, however, be emphasized that analytical error is such as to prevent any definite conclusions to be reached.
6.2.2. **Broken Hill**

Stanton and Rafter (1967) have reported on the fractionation of sulfur isotopes between co-existing galena, and sphalerite from Broken Hill, New South Wales.

The deposit occurs as thin lenses of sulfides, conformable to the stratification in the country rock. The enclosing country rock is intensely folded and metamorphosed to sillimanite grade assemblages. The ore consists principally of galena and sphalerite, but other sulfides are present in smaller amounts. The deposit is characterized by relatively uniform $\delta^{34}$S values and a mean value very close to meteoritic (Stanton and Rafter 1966).

Sixteen specimens of typically coarse lead-zinc ore from the "lead" lode were analyzed. Analyses for individual specimens as well as the mean value have been fitted to the experimental fractionation curve in Fig. 6-11. The standard deviation of these analyses is shown as vertical bars. The mean isotopic temperatures for all the specimens as well as the temperature range corresponding to one standard deviation are plotted in Fig. 6-12. It is immediately obvious that experimental accuracy is such as to prevent any meaningful conclusions to be drawn. Nevertheless, it should be noted that the average sphalerite-galena fractionation for all the specimens amounts to 0.8% $\delta^{34}$S corresponds...
ponding to a temperature of 590°C. The standard deviation of 0.4% for this value corresponds to a temperature range of 480°C to 920°C.

The lowest temperatures indicated in all the individual specimens is of the order of 250°C while most samples yield concordant temperatures over the range 500-650°C. In view of the large uncertainties in the reported analyses, it would seem that the agreement between the temperature corresponding to the average fractionation (590°C) and that indicated by the metamorphic grade of the country rock is largely fortuitous. No conclusions can be drawn regarding the degree of isotopic equilibrium in the individual specimens or the deposit.

6.2.3. **Japanese Tertiary deposits**

Fractionation of sulfur isotopes in low temperature sulfide assemblages representing deposits of the Late Tertiary metallogenic epoch of Japan has been investigated by Tatsumi (1965). Apparent equilibrium assemblages were selected for analysis on the basis of mineralogical and textural evidence.

Most of the deposits such as the Hanaoka, Kosawa, Osarizawa and Yakuno mines consist of massive to bedded Cu-Pb-Zn ore thought to have resulted from either hydrothermal replacement or exhalative sedimentation. Their mode of occurrence, mineral para-
FIG. 6-11 BROKEN HILL, N.S.W. - ISOTOPIC FRACTIONATION BETWEEN SPHALERITE AND GALENA
FIG. 6-12 BROKEN HILL - SPHALERITE-GALENA ISOTOPIE TEMPERATURES

(Temperature range corresponds to one standard deviation)
genesis and types of wall rock alteration suggest low temperatures of
formation, some of the deposits being classified as "epithermal" (50-
200°C as defined by Lindgren, 1933) vein filling deposits. The Taishu
deposit represents a higher temperature of formation being characteris-
tically rich in pyrrhotite, while the analyzed sulfide minerals from the
Chichibu mine were collected from pyrometasomatic (500-800°C) depo-
sits. Isotopic fractionation would be expected to have been generated
during crystallization from ore-forming fluids for all these deposits.

Analytical results representing measured fractionations
in individual mineral pairs have been fitted to fractionation curves in
Fig. 6-13 and corresponding temperatures are indicated in Fig. 6-14.
A clear distinction can be drawn between the high and low temperature
deposits and the isotopic temperatures appear in good agreement with
those inferred from geologic considerations. The Chichibu samples show
an identical fractionation of 0.4‰ between pyrite and sphalerite, cor-
responding to a temperature of 530°C which falls within the general
range of 500-800°C for pyrometasomatic deposits. The low temperature
deposits all fall between 120 and 260°C which agrees reasonably well with
the temperature range 50 to 200°C ascribed to epithermal deposits by
Lindgren. One specimen from the Yakomo mine containing two types
of sphalerite coexisting with galena yields isotopic temperatures of
FIG. 6-13 JAPANESE TERTIARY DEPOSITS - ISOTOPIC FRACTIONATION BETWEEN SULFIDES
FIG. 6-14 JAPANESE TERTIARY DEPOSITS- ISOTOPIC TEMPERATURES
240 and 570°C. Since the two sphalerites differ in isotopic composition by 1.5%, it is obvious that isotopic equilibrium has not been established in this specimen. It would appear, therefore, that the dimensions of isotopic equilibrium systems in hydrothermal mineral assemblages is small compared to that of a hand specimen. Since the size of the specimen is not indicated, it is not possible to arrive at a closer estimate of these dimensions.

Temperature estimates for these deposits appear surprisingly consistent considering that analyses were obtained from a variety of different deposits.

While the general mode of origin of the low temperature deposits would appear similar, it cannot be expected that they were emplaced at identical temperatures. The temperature estimates appear surprisingly consistent, therefore, compared to results obtained for single orebodies such as Heath Steele and Broken Hill which supposedly have undergone isotopic homogenization during metamorphism. If this close agreement is not fortuitous it would appear to result from (a) the care taken in selecting specimens, (b) good analytical techniques and sensitivity of isotopic geothermometers at low temperatures, and (c) close approach to equilibrium during hydrothermal crystallization.
6.3. **Chalcopyrite and Pyrrhotite**

6.3.1. **Equilibrium in natural sulfide assemblages**

Figure 6-15 represents a compilation of all reported values for $\Delta_{\text{Py-Gn}}$ and $\Delta_{\text{Sp-Gn}}$ from specimens where all three sulfides pyrite, sphalerite and galena coexist and have been analyzed. The experimentally determined equilibrium relationship between the two fractionation factors is indicated by the solid line. The two dashed lines represent least squares fits to the individual points, one corresponding to a fit of $\Delta_{\text{Py-Gn}}$ on $\Delta_{\text{Sp-Gn}}$ and vice versa. It can be seen that very close agreement exists between the experimental relationship and that determined from analyses of natural samples. This indicates that natural isotopic fractionations in the pyrite-sphalerite-galena assemblage show a symmetrical distribution around the equilibrium value so that if the mean values of a sufficiently large number of samples are considered, these will closely approximate the equilibrium fractionation factors.

6.3.2. **Chalcopyrite**

If the same is true for the assemblage pyrite-sphalerite-galena-chalcopyrite, the equilibrium fractionation of chalcopyrite with any of these sulfides can be estimated from analyses of natural assemblages. In order to consider all possible assemblages (e.g. chalcopyrite-sphalerite-galena, chalcopyrite-sphalerite-pyrite and
chalcopyrite-pyrite-galena) simultaneously it is necessary to employ a plot of the partition function ratios of the individual sulfides. Since these are not known, use can be made of the relative partition function ratios with respect to sulfur as determined experimentally (Fig. 5-48).

For an assemblage such as chalcopyrite-pyrite-sphalerite, the measured fractionation between pyrite and sphalerite is fitted to the appropriate fractionation curves and the chalcopyrite fractionation with respect to these two sulfides plotted as a single point at the same value of $T^{-2}$. Fig. 6-16 represents a compilation of all available analyses in the assemblage chalcopyrite-pyrite-sphalerite-galena. These points, therefore, represent the fractionation between chalcopyrite and sulfur at various temperatures as measured in natural assemblages. It can be seen that the chalcopyrite-sulfur fractionation is generally similar to that between sphalerite and sulfur. A least squares fit to these points yields the expression

$$\Delta_{Cpx-S} = 0.19 \times 10^{6} T^{-2}$$

where $Cpx =$ chalcopyrite, as compared to

$$\Delta_{Sp-S} = 0.21 \times 10^{6} T^{-2}$$
FIG 6-15 $\Delta_{\text{Py-Gn}}$ versus $\Delta_{\text{Sp-Gn}}$ COMPILATION OF AVAILABLE DATA FROM SAMPLES OF THREE OR MORE COEXISTING SULFIDES
FIG. 6-16 CHALCOPYRITE-SULFUR FRACTIONATION FROM NATURAL CHALCOPYRITE-PYRITE-SPHALERITE-GALENA ASSEMBLAGES.
derived experimentally. While the quantitative significance of this result probably is none too great in view of the limited number of points, it would appear very likely that the partition function ratios for chalcopyrite will closely approximate those of sphalerite. Chalcopyrite will therefore show approximately the same fractionation with respect to the other sulfides as sphalerite, while the fractionation between chalcopyrite and sphalerite can be expected to be very small.

6.3.3. Pyrrhotite

A single point has been determined experimentally on the pyrrhotite-sulfur fractionation curve. It appears probable that the pyrrhotite-sulfur fractionation will show similar behaviour to the fractionation of the other sulfides with sulfur and vary linearly with $1/T^2$. This relationship is illustrated in Fig. 6-16 and the pyrrhotite partition function ratio is seen to be very slightly larger than that for pyrite.

Results on natural specimens would seem to collaborate this. Three points representing coexisting sulfides in the assemblage pyrrhotite-pyrite-sphalerite-galena have been plotted in Fig. 6-16 in a way similar to that described for chalcopyrite. The number of points is too small to fit any curve to, but taking analytical precision into account, they are in general agreement with the experimental curve.
results from natural assemblages indicate again a very small fractionation effect between pyrite and pyrrhotite (Fig. 4-9) with either phase showing small enrichment in isotopic composition.

Pyrrhotite will therefore show fractionations with respect to the other sulfides similar to those of pyrite, while pyrite-pyrrhotite fractionations will be small unless very low temperatures are involved.
CHAPTER 7

SUMMARY AND CONCLUSIONS

This research set out to demonstrate the importance of equilibrium exchange reactions in producing fractionation of sulfur isotopes between coexisting sulfides in mineral assemblages.

A survey of fractionation data from natural assemblages indicates that on a statistical basis, systematic fractionations exist between several of the most common sulfide minerals. Such fractionations, though often disregarded by previous workers, may amount to a few permil and appear significant in the light of precision of isotopic analysis, which is of the order of 0.1 to 0.5 permil.

Since these fractionations would appear to depend only on the mineralogy of the sulfides between which they are measured and the probable temperature of their formation, and are not influenced by any other factors such as location or geologic mode of origin, they can reasonably be attributed to a process of equilibrium partitioning between sulfide phases in the solid state. Amongst the more common sulfide assemblages the largest fractionations are found between pyrite, sphalerite and galena.
with minor fractionations in assemblages involving pyrite, chalcopyrite and pyrrhotite. Pyrite appears almost invariably enriched in the heavier isotope while galena commonly shows enrichment in $S^{32}$ with respect to the other sulfides. In the pyrite-sphalerite-galena assemblage where fractionations are sufficiently large, a definite temperature effect is evident with the fractionation increasing with decreasing temperature.

Theoretical considerations suggest that equilibrium exchange fractionation of sulfur isotopes between sulfide minerals will generally amount to only a few permil at geologically reasonable temperatures. The fractionation factor, $\Delta$, can be expected to vary linearly as a function of $T^{-2}$ reaching a value of zero at very high temperatures. The equilibrium constant for such an exchange reaction has been shown to be essentially independent of pressure. The potential use of sulfur isotope fractionations for the purpose of geologic thermometry is therefore apparent, especially for fractionations between pyrite, sphalerite and galena. From theoretical considerations these sulfides would be expected to show the largest fractionations and the strongest temperature dependence in agreement with observations on natural assemblages.

Experimental calibration over the temperature range 300-725°C of the isotopic fractionation of these three sulfides with
respect to sulfur liquid yielded the expressions,

\[ 1000 \ln \alpha_{\text{Py-S}} = 0.49 \times 10^6 T^{-2} \]

\[ 1000 \ln \alpha_{\text{Sp-S}} = 0.21 \times 10^6 T^{-2} \]

\[ 1000 \ln \alpha_{\text{Gn-S}} = -0.42 \times 10^6 T^{-2} \]

while a single experimental point at 340°C would seem to indicate that the fractionation between pyrrhotite and sulfur is practically identical to that for pyrite-sulfur pairs.

From these results it is possible to derive the isotopic sulfide geothermometers,

\[ 1000 \ln \alpha_{\text{Py-Gn}} = 0.91 \times 10^6 T^{-2} \]

\[ 1000 \ln \alpha_{\text{Sp-Gn}} = 0.63 \times 10^6 T^{-2} \]

\[ 1000 \ln \alpha_{\text{Py-Sp}} = 0.28 \times 10^6 T^{-2} \]

These equations would appear good estimates of the equilibrium fractionation expression though experimental accuracy is such as to introduce an uncertainty of approximately ±0.1 \times 10^6 in each of the slopes of the reaction curves. Since all the fractionations appear to vary as a function of \( T^{-2} \) (within experimental accuracy over the tempera-
ture range investigated) and reach a value of zero at elevated temperatures, the temperature sensitivity is directly related to the magnitude of the fractionation effect for a particular sulfide pair. Pyrite-galena and sphalerite-galena pairs, therefore, show the greatest potential for use as isotope geothermometers. Analytical precision is such that the errors associated with the experimental calibration limit the accuracy of an absolute temperature determination from the pyrite-galena isotopic geothermometer to approximately 50°C between 300 and 400°C. At lower temperatures greater precision is possible.

Even greater uncertainty is introduced in temperature estimates from the sphalerite-galena and pyrite-sphalerite-geothermometers, owing to their smaller temperature sensitivity. While the uncertainty in absolute temperature determinations, therefore, is large, relative temperatures between mineral assemblages can potentially be determined to a much greater degree of accuracy and would only be limited by the analytical uncertainty associated with $^{32}S/^{34}S$ determination of the natural sulfides.

The experimentally determined geothermometers have been applied to natural occurrences to determine how the temperatures obtained compare with estimates based on other geologic criteria, and to what extent isotopic equilibrium may be approached and frozen in natural sulfide assemblages.
Averaged values of the isotopic fractionation for a large number of samples from the Heath Steele B-1 and Broken Hill deposits yield absolute temperatures consistent with an envisaged process of recrystallization of the ore bodies during a period of regional metamorphism. Analyses from individual specimens show a more complex behaviour though analytical inaccuracy is such that no definite conclusions can be drawn. The Heath Steele deposit, at least, would seem to represent a range of temperatures of equilibration. If this is indeed the case and the deposit has actually undergone metamorphism, it can only be concluded that solid state diffusion of sulfur isotopes in sulfide minerals is so slow that original disequilibrium effects in the assemblages may not be homogenized and may persist after metamorphism.

Isotopic temperatures obtained from Japanese Tertiary deposits of low temperature hydrothermal origin appear very consistent and in close agreement with other temperature estimates. Isotopic equilibrium would seem to be readily attained between two sulfides coprecipitating simultaneously from a hydrothermal fluid and frozen in at that temperature. Different generations of hydrothermal minerals show disequilibrium effects, probably representing changes in the overall isotopic composition of the hydrothermal fluid with time.
On the basis of fractionations measured between chalcopyrite and other sulfides in natural assemblages, it can be shown that,

\[ 1000 \ln \alpha_{\text{Cpx-S}} \sim 0.19 \times 10^6 T^{-2} \]

where Cpx = chalcopyrite; so that as far as isotopic geothermometry is concerned, chalcopyrite can be expected to closely resemble sphalerite.

Comparison of the experimentally determined isotope geothermometers and analytical results from natural assemblages lead to the following conclusions regarding the potential use of different sulfide pairs to serve as indicators of temperature.

(1) Pyrite-pyrrhotite and sphalerite-chalcopyrite fractionations appear extremely small and devoid of any practical importance in geothermometry.

(2) Fractionation between sphalerite and chalcopyrite on the one hand and pyrite and pyrrhotite on the other, under present conditions of analytical precision, can only give meaningful results at low temperatures (< 200°C). With improvement in analytical techniques their usefulness could be extended to higher temperature regions.
The greatest temperature sensitivity is associated with fractionations between pyrite, pyrrhotite sphalerite and chalcopyrite with galena. Meaningful results can probably be attained over the entire temperature range where these assemblages are found. Though it might be necessary to consider averaged fractionation values from a large number of specimens, multiple analyses from specimens containing three or more sulfides can give accurate information as to the degree of isotopic equilibrium in an assemblage and the uncertainty in the temperature of equilibration.
APPENDIX 1

COMPOSITION OF PYRITE-PYRRHOTITE MIXTURES

The composition of products resulting from the reaction of native iron and sulfur was determined by measuring the relative intensity of x-ray diffraction peaks. The reflections (114)(d=2.09 Å) in pyrrhotite and (211)(d=2.2118 Å) for pyrite peaks were measured. X-ray photographs were obtained from powder samples and the intensities of the two peaks measured in triplicate traces across the photograph through use of a densitometer. All the samples were ground to -200 mesh and Ni filtered FeKα radiation used.

A working standard was prepared by mixing natural pyrite and pyrrhotite samples in measured weight proportions. Pyrrhotite/pyrite peak height ratios are given in Table A-1 and plotted to give working curves shown in Figs. A-1 and A-2. The measured peak height ratios and the corresponding compositions of the synthetic pyrite-pyrrhotite mixtures, representing the longest reaction times, as determined from these curves, are presented in Table A-2.
FIG. A-1  PYRRHOTITE (114)/PYRITE (211) PEAK HEIGHT RATIOS FOR STANDARDS AND SAMPLES RICH IN PYRITE.
FIG. A-2 PYRITE (211)/PYRRHOTITE (114) PEAK HEIGHT RATIOS FOR STANDARDS AND SAMPLES RICH IN PYRRHOTITE.
Table A-1

Peak height ratios for standard pyrite-pyrrhotite mixtures

<table>
<thead>
<tr>
<th>Composition</th>
<th>Peak Height Ratio</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%Po-90%Py</td>
<td>0.21, 0.25, 0.23</td>
<td></td>
</tr>
<tr>
<td>20%Po-80%Py</td>
<td>0.51, 0.53, 0.48</td>
<td></td>
</tr>
<tr>
<td>30%Po-70%Py</td>
<td>1.46, 1.57, 1.35</td>
<td></td>
</tr>
</tbody>
</table>

Table A-2

Composition of Synthetic Pyrite-Pyrrhotite Mixtures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak Height Ratio</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>P690C</td>
<td>0.07, 0.11</td>
<td>&lt; 10%Po</td>
</tr>
<tr>
<td>P447C</td>
<td>0.14, 0.13</td>
<td>&lt; 10%Po</td>
</tr>
<tr>
<td></td>
<td>Py(211) / Po(114)</td>
<td></td>
</tr>
<tr>
<td>P340A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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Minor Typographical Errors, Grootenboer Thesis

Page 15, line 5 from bottom - as a model

Page 20, line 4 - level indicative

Page 21 - mobility of an ion is inversely proportional to the square root of its mass?

Page 50, line 7 from bottom - specimen of temperature colloform?

Page 62, line 1 - data were
   line 9 - Ryznar et al.

Page 74, line 3 - extent as to

Page 79 - Equation 5-1 two plus signs

Page 85 - Equation 5-16 bracket left off

Page 86, line 3 - elemental sulfur

Page 96, line 6 - compound of PbS

Page 100, figure 5-6 exaggerated

Page 113, line 7 - higher density

Page 135, line 3 - attempted

Page 136, Table 5-7 A15-4 551% recovery - should be 55%

Page 139, line 10 - Galena concentrates

Page 194, Figure 5-41 Semilogarithmic

Page 233, last line - being reached

Page 234, line 13 - lead lode

Page 235, line 4 from bottom - Kosaka

Page 236, figure 6-11 - Broken Hill

Page 254, line 2 - pyrrhotite

Page 255, Appendix 1, line 4 - Å

Page 260, line 6 - isotopic