The Barite-Celestite Solid Solution: Measurement of Thermodynamic Properties and Discussion of Their Geochemical Implications

A Thesis
Presented to the Graduate Faculty of the
New Mexico Institute of Mining and Technology

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
in Geoscience

by
H. Elise Brower
May 1971

TABLE OF CONTENTS

Part III GEOCHEMICAL CONSIDERATIONS

ACKNOWLEDGEMENT

I wish to thank Mr. Don Baker Jr., Director New Mexico State Bureau of Mines and Mineral Resources for the support of this research, Mrs. Lynn Brandvold and her staff for analysis of samples, and Frederic Laquer who helped as a student laboratory assistant. I appreciate the advice and criticism of my advisory committee: Drs. Gale Billings, Roshan Bhappu, and Kent Condie and the advice and technical assistance of Drs. Antonius Budding, Charles Chapin, Jacques Renault and Kay Brower who made the crystal-growing apparatus. Others who have helped me by critically reading the manuscript are Dr. Gerardo Gross, Dr. Carl Popp, and Mr. Kelley Summers.

ABSTRACT

Strontium sulfate in equilibrium with aqueous solution leaches selectively from barium sulfate-strontium sulfate solid solutions at 25° C and 1 atmosphere. Equilibrium concentrations of Sr^{++} and Ba^{++} in aqueous solution are not significantly different from values calculated on the assumption that the chemical activity of each component is proportional to its mole fraction in the solid. The enthalpy of mixing for $(Ba,Sr)SO_4$ solid solutions was determined by calorimetry to be approximately zero at 25 and 61° C. The thermodynamic properties are therefore characteristic of an ideal solution.

Crystals of synthetic barite and celestite and their solid solutions were prepared by recrystallization in brine by the process of thermal cycling. The maximum sizes of the crystals are: $BaSO_4$ - 500 microns, $SrSO_4$ - 70 microns, and $(Ba,Sr)SO_4$ - 50 microns. The possibility of forming pure barite deposits by recrystallization of a natural solid solution was demonstrated by an experiment in which Sr was removed from a 90 mole percent $BaSO_4$ solid solution by the process of recrystallization.

Nearly pure barite occurs frequently in hydrothermal deposits whereas celestite and $(Ba,Sr)SO_4$ solid solutions of intermediate composition are scarce. Separation of the two sulfates could be the result of fractional precipitation in the presence of low sulfate concentrations, leaching of an antecedent solid solution, or by removal of strontium as $SrCO_3$. Selective leaching of $SrSO_4$ contributes to the separation of barium and strontium sulfates in the sedimentary environment and to the concentration of Sr^{++} in sea water and $BaSO_4$ in residual deposits.

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

The ratio of barium to strontium concentrations in the earth's crust is 1.13, and the two elements exhibit a similar geochemistry in igneous rocks (Mason, 1966; Rankama, 1950; Hanor, 1966). However, barite, $BaSO_4$, is a common mineral in hydrothermal deposits whereas celestite, $SrSO_4$, and $(Ba,Sr)SO_4$ solid solutions of intermediate composition are rare (Deer et al., 1962; Palache et al., 1951). Both celestite and barite are commonly found in sedimentary deposits but intermediate $(Ba,Sr)SO_4$ is apparently rare in these rocks also. Although the $BaSO_4$-$SrSO_4$ system has been studied by others, some of the factors which may govern the geochemical distribution of barite and celestite are not well understood. There was a need to study those physicochemical properties which are pertinent to the precipitation and dissolution of $(Ba,Sr)SO_4$ in order to understand the conditions in which hydrothermal and sedimentary sulfates are deposited and recrystallized.

Part I

SOLUBILITY AND ENTHALPY OF THE (Ba,Sr)SO_4 SOLID SOLUTION SERIES

Purpose

Previous workers have shown by X-ray analysis that a complete series of synthetic solid solutions exist between $BaSO_4$ (barite) and $SrSO_4$(celestite) in which Ba^{++} and Sr^{++} substitute one for another in the orthorhombic lattice (Bostrom et al.,1968). Some investigators have reported that it is not experimentally feasible to establish a true thermodynamic equilibrium between the solid solution and the aqueous solution of (Ba,Sr)SO_4 (Gordon et al., 1954; Cohen and Gordon, 1961; and Starke, 1964). It should be mentioned, however, that their conclusions are based solely on data obtained by precipitation from aqueous solution. One purpose of this study is to remove all doubt concerning the establishment of equilibrium between the solid and aqueous solutions of (Ba,Sr)SO_4 by an approach from the opposite end-point, namely by dissolving solid (Ba,Sr)SO_4.

Previous Studies

Because of the difference in solubility products of the two end-members, $K_{BaSO_4} = 10^{-10}$ and $K_{SrSO_4} = 10^{-6.4}$, Ba^{++} is preferentially concentrated in the solid phase and Sr^{++} in the aqueous phase in the precipitation of $(Ba,Sr)SO_4$ as shown by the experimental work of Gordon et al. (1954), Cohen and Gordon (1961), and Starke (1964). Gordon et al. (1954) slowly precipitated a solid solution of $(Ba,Sr)SO_4$ and analyzed the aqueous solution at intervals during the precipitation. The results suggested that Sr is heterogeneously distributed throughout the $(Ba,Sr)SO_4$ solid solution. This heterogeneity is presumed to result from each successive surface layer growing in response to an aqueous phase of progressively increasing strontium content.

Hanor (1968) interpreted the data of Gordon et al. (1954) and Cohen and Gordon (1961) to mean that $(Ba,Sr)SO_4$ is an inert substance which fails to re-equilibrate in response to changes in the composition of the liquid, and he constructed a precipitation model that agreed with the observed frequency distribution in nature.

During the course of a contract research project to develop a commercial process for the chemical separation of barium and strontium in the Mountain Pass, California deposit, the author discovered that finely divided $(Ba,Sr)SO_4$ is not chemically inert to aqueous barium ion (Brower and Bhappu, 1969). This study showed that when either fine-grained solid $(Ba,Sr)SO_4$ or pure $SrSO_4$ is equilibrated with an amount of barium chloride in aqueous solution equivalent to the $SrSO_4$ in the solid phase, nearly all the barium is in the solid phase and approximately 98% of the strontium is in solution at the end of 24 hours. The metatheses are illustrated by the following equations:

$$\underset{\text{(solid)}}{(Ba,Sr)SO_4} + \underset{\text{(aqueous)}}{BaCl_2} \longrightarrow \underset{\text{(solid)}}{BaSO_4} + \underset{\text{(aqueous)}}{SrCl_2} \quad (1)$$

$$\underset{\text{(solid)}}{SrSO_4} + \underset{\text{(aqueous)}}{BaCl_2} \longrightarrow \underset{\text{(solid)}}{BaSO_4} + \underset{\text{(aqueous)}}{SrCl_2} \quad (2)$$

The process goes nearly to completion because $BaSO_4$ is more insoluble than $SrSO_4$, and the system is sulfate-deficient: the molar quantity of sulfate ion in the solid and aqueous phases is less than the sum of the molar quantities of barium and strontium ion in the two phases. If the Law of Mass Action determines the outcome of the competition of Ba^{++} and Sr^{++} for $SO_4^{=}$, the partitioning of barium and strontium between aqueous and solid solutions will be determined by the ratio of the equilibrium constants:

$$\frac{a_{Sr^{++}}/a_{Ba^{++}}}{N_S/N_B} = \frac{K_{SrSO_4}}{K_{BaSO_4}} \approx 4000\ (25^{\circ}\ C)$$

where N_S is the mole fraction of strontium in the solid and N_B is the mole fraction of barium in the solid.

Thermodynamic Stability of $(Ba,Sr)SO_4$

Three hypotheses that might explain the scarcity of natural $(Ba,Sr)SO_4$ of intermediate compositions are (1) a deficiency of any one of the component ions, (2) removal of strontium by the process shown in equation (3)

$$\underset{\text{(solid)}}{(Ba,Sr)SO_4} + \underset{\text{(aq.)}}{CO_3^{=}} \longrightarrow \underset{\text{(solid)}}{BaSO_4} + \underset{\text{(solid)}}{SrCO_3} + \underset{\text{(aq.)}}{SO_4^{=}} \quad (3)$$

or, (3) the thermodynamic instability of intermediate $(Ba,Sr)SO_4$ relative to the end-members. Since the first two hypotheses could occur under particular geological circumstances, this investigation attempts to evaluate hypothesis (3). Is the formation of intermediate $(Ba,Sr)SO_4$ from barite and celestite a spontaneous process, and if so how closely does the solid solution approach ideality?

The free energy of mixing pure barite and celestite to form one mole of solid solution is given by the following expression:

$$\Delta F_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (4)$$

If the process is spontaneous, then ΔF_{mix} must have a negative value. For an ideal solution there is no difference in the interaction energy between like and unlike molecules, therefore the heat of mixing is zero. If the heat of mixing is zero for the $(Ba,Sr)SO_4$ solid solution, then the heat evolved in the precipitation of one mole of $(Ba,Sr)SO_4$ should be the sum of the molar heats for precipitating the individual components.multiplied by their mole fractions as illustrated in equations (5) and (6) where N_B and N_S are the mole-fractions of $BaSO_4$ and $SrSO_4$ in the solid solution respectively.

$$\Delta H_{mix} = 0 \qquad (5)$$

$$\Delta H_{ppt(Ba_{N_B},Sr_{N_S})SO_4} = N_B \Delta H_{ppt(BaSO_4)} + N_S \Delta H_{ppt(SrSO_4)} \quad (6)$$

When the enthalpy of mixing is zero, the only contribution to the free energy of mixing is the entropy term, $-T\Delta S_{mix}$. The entropy of mixing one mole of solid solution is given in (7) and the free energy of mixing in (8).

$$\Delta S_{mix} = -R(N_B \ln N_B + N_S \ln N_S) \quad (7)$$

$$\Delta F_{mix} = RT(N_B \ln N_B + N_S \ln N_S) \quad (8)$$

Therefore when $\Delta H = 0$, regardless of the values of the respective mole fractions, the value of ΔF_{mix} is always negative and the formation of an ideal solid solution is a spontaneous process. A more extensive treatment of the thermodynamics of mixing is given in Hildebrand and Scott (1964).

To determine how closely the $(Ba,Sr)SO_4$ solid solution approaches ideality, an expression for equilibrium between a solid solution and an aqueous solution was derived as follows, where

ΔF_S = standard free energy of pure $SrSO_4$

K_S = equilibrium constant for pure $SrSO_4$ in equilibrium with its aqueous solution

F_S' = standard free energy of one mole of $SrSO_4$ as a component of $(Ba,Sr)SO_4$ with mole-fraction N_S: chemical potential

K_S = equilibrium constant for $SrSO_4$ as a component of a solid solution in equilibrium with its aqueous solution

$\Delta F_S^{(mix)}$ = change in ΔF_S when one mole of $SrSO_4$ is mixed in a solid solution of mole fraction N_S

The free energy of mixing per mole of $SrSO_4$ is the difference between the standard free energy of pure $SrSO_4$ and $SrSO_4$ as a component in $(Ba,Sr)SO_4$ as given in (9).

$$\Delta F^{mix} = \Delta F_S - \Delta F_S{}' \qquad (9)$$

For an ideal solution ΔH^{mix} is zero and ΔS^{mix} is $-R\ln N_S$, therefore, $\Delta F_S{}^{mix}$ is given by equation (10).

$$\Delta F_S{}^{mix} = RT\ln N_S \qquad (10)$$

Combining equations (9) and (10) with (11) and (12) which relate the equilibrium constant of $SrSO_4$ in solid solution to that of the pure substance.

$$\Delta F_S = -RT\ln K_S \qquad (11)$$

$$\Delta F_S{}' = -RT\ln K_S{}' \qquad (12)$$

$$K_S{}' = N_S K_S \qquad (13)$$

The derivation of an equilibrium expression for $BaSO_4$ is analagous to that for $SrSO_4$.

Equilibrium expressions (14) and (15) apply to the dissolution of $(Ba_{N_B}, Sr_{N_S})SO_4$ in water if the solid solution is ideal.

$$(Sr^{++})(SO_4{}^{=}) = N_S K_S \qquad (14)$$

$$(Ba^{++})(SO_4^{=}) = N_B K_B \qquad (15)$$

EXPERIMENTAL PROCEDURES

Enthalpy Measurements

The calorimeter and experimental procedure was borrowed from Brower (1969) and modeled after that of O'Hara et al. (1961).

Barium and strontium chloride solutions were pipetted into the Dewar flask, and a 15 ml. sample of 1.0 M Na_2SO_4 was introduced in a sealed glass ampoule. After thermal equilibrium had been established, the ampoule was broken and the change of enthalpy was measured. The heat of dilution of 1.0 M Na_2SO_4 was also measured, and the result used to calculate enthalpies of precipitation at infinite dilution. Experimental error in repeated runs was ± 0.2 kcal/mole.

X-ray Diffraction Measurements

X-ray powder diffraction patterns were obtained using K_α radiation from a copper target. The Norelco diffractometer was run at $1/8^\circ$ min^{-1} and the recorder at 0.25°/inch. Ultrapure RbI was used as an internal standard since the 200 peak at $2\theta = 24.22$ is well defined and located between the 111 and 002 peaks of $BaSO_4$ and $SrSO_4$ respectively. Each 111 diffraction peak was scanned twice in both directions, and the d-spacing of this peak versus mole percent $BaSO_4$ is plotted in Figure 1. The angle 2 θ was measured to ± 0.01° which gives a relative error of 1% in composition between the barium and strontium end-members of the system.

Equilibration Experiments

Solid solutions were prepared at 25° C by instantaneous precipitation from solutions containing barium and strontium chloride on addition of excess Na_2SO_4 solution. Digestion time was less than 30 minutes. X-ray diffraction patterns showed that the precipitates were composed of a single phase for each $(Ba,Sr)SO_4$ composition.

Four grams of each $(Ba,Sr)SO_4$ precipitate were equilibrated in 2 liters of distilled water for one week. During equilibration the vessels were continuously rotated.

Concentrations of Ba^{++} and Sr^{++} in solution were determined by atomic absorption with a model 303 Perkin-Elmer spectrometer. Wherever possible, analyses were checked by the conductimetric method. The maximum relative error for the atomic absorption analysis was ± 10%. Analyses by the two methods agreed within 5%.

To analyze for sulfate and for barium in solutions containing less than 1 ppm, 2 liters of the solution were evaporated to dryness and the residue fused with Na_2CO_3. The sulfate was determined gravimetrically as $BaSO_4$ and the barium determined by atomic absorption.

Serial Leaching Experiment

A 12 gram sample of $(Ba_{0.25},Sr_{0.80})SO_4$ and 15 liters of distilled water were placed in a 20 liter bottle which was rotated for a month. A 0.5 gram sample of solid and most of the liquid were then removed for analysis. A fresh portion of distilled water was added to the bulk of the solid and the extraction repeated seven times. Since the amount of solid removed represented a significant fraction of the total, the volume of fresh water added was also reduced for subsequent leachings by an appropriate amount.

Particle size of the starting material as well as the leached solid was below the limits of resolution with an optical microscope at 500x.

The composition of the solid phase was determined from the value of the d-spacing of the 111 X-ray diffraction peak by using Figure 1 as a calibration curve. The Sr^{++} concentration in the aqueous phase was determined by atomic absorption spectrometry.

Solubility Measurements

The concentrations of $SrSO_4$ and $BaSO_4$ at the various temperatures were determined conductimetrically between 2^o and 95^o C. A beaker just slightly larger than the conductivity cell was nearly filled with a slurry of water and either barium or strontium sulfate, and the conductivity was measured at each degree change in temperature. A calibration curve to convert conductance to concentration was prepared from handbook data on equivalent conductance of separate ions at various temperatures (Steinbach and King, 1950).

Solutions containing added electrolytes (data in Tables I and II) were analyzed for Sr^{++} and Ba^{++} by atomic absorption spectrometry.

DISCUSSION

Enthalpy Measurements

The enthalpies of mixing were evaluated in this study by direct calorimetric measurements of the heat of precipitation of solid solutions of $SrSO_4$ and $BaSO_4$ at 25° and 61° C.

The chemical reaction that takes place in the calorimeter is given in equation (16).

$$N_B \underset{\text{(aq.)}}{BaCl_2} + N_S \underset{\text{(aq.)}}{SrCl_2} + \underset{\text{(aq.)}}{Na_2SO_4} \longrightarrow \underset{\text{(solid)}}{(Ba_{N_B},Sr_{N_S})SO_4} + \underset{\text{(aq.)}}{2NaCl} \quad (16)$$

That the precipitates formed in the calorimetry experiments were true solid solutions was determined by X-ray diffraction. The $(Ba,Sr)SO_4$ precipitates gave single-phase patterns whose diffraction peaks were shifted in proportion to the change in mole composition as the series progressed from one end-member to the other. The d-spacing of the 111 diffraction peak is plotted versus mole percent $BaSO_4$ in Figure 1.

The data obtained from the calorimetry experiments

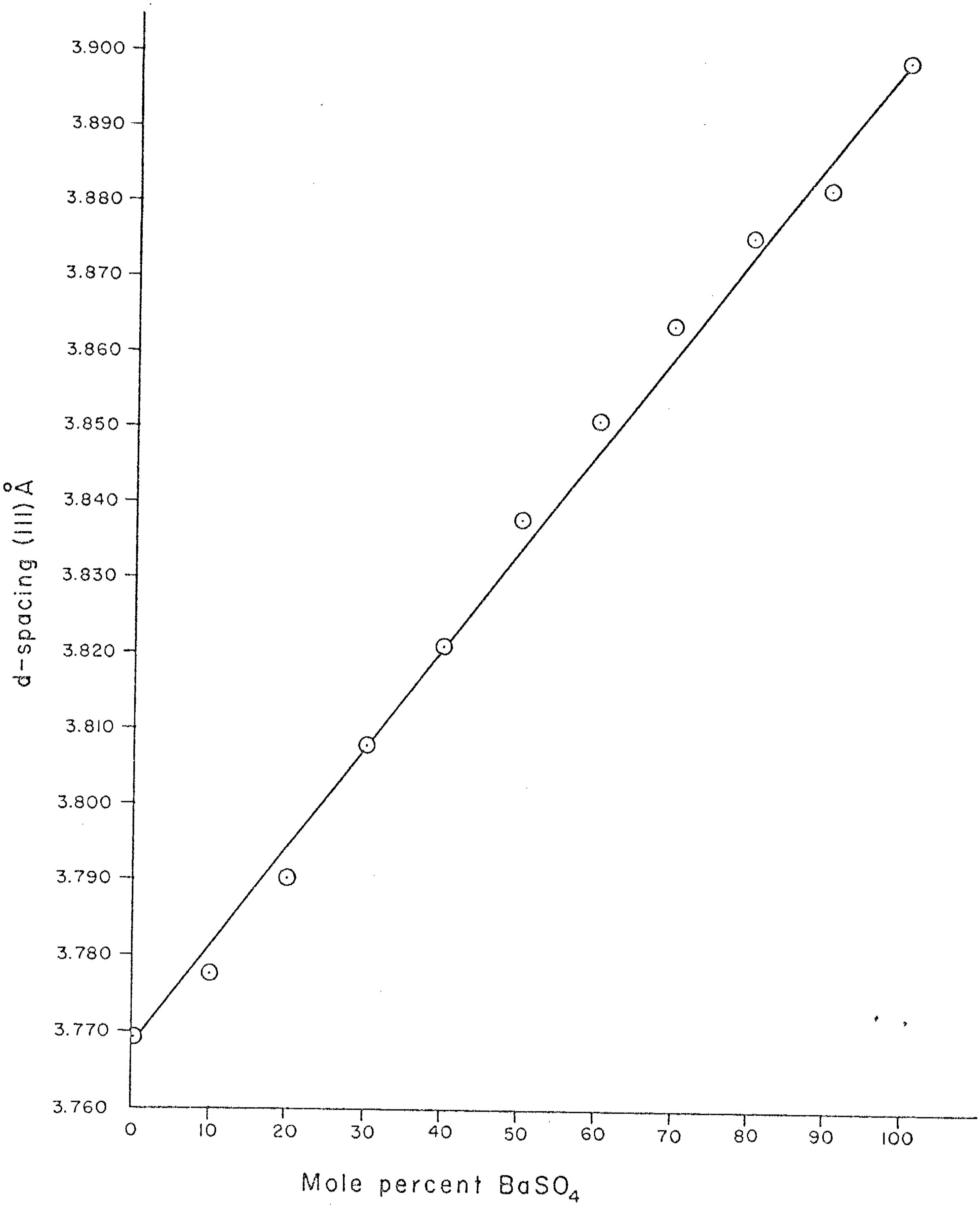


Figure 1. d-spacing (111)Å versus mole percent $BaSO_4$ in $(Ba, Sr)SO_4$.

are summarized in Figures 2 and 3. A plot of enthalpy of precipitation versus mole fraction of either component should give a straight line for an ideal solid solution. The theoretical lines representing $\Delta H_{mix}=0$ are shown for comparison with the analytical results. The mean ΔH of precipitation for $BaSO_4$ and $SrSO_4$ is - 3.7 and + 0.45 kcal/mole respectively at 25° C and - 2.0 and + 3.1 kcal/mole at 61° C. The values of ΔH for intermediate composition have a mean deviation of 0.2 kcal/mole from the theoretical lines; thus, the $(Ba,Sr)SO_4$ solid solution is nearly ideal. Ludd and Lee (1961) give the lattice energies of $BaSO_4$ and $SrSO_4$ as 578 and 591 kcal/mole respectively. The deviation of the experimental values of ΔH from the theoretical line representing $\Delta H_{mix}= 0$ is less than 0.04% of the crystal lattice energy.

The linearity of the enthalpy of precipitation with respect to mole fraction is also a measure of the true linearity of d-spacing in the crystal lattice as shown by the following: The lattice energy of a crystal, U_o, is related to the internuclear separation, d_o, by equation (17) where N = Avogadro's number, A = Madelung constant, e = charge on the electron, Z = integral charge on the ions, and n = Born exponent

$$U_o = \frac{N A e^2 Z^2}{d_o} (1 - \frac{1}{n}) \qquad (17)$$

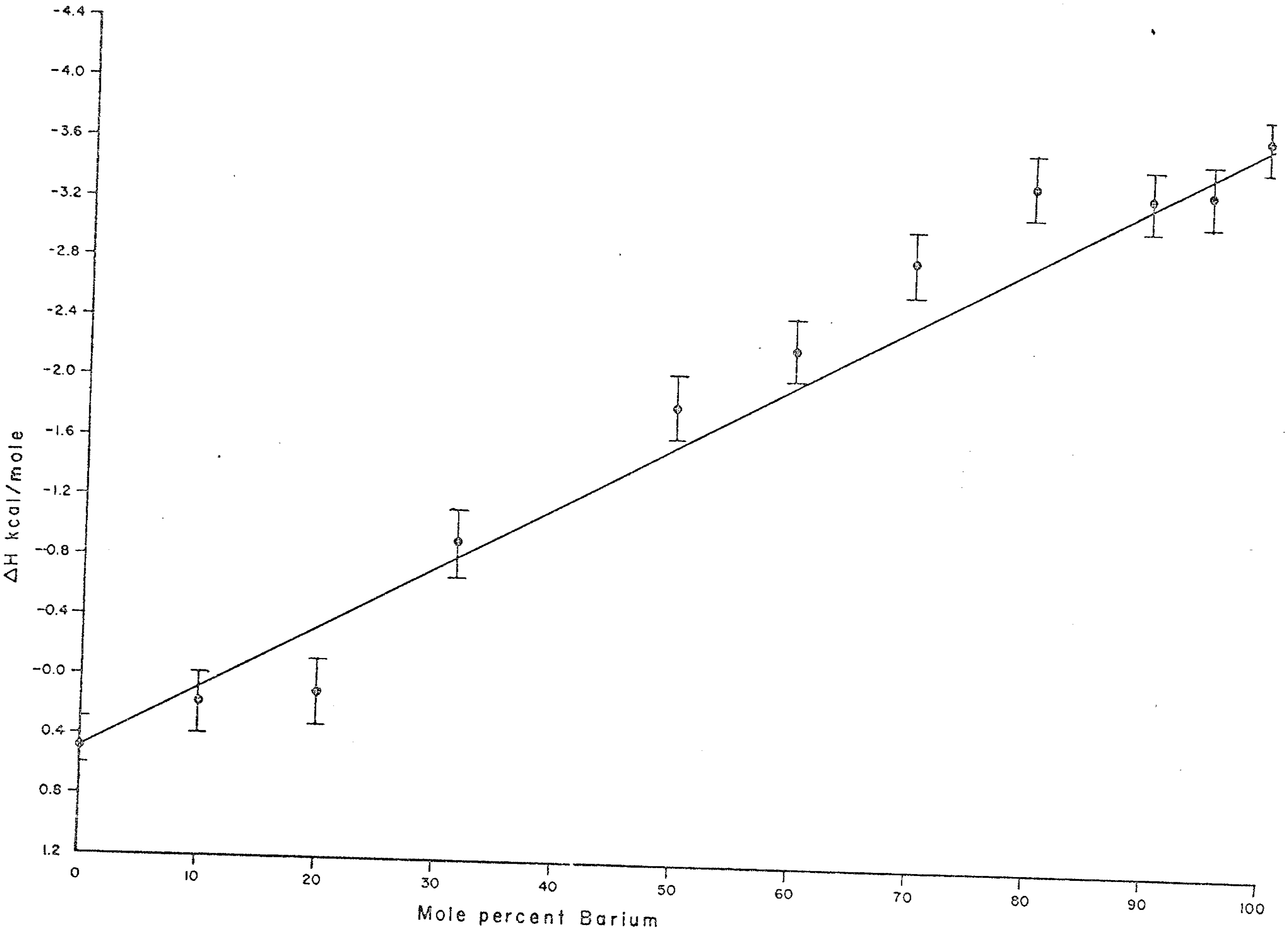


Figure 2. Enthalpy of precipitation of $(Ba, Sr)SO_4$ in kcal/mole at 25°C.

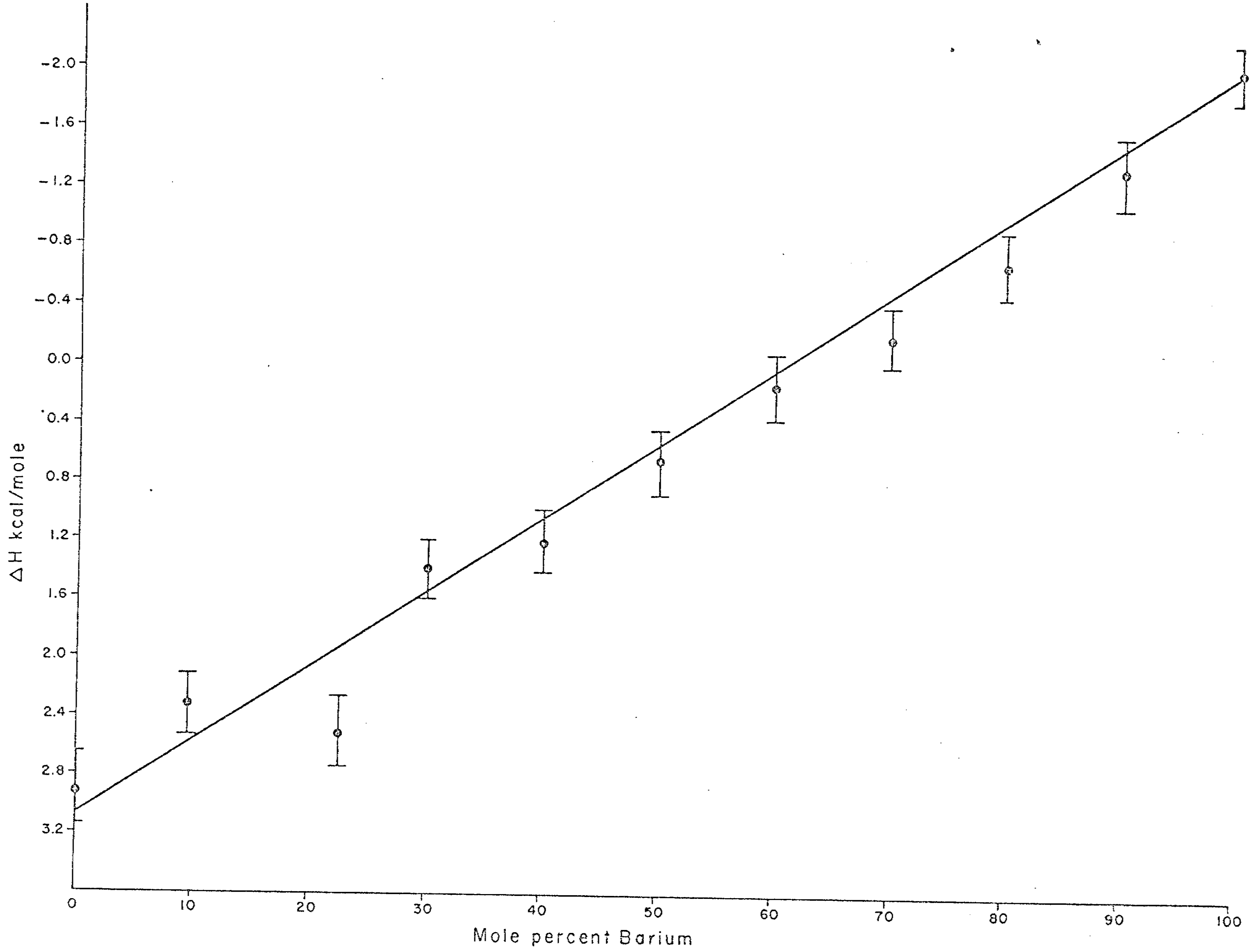


Figure 3. Enthalpy of precipitation of (Ba, Sr)SO_4 in kcal/mole at 61°C.

Assuming that a deviation in crystal lattice energy in the mixed crystal would be manifested as a deviation in ΔH_{mix}, the relative deviation from linearity in d-spacing should not be greater than $\frac{0.2 \text{ kcal}}{U_o} = 0.04\%$. Since the measurement of d-spacing (Figure 1) is subject to 1% instrumental error, the linearity of enthalpy versus mole fraction imposes a stricter limit on the linearity of d-spacing.

Equilibration Experiments

The ideality of the $(Ba,Sr)SO_4$ solid solution was further tested by determining the concentration of Sr^{++} ion in solution in equilibrium with solid $(Ba,Sr)SO_4$ of various compositions. The data for barium concentrations in solutions saturated with $(Ba,Sr)SO_4$ or mixtures of pure $BaSO_4$ and $SrSO_4$ are relatively inaccurate because the high sulfate concentrations depress the barium concentration to levels below the limits of detection with the atomic absorption spectrophotometer. The data for Ba^{++}, however, are all within an order of magnitude of the values predicted by equation (15).

For an ideal solid solution in which $N_S \geq 0.1$ the Sr^{++} concentration should be approximately equal to that of sulfate since $K_S \gg K_B$. For aqueous solutions saturated with respect to solid solutions having compositions clustered about $(Ba_{0.75}, Sr_{0.25})SO_4$, the strontium ion concentration was found to be nearly equal to the sulfate as predicted by the solubility products. Strontium ion concentration versus $\sqrt{N}$ is plotted for a series of solid solutions in Figure 4.

For an ideal solid solution the activity of the solute in the aqueous phase is equal to its concentration , and the activity in the solid is equal to its mole fraction. A plot of Sr^{++} concentration versus the square root of the mole fraction in the solid should give a straight line for an ideal solid solution. The graph in Figure 4 shows that ideality is closely approached for strontium mole fractions above 0.30. The mean deviation for the cluster of points at $\sqrt{N} = 0.45$ from the line representing the ideal solution is approximately 33% and corresponds to an activity coefficient of 0.5 for the solid in the solid solution or 1.5 for the ions in solution. Assuming the discrepency is real and not the result of imperfect equilibration, there would be a difference of only 0.4 kcal/mole between the real and ideal chemical potentials as calculated from (18).

$$\Delta F'_{real} - \Delta F'_{ideal} = -RT\ln\frac{(Sr^{++}ideal)^2}{(Sr^{++}meas.)^2} \tag{18}$$

Serial Leaching Experiments

The solubility of intermediate $(Ba,Sr)SO_4$ is pertinent to the problems of barite-celestite deposition in hydrothermal veins and marine environments. If $(Ba,Sr)SO_4$ remains inert after being precipitated, its composition is an indicator of initial depositional conditions, but if it equilibrates freely with its environment its composition is determined by the post-depositional history. This problem was investigated by following the change in composition of a Sr-rich solid solution as it progressively leached in successive portions of distilled water. Data at 25° C for serial leaching are summarized in Figure 4.

The experimental values of the strontium concentration in aqueous solution in the series of leachings of a strontium-rich $(Ba,Sr)SO_4$ sample are in close agreement with the theoretical values calculated from equation (14). Although the Sr^{++} concentrations for leaching a barium-rich solid solution were lower than the theoretical values, the change in concentration from one leach solution to the next in the series was in agreement with that predicted by theory.

The X-ray diffraction patterns of solid $(Ba,Sr)SO_4$ obtained after each equilibration show that the mole fraction of barium sulfate increased systematically and that finely powdered strontium-rich $(Ba,Sr)SO_4$ can be converted to a single phase homogeneous solid solution of higher barium composition by leaching.

The diffraction peaks of all the solid solutions of

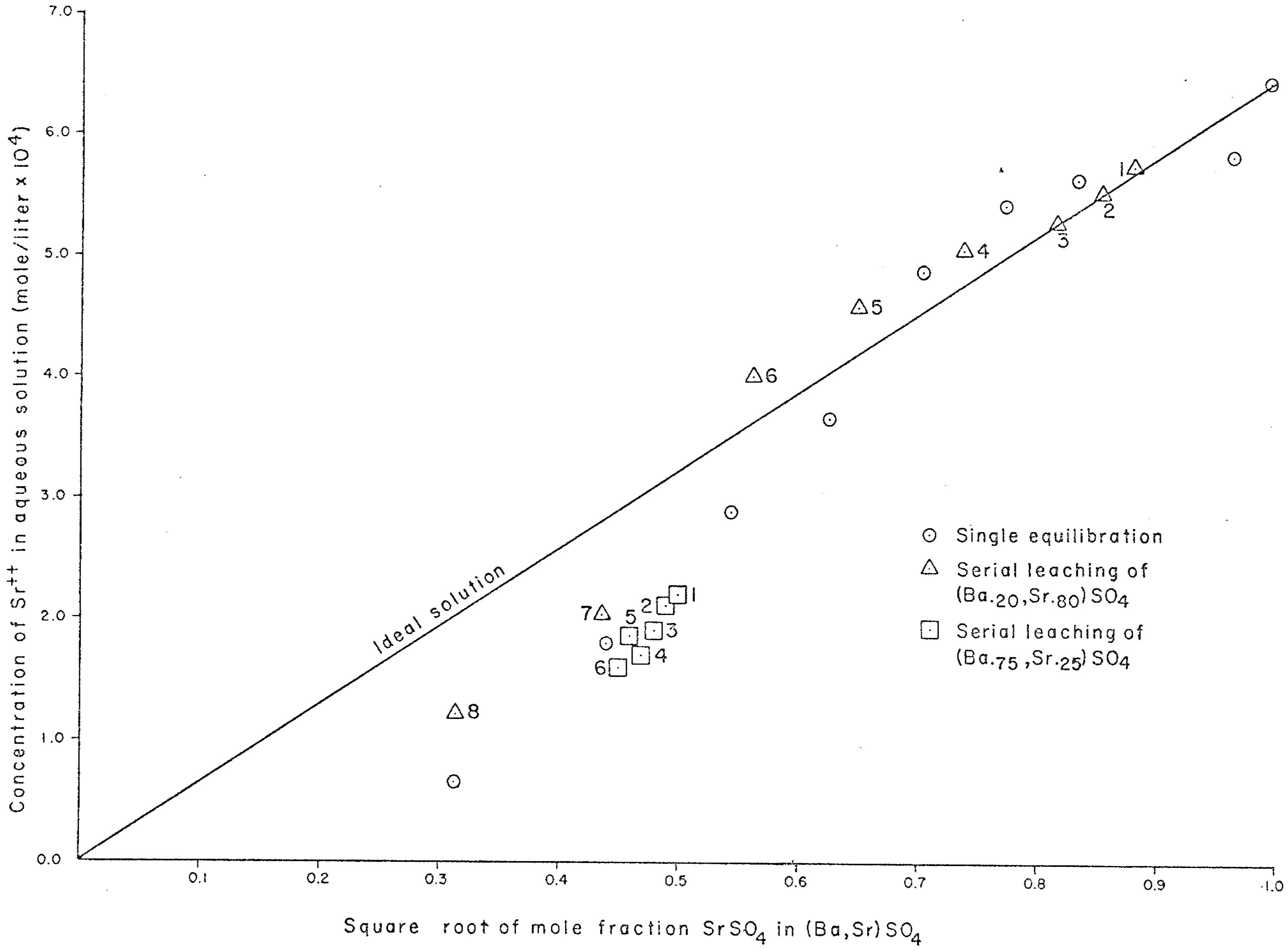


Figure 4. Equilibration of $SrSO_4$ between solid solution $(Ba, Sr)SO_4$ and aqueous solution at 25°C.

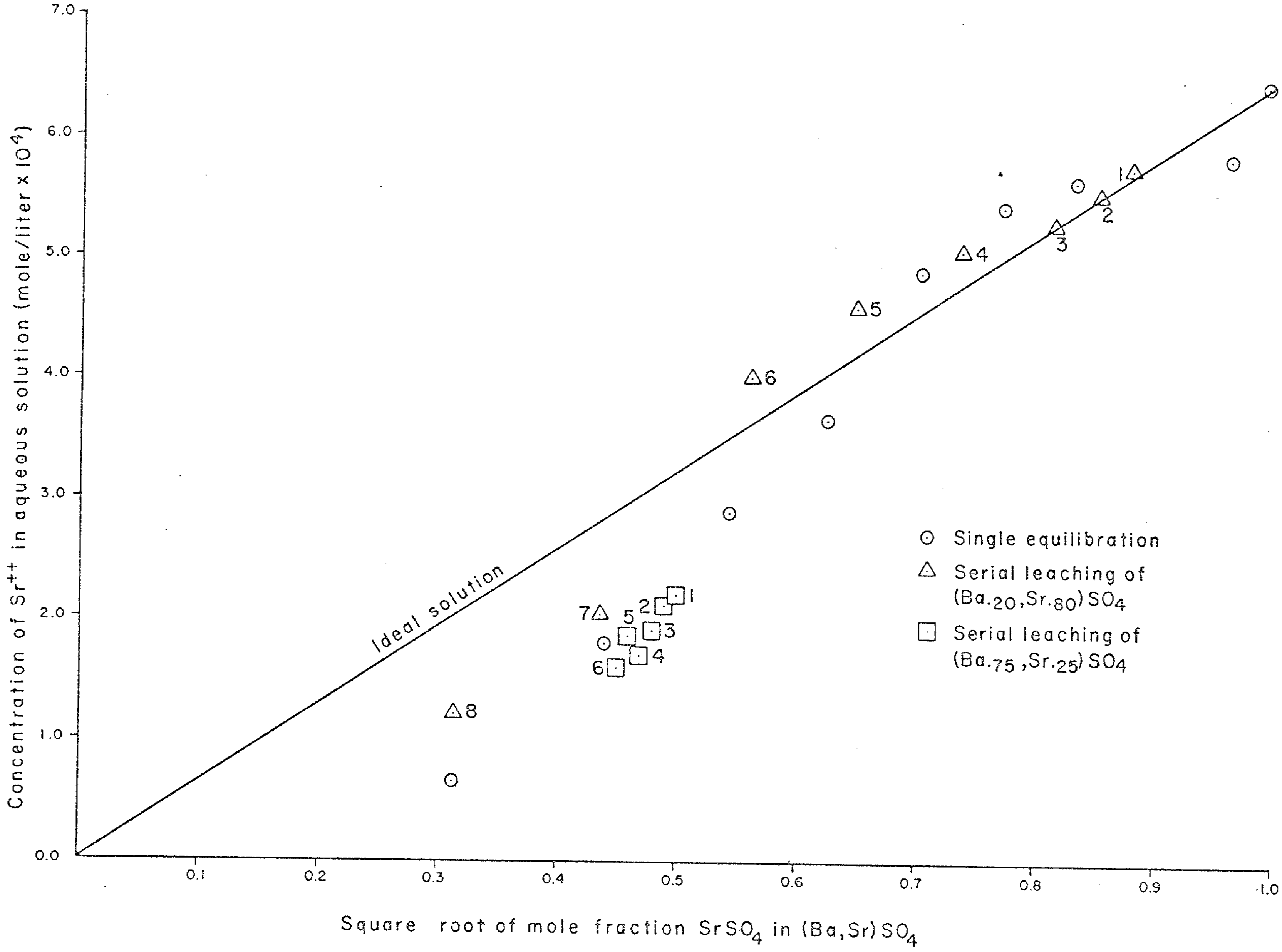


Figure 4. Equilibration of $SrSO_4$ between solid solution $(Ba, Sr)SO_4$ and aqueous solution at 25°C.

intermediate composition were broadened relative to the end-members as shown in Figure 5, and the broadening was most extreme for equimolar (Ba,Sr)SO_4. The diffraction peaks of the leached series were also broadened and appeared nearly identical to the peaks of the freshly precipitated (Ba,Sr)SO_4 of the same molar composition.

Two factors which influence the broadening are crystallite size and strain, and these have been examined in another study (Renault and Brower, in press). Only the crystallite size was found to be an important cause of broadening.

The results of the serial leaching experiment show clearly that fine-grained (Ba,Sr)SO_4 solid solutions of intermediate composition are not chemically inert with respect to distilled water. Consequently, under the conditions of the experiment, the composition of the solid phase reflects the final rather than the initial environmental conditions.

Solubility Measurements

Widely different results for the temperature dependence of the solubility of $SrSO_4$ in water have been reported (Holland, 1967). The disagreement may be due to difficulty in achieving saturation; therefore, in this study the measurements were repeated in the temperature range 2 - 95° C being careful to verify the attainment of equilibrium by approach from both higher and lower concentrations. Monitoring conductivity as a function of

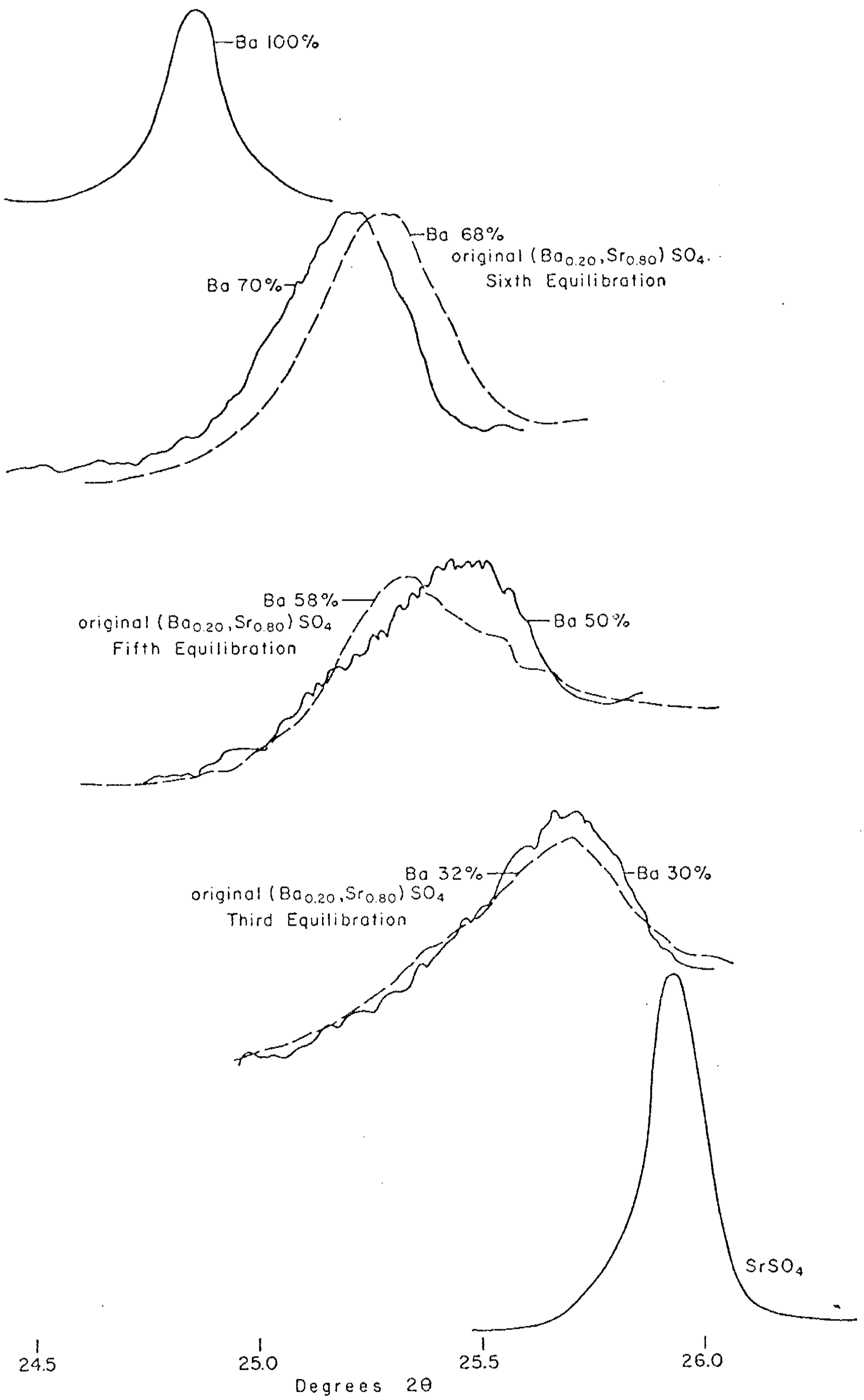


Figure 5A. Variation in shape of 111 diffraction peak with change in mole fraction.
—— freshly precipitated sample; ..... leached sample
$BaSO_4$ and $SrSO_4$, 500 cps = full scale
$(Ba, Sr)SO_4$, 200 cps = full scale.

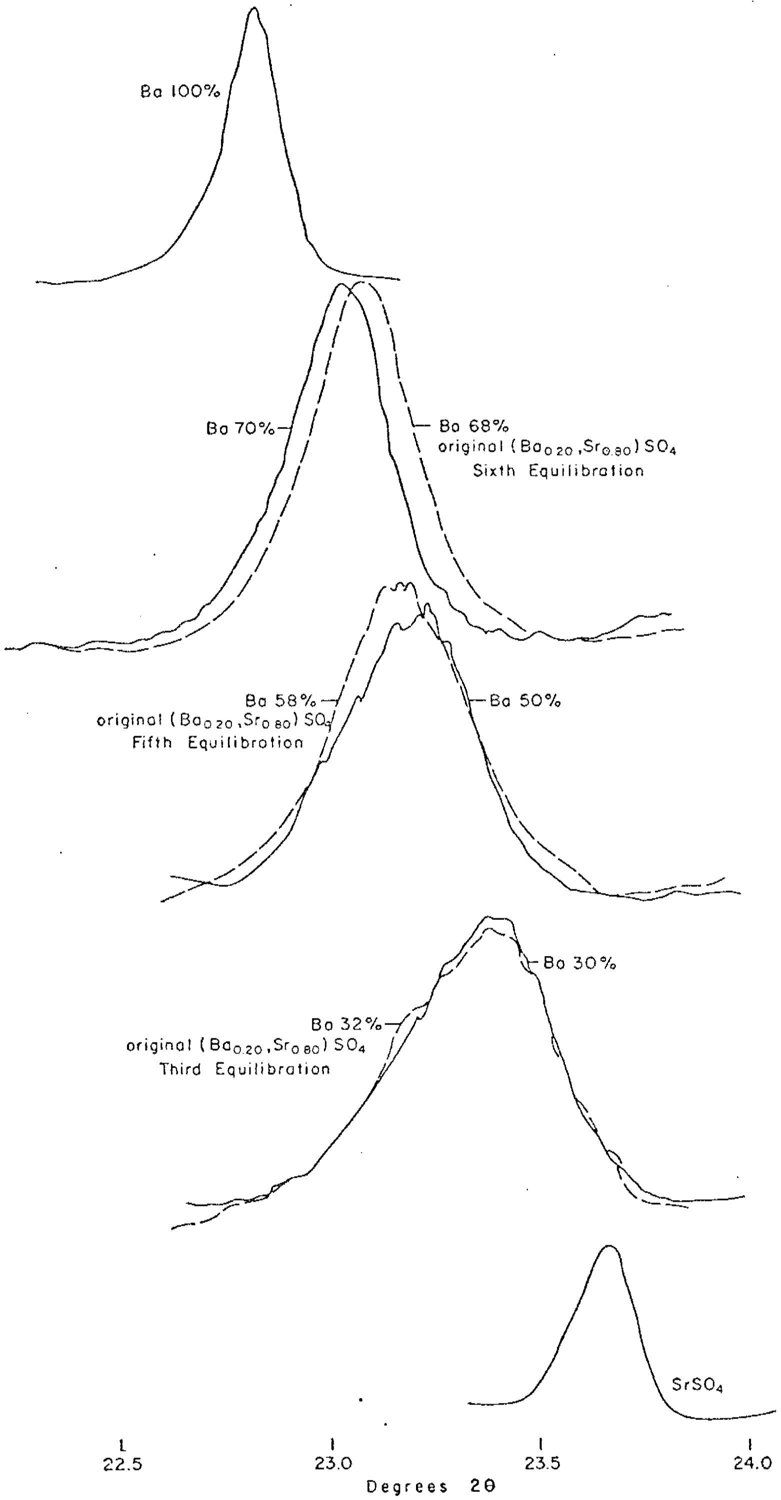


Figure 5B. Variation in shape of 002 diffraction peak with change in mole fraction.
—— freshly precipitated sample; ..... leached sample
$BaSO_4$ and $SrSO_4$, 500 cps = full scale
(Ba, Sr)SO_4, 200 cps = full scale.

as a function of time, the author has found that equilibrium is reached in less than one minute by dissolution but may be much slower by precipitation. Because the solubility of $SrSO_4$ is greater at lower temperature, accurate solubility values were obtained rapidly by saturating first at high temperatures, measuring conductivity, and then gradually cooling to lower temperatures and higher concentrations of Sr^{++}.

The solubilities of $BaSO_4$ and $SrSO_4$ were measured in a variety of electrolyte solutions. Although NaCl is the only uni-univalent salt that is geochemically important, ammonium nitrate and chloride were used to measure solubility at high ionic strengths because they caused much less interference with the atomic absorption analyses than metallic salts. The solubility data at various ionic strengths are given in Tables I and II.

The temperature dependence of $SrSO_4$ solubility is shown by a plot of log K versus $\frac{1000}{T}$ in Figure 6 where T is absolute temperature. The slope was determined at points corresponding to 25° and 61° C. The enthalpies calculated from equation (19) are + 0.54 and + 3.8 kcal/mole respectively and agree within 20% of the calorimetry values.

$$\frac{d(\log K)}{d(1/T)} = -\frac{H}{2.3R} \qquad (19)$$

The temperature dependence of $BaSO_4$ solubility was measured and log K plotted versus $\frac{1000}{T}$ as shown in Figure

TABLE I

Solubility of $SrSO_4$ (in moles x 10^3/liter) in electrolyte solutions at various concentrations at 25° C

Molarity of Electrolyte	NaCl	KCl	NH_4Cl	NH_4NO_3	$CaCl_2$
0.00	0.66	0.66	0.66	0.66	0.66
0.001	0.72	0.76	0.70	0.74	—
0.01	0.96	0.97	0.83	0.92	1.36
0.025	1.3	—	—	—	—
0.1	1.7	1.7	1.4	1.7	—
0.5	—	—	3.1	3.9	—
1.0	4.5	4.0	4.1	5.1	9.6
2.0	—	—	4.9	7.3	—
3.0	—	—	5.7	8.9	—
4.0	—	—	5.7	—	—
5.0	—	—	10.3	—	—

Molarity of Electrolyte	$MgCl_2$	Na_2SO_4	$CaSO_4$	$MgSO_4$
0.00	0.66	0.66	0.66	0.66
0.01	0.84	—	0.40	0.21
0.5	—	0.1	—	—
1.0	9.1	—	—	0.1

TABLE II

Solubility of $BaSO_4$ (in moles/liter x 10^4)
in electrolyte solutions at various concentrations
at 25° C

Molarity of Electrolyte	Electrolyte NaCl	KCl	NH_4Cl	NH_4NO_3	$SrCl_2$
0.00	0.1	0.1	0.1	0.1	0.1
0.1	—	—	0.2	0.14	0.4
0.5	—	—	0.6	0.2	—
1.0	0.3	0.4	1.0	1.5	1.5
2.0	—	—	1.4	2.6	—
3.0	—	—	1.5	3.8	—
4.0	—	—	1.6	—	—
5.0	—	—	1.5	5.6	—

7. Enthalpies calculated from the slope at 25° and 61° C are - 5.2 and - 2.3 kcal/mole respectively and agree within 25% of those determined by calorimetry.

The solubilities of $BaSO_4$ and $SrSO_4$ are markedly increased by a rise in ionic strength, and the molar solubility of $BaSO_4$ is increased somewhat more than that of $SrSO_4$. Preliminary experiments show that in the presence of sodium chloride $SrSO_4$ will be selectively leached from $(Ba,Sr)SO_4$. Roedder et al. (1968) report that fluid inclusions in barite are saline; therefore, barite either formed or recrystallized from a saline medium.

Since an increase in temperature up to the boiling point of water decreases K_{SrSO_4} and increases K_{BaSO_4}, the possibility exists that at temperatures consistent with hydrothermal vein deposition the two values could be equal and intermediate $(Ba,Sr)SO_4$ could precipitate from a sulfate-deficient system. In Figure 8 the log K versus $\frac{1000}{T}$ data have been extrapolated to their temperature of intersection. Barium sulfate and strontium sulfate would have the same solubility in water at not less than 360° C.

Helgeson (1969) has calculated from thermodynamic data values of K_{BaSO_4} at high temperature which are listed as follows:

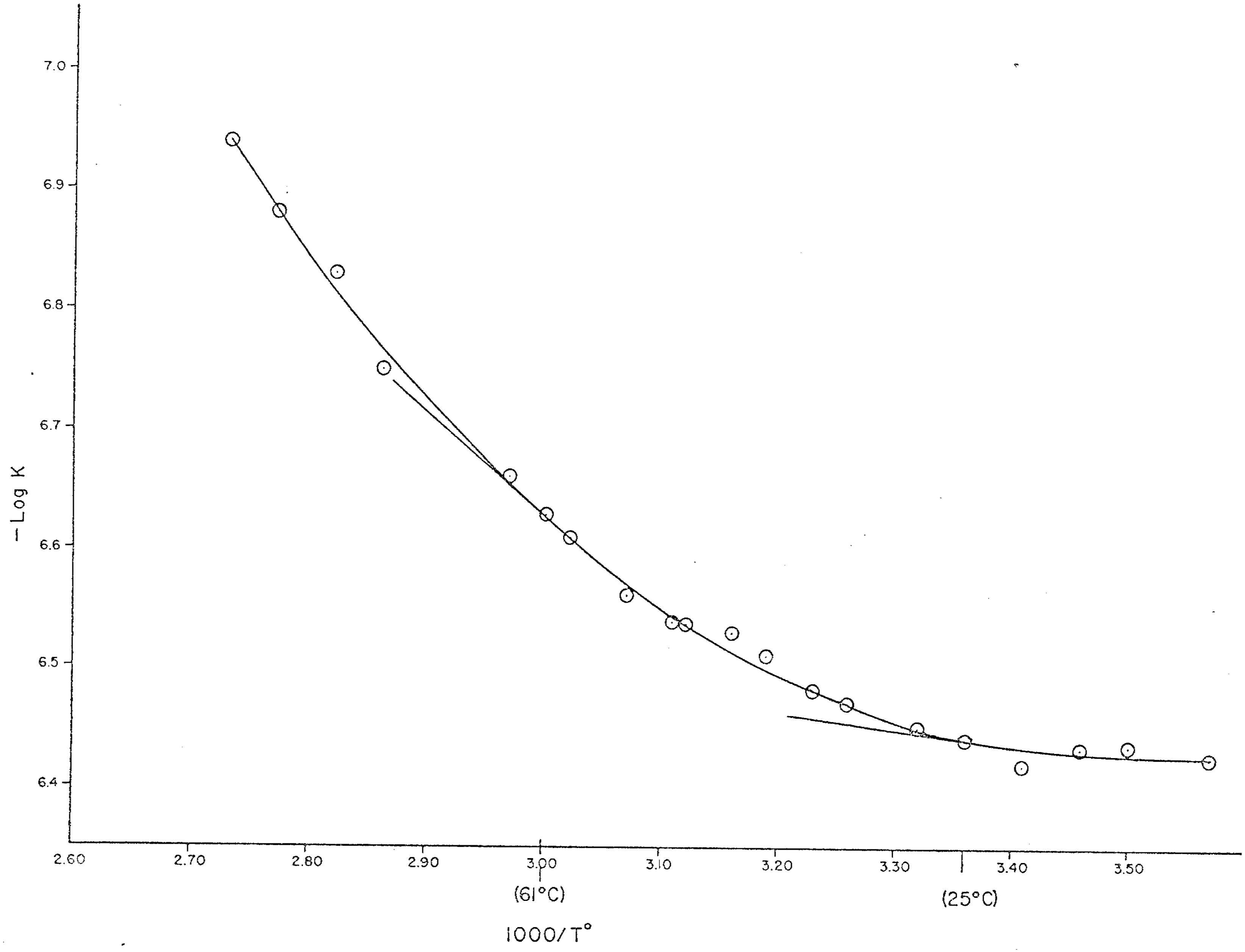


Figure 6. −Log K versus $\frac{1000}{T}$ for $SrSO_4$.

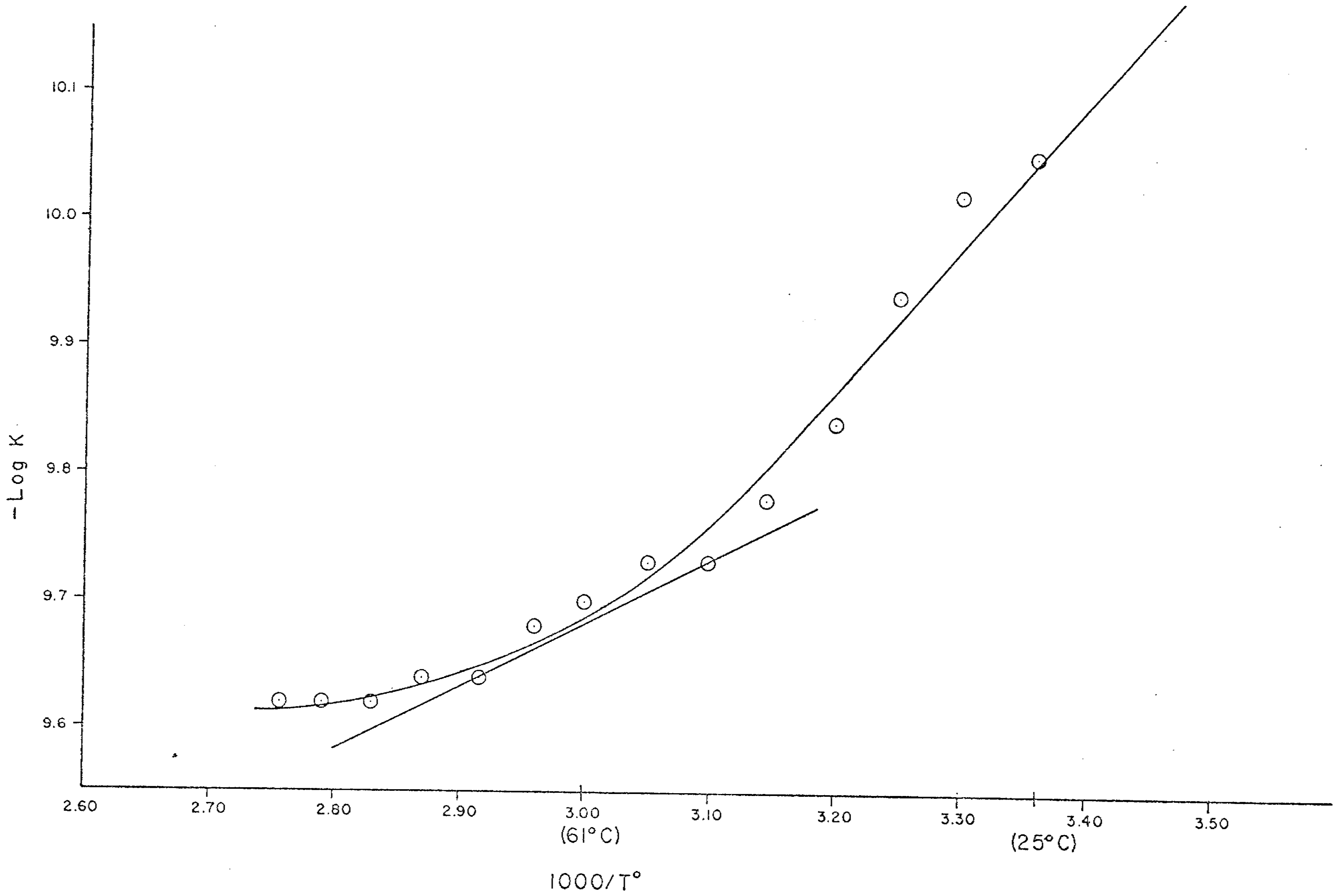


Figure 7. −Log K versus $\frac{1000}{T}$ for $BaSO_4$.

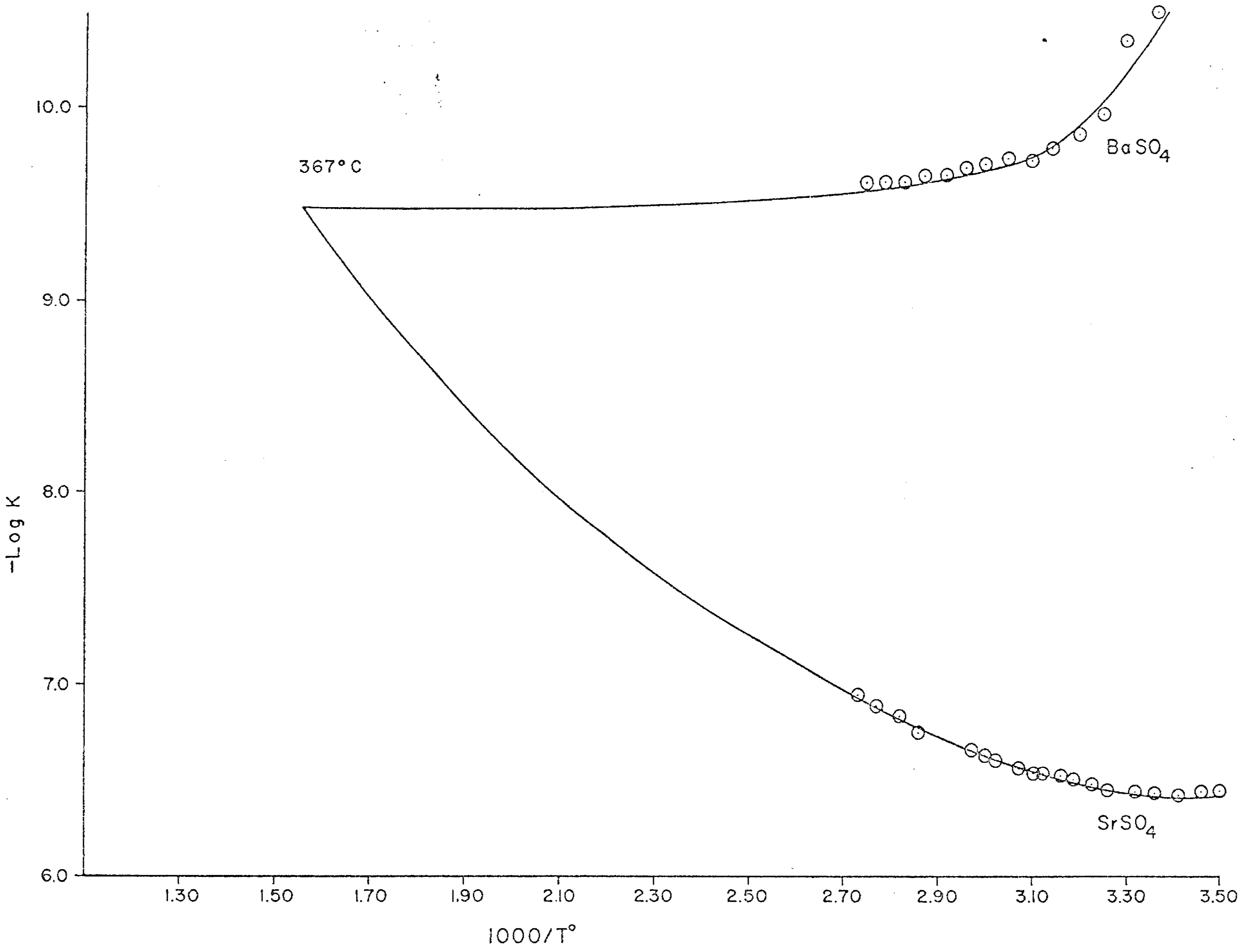


Figure 8. Extrapolation of $-\log K$ versus $\frac{1000}{T}$ to 367°C for BaSO$_4$ and SrSO$_4$.

T °C	Log K
25	9.7
50	9.42
60	9.34
100	9.22
150	9.34
200	9.76
250	10.34
300	11.05

The trend of increased solubility with rise in temperature reverses at approximately 125° C. If Helgeson's calculated values are correct, the equilibrium constants for barium sulfate and strontium sulfate probably do not intersect at any temperature.

Data given by Roedder et al. (1968) determined by fluid inclusion thermometry indicate that barite deposition occurs between 130 - 170° C. Thus, in low temperature hydrothermal environments, the solubilities of barite and celestite are probably not equal, and except in the case of a stoichiometric excess of $SO_4^=$ one would not expect celestite to precipitate.

CONCLUSIONS

The enthalpy of mixing $BaSO_4$ and $SrSO_4$ is nearly zero at 25° and 61° C. The entropy of mixing should closely approximate the ideal value, $-R(N_B \ln N_B + N_S \ln N_S)$, and the mixing process should be spontaneous over the entire range of compositions. This implies that in nature the solid solution $(Ba,Sr)SO_4$, should precipitate from an aqueous solution of Sr^{++} and Ba^{++} in any proportion provided that a stoichiometric amount of sulfate ion is available. However, the rarity of intermediate composition in nature suggests that $SO_4^{=}$ is often deficient during the deposition of barite or that $SrSO_4$ is removed following deposition.

Strontium sulfate leaches selectively from the solid solution at 25° C, and Sr^{++} and Ba^{++} concentrations in aqueous solution approach the ideal value calculated from the assumption that the chemical activity of each component is proportional to its mole fraction in the solid. In natural systems strontium sulfate should be leached from the solid solution which then becomes enriched in barium sulfate because surface waters are undersaturated with respect to $SrSO_4$. These experiments were based on fine-grained material so that the aqueous solution was rapidly saturated with $SrSO_4$; however, if natural crystals are coarse-grained, the process might go very slowly.

Optimum conditions for leaching $SrSO_4$ from $(Ba,Sr)SO_4$ are low temperature and high ionic strength. Carbonate ion, if it were present and equal in concentration to sulfate ion, would have a profound effect by forming the more insoluble $SrCO_3$ as shown in equation (3).

The separation of barium and strontium in nature could result from leaching $(Ba,Sr)SO_4$ possibly in conjunction with metathesis by carbonate ion. Strontianite is frequently associated with barite, celestite, and calcite in veins either in limestone or in sulfide veins (Palache et al., 1951). Schraut (1951) reports the occurence of strontianite with barite, witherite, and celestite in the Rosiclare fluorite district, and Grawe and Nackowski (1949) report the occurence of strontianite with fluorite, chalcopyrite, sphalerite, calcite, barite, and witherite in the Southern Illinois fluorspar district.

Part II

DEVELOPMENT OF A TECHNIQUE FOR GROWING BARIUM-STRONTIUM SULFATE CRYSTALS

Purpose

It is possible that natural macroscopic specimens of intermediate barium-strontium sulfate solid solutions are rare because the crystal lattice of either $BaSO_4$ or $SrSO_4$ is strained by substitution of the opposite end-member. Strain in the lattice may inhibit the growth of the crystal regardless of the availability of the required Ba^{++}, Sr^{++}, or $SO_4^{=}$ ions.

A complete series of synthetic solid solutions has been shown to exist between $BaSO_4$ and $SrSO_4$ by X-ray studies, but the synthetic materials are fine-grained precipitates. The diffraction peaks of all the intermediate members in this study were broadened relative to the end-members, and the broadening was most extreme for equimolar $(Ba,Sr)SO_4$.

The results of electron-microprobe analyses of single crystals of barium-rich $(Ba,Sr)SO_4$ are available in the literature (Hanor, 1966). The crystals Hanor analyzed contained no more than 9 mole% strontium. To the knowledge of the author there are no published chemical analyses of single crystals of $(Ba_{N_B},Sr_{N_S})SO_4$ for which $0.1 < N_B < 0.9$.

Thus it is desirable to synthesize large homogeneous crystals of the $BaSO_4$-$SrSO_4$ series and study their physical and chemical properties.

Methods of Crystal-Growing

The most important step in growing large crystals is the choice of a suitable solvent. Crystals grow most easily from very concentrated solutions, and workers who are experienced in the art of crystal-growing recommend a solvent capable of dissolving 10-60 weight percent solute (Kohman, 1963). Crystal growth in the solvent is controlled by the rate at which the solvent becomes supersaturated with respect to the solute; therefore, it is important to choose a solvent that can be supersaturated easily by a physical or chemical process such as evaporation, heating, cooling, or change in pH (Buckley, 1951).

It is difficult to grow large crystals of a substance that is just slightly soluble in all solvents even when the solubility can be either increased or decreased rapidly with a rise in temperature. When a solvent containing solute at low concentration is gradually supersaturated either by a temperature change or evaporation, a copious fine-grained precipitate may form instead of a small number of large crystals. The exlanation may be that nutrient cannot diffuse rapidly enough to reach the sites of the seed crystals already available in the solvent before a large number of new crystallites are nucleated. Spontaneous nucleation can be prevented by controlling the rate of supersaturation in the solvent. The usual technique for growing large crystals of a slightly soluble substance is to place seed crystals in a compartment of the crystal-growing apparatus separate from that of the nutrient (Buckley, 1951; Ballman and Laudise, 1963).

The solvents considered for crystallization of barium sulfate and strontium sulfate were the following acids and salt solutions: concentrated H_2SO_4, 6N HCl, 5M NaCl, 5M $CaCl_2$, 3.5M $MgCl_2$, 10M NH_4Cl, and 10M NH_4NO_3. The formation of bisulfate ion is responsible for the dissolution of barium or strontium sulfate in the concentrated acid solutions as shown in equations (20) and (21), and the high ionic strength is responsible for the enhanced solubility of $BaSO_4$ and $SrSO_4$ in salt solutions.

$$BaSO_4 + HCl \longrightarrow Ba^{++} + HSO_4^{-} + Cl^{-} \qquad (20)$$

$$SrSO_4 + HNO_3 \longrightarrow Sr^{++} + NO_3^{-} + HSO_4^{-} \qquad (21)$$

Experimental Procedures

Solubility measurements

The solubility of barium sulfate was determined in each of the solvents mentioned above, except concentrated H_2SO_4, and the values are given in Table III. The solubility of $BaSO_4$ was estimated by putting a measured volume of a particular solvent in each of a series of flasks and then adding to each a different amount of

TABLE III

Solubility of $BaSO_4$ and $SrSO_4$ in concentrated acids and salt solutions in moles x 10^3/liter at 25° C

Solvent	Solute	
	$BaSO_4$	$SrSO_4$
6N HCl	2	10
6N HNO_3	10	40
5M NaCl	0.5	5
3.5M $MgCl_2$	0.5	10
5M $CaCl_2$	1	—
10M NH_4NO_3	5	—

equivalent portions of aqueous H_2SO_4 and $BaCl_2$. The solubility of $BaSO_4$ in the solvent was estimated to be the starting concentration of Ba^{++} and $SO_4^{=}$ in the flask in which a precipitate just barely formed on standing 24 hours. The experiment was repeated for $SrSO_4$ in several of the solvents, and the values of the estimated solubilities are given in Table III.

Recrystallization of barium sulfate and strontium sulfate under hydrothermal conditions

The most successful method for growing synthetic barite and celestite crystals was by recrystallization under hydrothermal conditions.

In order to recrystallize under hydrothermal conditions a special apparatus was designed to permit thermal cycling. The apparatus consisted of an aluminum block, 14"x3"x3", with 12"x5/8" cylindrical holes for the glass sample tubes, a hot plate for heating the metal block, and a timer which turned the hot plate on for 3 hours and off for 3 hours.

Approximately 5-7 mg. of finely-powdered barium sulfate and 12 ml. of 5M NaCl were sealed in a heavy glass tube, and the tube was inserted in a hole in the aluminum block. The maximum temperature measured by a thermometer inserted in the block was 220° C and the minimum 35° C.

Each week the sample tubes were removed from the block and the crystals examined through the glass with a hand lens. Shiny, crystal faces appeared as the material coarsened with time. The finely-powdered barium sulfate dissolved, and the larger crystals grew.

The largest barium sulfate crystal was 500 microns and had been recrystallizing for 2 months. Most of the large crystals were 100 - 250 microns. The crystals seem to grow outward from aggregates of finely-powdered starting material. An aggregate with crystals radiating outward is marked with an arrow in picture 2 of Figure 9.

Samples of strontium sulfate were prepared for thermal cycling by sealing 15 mg. of finely powdered $SrSO_4$ and 12 ml. of 5M NaCl in a glass tube. The largest $SrSO_4$ crystals grown were 40 - 70 microns.

Samples of solid solution of various molar composition were prepared for recrystallization by sealing 8-12 mg. of finely powdered $(Ba,Sr)SO_4$ and 12 ml. of 5M NaCl in a glass tube. The starting material was prepared by the instantaneous precipitation of an aqueous solution of barium and strontium with a stoichiometric excess of sulfuric acid. Most of the solid solutions did not form crystals larger than 50 microns after 2 months of thermal cycling. A preliminary examination of the solid solutions with a Philips Electron Microprobe Analyzer AMR/3 suggests that indiv-

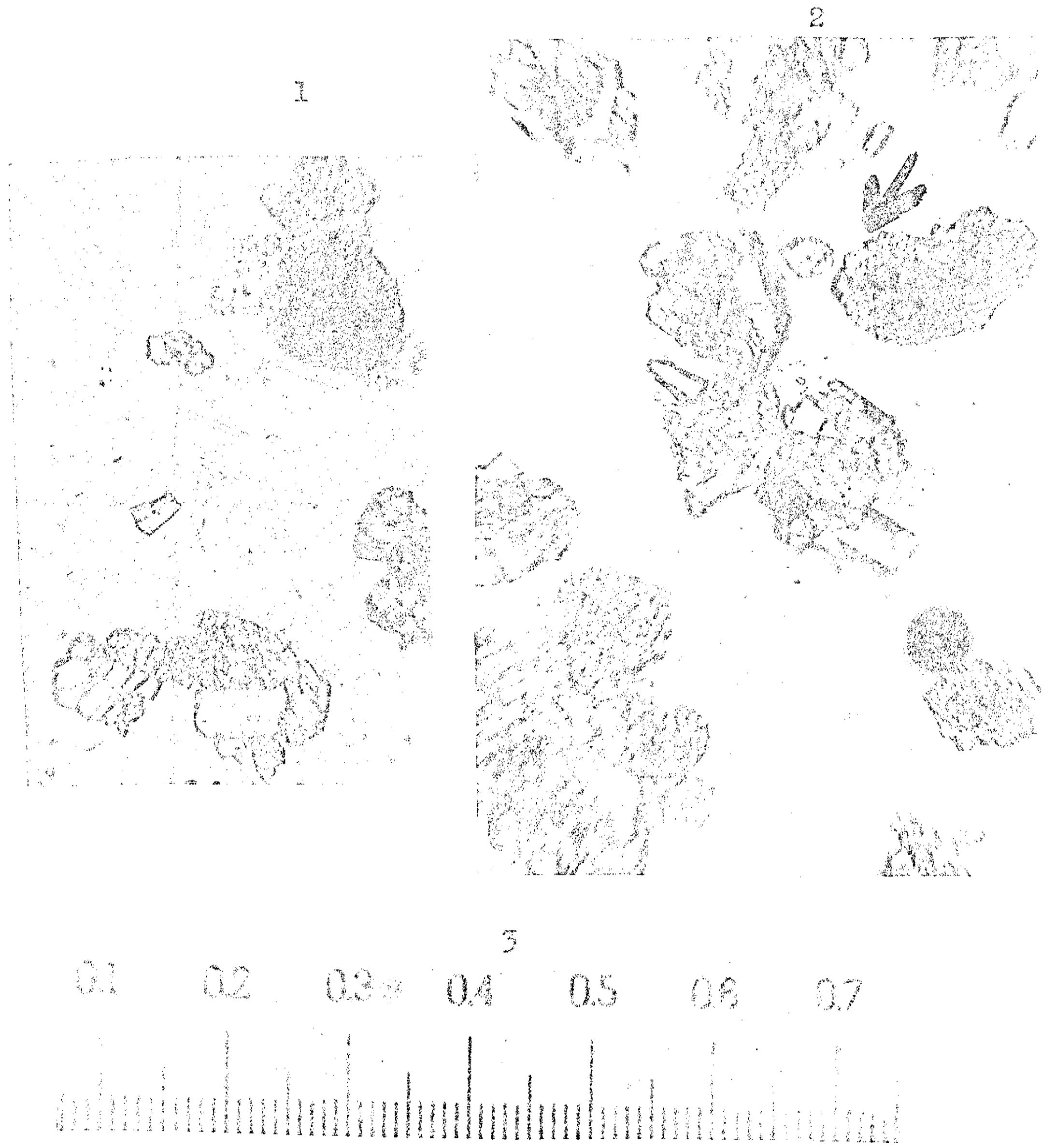


Figure 9. Synthetic barite crystals, grown by recrystallization of finely-powdered $BaSO_4$ in brine by thermal cycling. Photographs taken with an optical microscope.

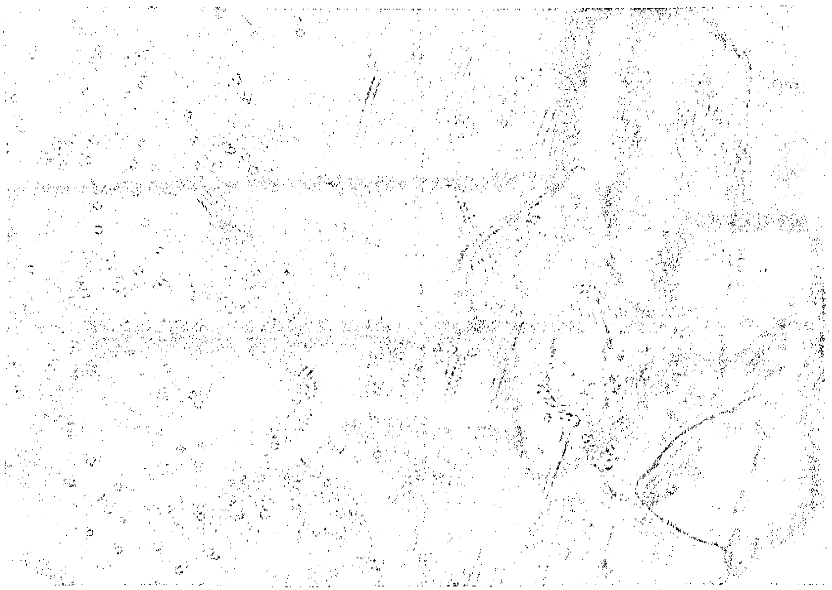
1&2. clusters of crystals, medium power, field of view ~ 700 microns

3. micrometer, medium power, scale = 0.1 mm

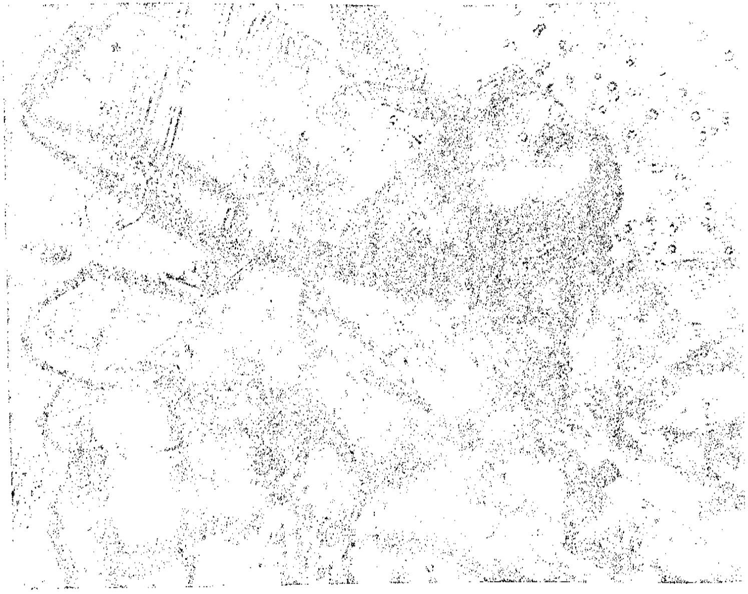
4. large crystal, high power, field of view ~ 180 microns

5. cluster of crystals, high power

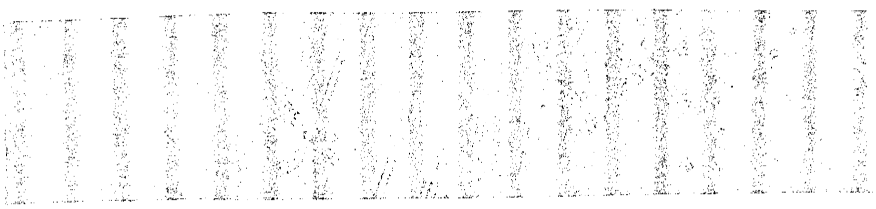
6. micrometer, high power, scale = 0.01 mm



4



5



6

idual crystals contain both barium and strontium. At present the results are not quantitative.

Robert Horrigan of the metallurgical laboratory at the White Sands Missile Range reported strontium below the limits of detection by electron microprobe analysis in crystals formed by recrystallizing 10 mg. of finely-powdered $(Ba_{0.9},Sr_{0.1})SO_4$ in 12 ml of 5M NaCl. The limits of detection are approximately 0.1%.

Preliminary experiments

Crystallization of barium sulfate from salt solutions:

Each solution was heated to the boiling point, stoichiometric amounts of $BaCl_2$ and H_2SO_4 solutions were added, and the solution was cooled with stirring to either room temperature or 7° C (refrigerator temperature). The cooling period varied from 20 minutes to 2 weeks. The maximum size of the crystals was 20 microns, and the size showed no clear relation to the rate of cooling. The temperature of the solutions was regulated by means of a thermostatic water bath.

Eventually it was possible to obtain crystals up to 30 microns by the method of recrystallization. The solution was heated to the boiling point and saturated with $BaSO_4$ by the addition of stoichiometric amounts of $BaCl_2$ and H_2SO_4 solutions. When the solution cooled, most of the fine precipitate was removed by decantation. On reheating to the boiling point the solution became nearly clear. The solution was cooled to room temperature again, but this time the precipitate was coarser and was not decanted. The process of heating to dissolve the finest precipitate and then cooling to supersaturate the solution so that the coarsest crystals could grow was repeated until shiny, crystal faces could be observed in the precipitate with a hand lens.

The salt solutions used in this series of preliminary experiments include 3.5M $MgCl_2$, 5M $CaCl_2$, 5M NaCl, and 10M NH_4NO_3. The coarsest crystals were grown in 5M NaCl. The other salt solutions seemed to be nearly equal in value as a solvent for recrystallizing $BaSO_4$.

Crystallization of barium sulfate and strontium sulfate from concentrated acids:

The supersaturation of concentrated acids with $BaSO_4$ or $SrSO_4$ resulted in the precipitation of a poorly crystallized material as shown by optical examination. The method of supersaturating each acid with $BaSO_4$ is summarized as follows:

(1) concentrated sulfuric acid

A beaker containing 50 ml of concentrated sulfuric acid saturated with solid $BaSO_4$, and an evaporating dish containing 50 ml of water were enclosed in a glass container. The solution became supersaturated as the acid absorbed water. The solubility changes from 7.05 weight percent barium sulfate in 96% sulfuric acid to 0.05 weight percent barium sulfate in 83% sulfuric acid (Seidell,1940)

(2) 6N HCl

(a) Equivalent portions of aqueous $BaCl_2$ and H_2SO_4 were added to 100 ml of 6N HCl in an open beaker. The acid was supersaturated by enclosing the beaker in a dessicator with an evaporating dish containing an equivalent amount of NaOH.

(b) Two sealed flasks, one containing 100 ml of $BaSO_4$ in 6N HCl and the other an equivalent amount of NH_4OH, were connected by a glass tube, and the system was evacuated.

(3) 6N HNO_3

A slightly undersaturated solution of $BaSO_4$ in 6N HNO_3 was supersaturated by neutralization of the acid with ammonia. An open beaker containing 50 ml of nitric acid and an evaporating dish containing an equivalent amount of ammonium hydroxide were placed in a dessicator.

Conclusions

When a variety of concentrated acids were saturated with $BaSO_4$ and $SrSO_4$ and supersaturated by slow neutralization, the resulting precipitates were poorly crystallized. Concentrated sulfuric acid is a good solvent for both sulfates, but the high viscosity may have interfered with crystal growth. Poor crystal growth in 6N HCl and 6N HNO_3 could be attributed to low concentrations and the fact that the solvent was not stirred during chemical neutralization.

Small crystals, 10-30 microns, of $BaSO_4$ were grown by recrystallization from concentrated salt solutions. Finely-powdered $BaSO_4$, $SrSO_4$, and $(Ba,Sr)SO_4$ were recrystallized in brine by the process of thermal cycling in a hydrothermal apparatus. The maximum size of the crystals are: $BaSO_4$, 500 microns, $SrSO_4$, 70 microns, and $(Ba,Sr)SO_4$, 50 microns. Qualitative analysis by the electron microprobe of the solid solution crystals show that individual crystals contain both barium and strontium.

The preliminary results suggest $BaSO_4$ grows faster by recrystallization than either $SrSO_4$ or $(Ba,Sr)SO_4$.

The conversion of $(Ba_{0.9},Sr_{0.1})SO_4$ to 100% $BaSO_4$ by recrystallization is consistent with the Law of Mass Action because the volume of brine solution in the tube was sufficient to dissolve all of the $SrSO_4$ contained in the original finely-powdered precipitate. This conversion shows that a barium-strontium sulfate solid solution can achieve equilibrium with its aqueous solution by the process of recrystallization. Crystallization of $(Ba,Sr)SO_4$ by slow cooling in a hydrothermal environment should also enable a crystal to achieve equilibrium with the ore solution.

Part III

GEOCHEMICAL CONSIDERATIONS

Introduction

The purpose of this section is to relate the geological occurence of the barite-celestite series to the thermodynamic properties.

The hydrothermal environment

The nearly ideal behavior of the barite-celestite solid solution series is consistent with the observed relative scarcity of celestite in hydrothermal deposits and the rarity of intermediate $(Ba,Sr)SO_4$ members in both hydrothermal and sedimentary environments.

Consider a single hydrothermal ore solution. The compositions of a solid solution formed from this ore solution can be calculated by estimating activities for Ba^{++}, Sr^{++}, and $SO_4^{=}$ in the aqueous phase. The following three cases show how the composition of the solid solution varies with change in values of the activities of Ba^{++}, Sr^{++}, and $SO_4^{=}$.

Case #1

$$
\begin{aligned}
a_{Sr^{++}} &= a_{Ba^{++}} \\
a_{SO_4^{=}} &\geqq a_{Ba^{++}} + a_{Sr^{++}} \\
a_{Ba^{++}} \times a_{SO_4^{=}} &\geqq K_{BaSO_4} = 10^{-10} \\
a_{Sr^{++}} \times a_{SO_4^{=}} &\geqq K_{SrSO_4} = 10^{-6.4}
\end{aligned}
$$

The products of the ionic activities are equal to or greater than the equilibrium constants, and sulfate activity is equivalent to barium plus strontium activities. Therefore, barium and strontium coprecipitate as $(Ba_{N_B}, Sr_{N_S})SO_4$, and the mole fraction of each component in the solid solution is related to its activity in the aqueous solution as follows:

$$N_B = \frac{a_{Ba^{++}}}{a_{Ba^{++}} + a_{Sr^{++}}} \qquad N_S = \frac{a_{Sr^{++}}}{a_{Ba^{++}} = a_{Sr^{++}}}$$

Assume, for example, that the activities in the ore-forming solution are as follows:

$$a_{Ba^{++}} = 0.002$$

$$a_{Sr^{++}} = 0.001$$

$$a_{SO_4^{=}} = 0.003$$

The activity of sulfate is equivalent to that of barium plus strontium. The product $a_{Ba^{++}} \times a_{SO_4^{=}}$ is 6×10^{-6} which greatly exceeds the equilibrium constant of 10^{-10}, and the product $a_{Sr^{++}} \times a_{SO_4^{=}}$ is 3×10^{-6} which exceeds the equilibrium constant of $10^{-6.4}$. Because the aqueous solution is saturated with respect to both end-members a solid solution precipitates having the same molar composition as the aqueous phase, 33 mole% $SrSO_4$ and 67 mole% $BaSO_4$.

Case #2

$$a_{Ba^{++}} \approx a_{Sr^{++}}$$

$$a_{SO_4^{=}} \geqq a_{Ba^{++}} + a_{Sr^{++}}$$

$$a_{Ba^{++}} \times a_{SO_4^{=}} \geqq K_{BaSO_4}$$

$$a_{Sr^{++}} \times a_{SO_4^{=}} < K_{SrSO_4}$$

This ore solution is saturated with respect to pure barium sulfate and undersaturated with respect to pure strontium sulfate. The mole fraction of strontium sulfate in the solid solution is determined by the activity of strontium sulfate in the aqueous solution given by the following:

$$N_S = \frac{a_{Sr^{++}} \times a_{SO_4^{=}}}{K_{SrSO_4}}$$

For example if all activities given in case #1 are reduced by a factor of 10, they will be:

$$a_{Ba^{++}} = 0.0002$$

$$a_{Sr^{++}} = 0.0001$$

$$a_{SO_4^{=}} = 0.0003$$

This solution is saturated with respect to barium sulfate and undersaturated with respect to strontium sulfate:

$$a_{Ba^{++}} \times a_{SO_4^{=}} = 6 \times 10^{-8} > 10^{-10}$$

$$a_{Sr^{++}} \times a_{SO_4^{=}} = 3 \times 10^{-8} < 10^{-6.4}$$

The mole fraction of $SrSO_4$ co-precipitated in solid solution with barium sulfate is calculated as follows:

$$N_S = \frac{10^{-7.5}}{10^{-6.4}} = 10^{-1.1} = 0.08$$

Case #3

$$a_{Ba^{++}} + a_{Sr^{++}} > a_{SO_4^{=}} \approx a_{Ba^{++}}$$

In this ore solution Ba^{++} and Sr^{++} must compete for $SO_4^{=}$ because the sulfate activity is deficient with respect to the sum of the cation activities. The partitioning of barium and strontium between aqueous and solid solutions is determined by the relative activities of Ba^{++} and Sr^{++} and the ratio of the equilibrium constants assuming that equilibrium is achieved:

$$\frac{a_{Sr^{++}} \times a_{SO_4^{=}}}{a_{Ba^{++}} \times a_{SO_4^{=}}} = \frac{N_S K_{SrSO_4}}{N_B K_{BaSO_4}}$$

$$\underset{\text{(aqueous)}}{\frac{a_{Sr^{++}}}{a_{Ba^{++}}}} = \underset{\text{(solid)}}{\frac{N_S}{N_B}} \times 10^{3.6}$$

For example if the activities of Ba^{++} and Sr^{++} are equal, the ratio $N_B/N_S = 4{,}000$, and the mole% $SrSO_4$ precipitated in solid solution will be 0.025%. To precipitate a solid solution containing 1% $SrSO_4$ would require a ratio of $Sr^{++}/Ba^{++} = 40$ in the aqueous solution, 9% $SrSO_4$ in the solid would require a ratio of 400, and 50% $SrSO_4$ in the solid a ratio of $Sr^{++}/Ba^{++} = 4000$. If Sr^{++}/Ba^{++} in the aqueous phase is smaller than 1, only a negligible amount of $SrSO_4$ would coprecipitate. Although these calculations have not been adjusted for temperature, the adjusted values should not be different from those calculated by more than one order of magnitude.

These examples suggest that nearly pure barite should precipitate preferentially from a single hydrothermal ore solution. Formation of intermediate $(Ba_{N_B}, Sr_{N_S})SO_4$ compositions, $N_B \approx N_S$, are improbable because the required conditions for deposition are very special. To precipitate intermediate $(Ba,Sr)SO_4$ from a single ore-forming solution would require either a very high ratio of Sr^{++}/Ba^{++} for low $SO_4^{=}$ activity as shown in case #3 or supersaturation with respect to $BaSO_4$ and saturation with respect to $SrSO_4$ for high sulfate activity as in case #1.

Another possible origin of a barite-celestite deposit is the mixing of a hydrothermal solution containing $Ba^{++}$and Sr^{++} ions with connate water containing sulfate ion. The composition of $(Ba,Sr)SO_4$ formed depends not only on the activities of the ions in solution but also on the order and speed of mixing the two solutions as shown in the following cases.

Case #1

One solution containing $SO_4^{=}$ is added gradually to a reservoir containing nearly equal activities of Sr^{++} and Ba^{++}. If the mixing process is slow enough, the $SO_4^{=}$ activity in the reservoir will be much lower than the sum of $Ba^{++} + Sr^{++}$activities. When the two solutions begin to mix, barium sulfate will be preferentially partitioned into the solid phase, and only a small amount of $SrSO_4$ will be incorporated into the solid solution. If sufficient sulfate is added to the reservoir and $a_{Sr^{++}} \times a_{SO_4^{=}} = K_{SrSO_4}$, strontium sulfate will begin to precipitate after nearly all of the barium has been removed from aqueous solution.

Case #2

A solution containing nearly equal activities of Sr^{++} and Ba^{++} is gradually added to a $SO_4^{=}$ hydrothermal solution. The molar composition of the solid solution will be comparable to that of the aqueous solution only if the mixing is very rapid and the solutions highly concentrated. The formation of a $(Ba_{N_B}, Sr_{N_S})SO_4$ solid solution of intermediate composition, $N_B \approx N_S$, requires that the aqueous solution be just saturated with $SrSO_4$ and supersaturated with $BaSO_4$; therefore, only instantaneous mixing of concentrated solutions will yield a ratio of Sr/Ba in the solid equal to that of the aqueous solution.

If the solutions are dilute and the Sr^{++}, Ba^{++} solution gradually added to the $SO_4^{=}$ solution, barium sulfate will be preferentially partitioned into the solid phase and the mole fraction of $SrSO_4$ incorporated in the solid solution is calculated as follows:

$$N_S = \frac{a_{Sr^{++}} \times a_{SO_4^{=}}}{K_{SrSO_4}}$$

These examples suggest that separate barite and celestite deposits rather than $(Ba,Sr)SO_4$ of intermediate composition are more likely to form when the source of the ore is a mixture of two solutions, one containing Ba^{++} and Sr^{++} and the other $SO_4^{=}$. Formation of intermediate $(Ba,Sr)SO_4$ would require the improbable instantaneous mixing of concentrated ore solutions.

The mineral associations of hydrothermal barite and celestite ores give important evidence for the physico-chemical nature of the depositional environment. Fluorite, quartz, calcite, galena, and sphalerite are common associates of barite and celestite (Bateman, 1950; Berry and Mason, 1959; Heyl, 1968). Although the entire assemblage of minerals does not always occur in each deposit, the sequence of minerals is usually the same from one deposit to another. Whenever sphalerite and barite are found together in a hydrothermal deposit, for example, the barite is either with or above the sphalerite but never below it (Barnes and Czamanske, 1967). The fact that barite is commonly associated with sulfide minerals sets limits on the probable range of values for the ratio $a_{SO_4^=}/a_{S^=}$ and the oxygen fugacity in the ore solution at the time of deposition.

A hydrothermal ore solution is likely to become progressively oxidized as it rises in the crust. The oxidation state of a particular chemical species may increase as the ore solution progresses from a reduced to an oxidized environment. The sulfur species that predominate in the ore solution at depth ($P_{O_2} = 10^{-35}$ atmospheres, $T = 250^\circ$ C), for example, are probably H_2S, HS^-, or $S^=$, whereas in the oxidizing environment at the earth's surface and $T = 25^\circ$ C the only important sulfur species are HSO_4^- and $SO_4^=$ (Barnes and Czamanske, 1967). Each hydrothermal environment can be characterized by a definite value of the ratio $a_{SO_4^=}/a_{S^=}$ if T, P, pH, and total sulfur in solution are known.

A mineral should form whenever the activity of the mineral in solution exceeds the saturation value given by the thermodynamic equilibrium constant. A change in temperature from T_1 to T_2 may decrease the value of the equilibrium constant from K_1 to K_2 so that the product of the activities of the ions in solution which was smaller than K_1 now exceeds K_2, and the mineral precipitates. The activity of one or more ions that participate in the formation of the mineral may be increased by some physico-chemical change in the ore solution such as a chemical reaction of the solution with the wall rock, a change in temperature, or a change in the partial pressure of H_2S, CO_2, or O_2. If the product of the ionic activities following the physico-chemical change exceeds the equilibrium constant, the mineral will be deposited.

A probable mechanism for the deposition of a sulfide mineral from ore solution is by cooling because the solubility of sulfide minerals in aqueous solution increases with rising temperature (Czamanske, 1959). Cooling the ore solution below 100° C also causes barite to precipitate because its solubility increases with rising temperature between 0 and 100° C. Another possible mechanism for barite deposition is the gradual increase in sulfate activity caused by oxidation of sulfide ion. Barium sulfide at 100° C is approximately 10^5 times more soluble than barium sulfate (Seidell, 1940).

If the source of barite and contemporaneous sulfide minerals is a single, rising hydrothermal solution containing both metal ions and sulfur, the value for the $a_{SO_4^=}/a_{S^=}$ ratio and the oxygen fugacity at the time of deposition can be calculated whenever it is possible to estimate values for the total sulfur activity, pH, and the temperature of deposition. The fact that barite occurs above the sulfides in the sequence of minerals suggests that the activity of $SO_4^=$ is equal to but not larger than the minimal value for deposition of barite, $a_{SO_4^=} = \frac{K}{a_{Ba^{++}}}$, where K is the equilibrium constant for barium sulfate at the temperature of deposition. Barnes and Kullerud (1961) estimated activities for sulfate ion in the ore solution of a Mississippi Valley deposit in which barite is nearly contemporaneous with spalerite. They calculated a value of $10^{-4.4}$ for $SO_4^=$ if $Ba^{++} = 0.001$, using $K_{250^\circ C} = 10^{-7.4}$.

The value for $K_{250^\circ C}$ was calculated by Barnes and Kullerud from the data of Latimer (1952). The value calculated by Helgeson, $K_{250^\circ C} = 10^{-10.34}$, gives a value $SO_4 = 10^{-7.3}$ if $Ba^{++} = 0.001$.

Thus some geological evidence suggests that barite is formed from an ore solution containing a low activity of $SO_4^=$ so that the ore solution is saturated but not supersaturated with respect to barium sulfate. If the Ba^{++} and Sr^{++} activities are nearly the same, formation of $(Ba_{N_B},Sr_{N_S})SO_4$ of intermediate composition, $N_B \gtrsim N_S$, is not possible because the solution is undersaturated with respect to pure $SrSO_4$. If the $SO_4^=$ activity is the minimum required for barite deposition and $Ba^{++} \approx Sr^{++}$, the sulfate activity is much smaller than the minimum value required for $SrSO_4$ deposition, $a_{SO_4^=} = \frac{K_{SrSO_4}}{a_{Sr^{++}}}$.

Assume, for example, the following:

$$a_{Sr^{++}} = a_{Ba^{++}} = 0.001$$

$$T = 150^{\circ}\ C$$

$$K_{BaSO_4} = 10^{-9.8}$$

$$K_{SrSO_4} = 10^{-7.2}$$

where values are given by the following: K_{BaSO_4}, (Figure 8, this paper; Templeton, 1960; Mosebach and Strubel, 1962) and K_{SrSO_4}, (Figure 8, this paper; Strubel, 1962).

Then

$$a_{SO_4^=} = \frac{10^{-9.8}}{10^{-3}} = 10^{-6.8}$$

$$N_S = \frac{10^{-3} \times 10^{-6.8}}{10^{-7.2}} = 10^{-2.6}$$

Thus the composition of a solid solution deposited at 150° C from an ore-solution containing equal activities of barium and strontium and sulfate activity minimal for $BaSO_4$ precipitation will be 99.75 mole% barium sulfate

and 0.25 mole% strontium sulfate.
The estimated value of 1 for the ratio of Ba^{++}/Sr^{++} in the ore-forming solution is based on the fact that the crustal abundances of barium and strontium are approximately the same, and the two elements follow a similar geochemistry in igneous rocks.

The rarity of celestite in hydrothermal deposits has several explanations that are consistent with the ideality of the $(Ba,Sr)SO_4$ series: (1) Sulfate ion activity in most ore-forming deposits may be too low to precipitate Sr^{++} ; (2) celestite deposits may have been removed by weathering because of the high solubility of $SrSO_4$ relative to other hydrothermal ores; (3) carbonate ion may have precipitated the more insoluble $SrCO_3$, $K_{SrCO_3} = 10^{-9.2}$.

Although strontianite, like celestite, is a rare hydrothermal mineral (Helz and Holland, 1965), strontium carbonate coprecipitates with $CaCO_3$ to form a solid solution. Strontium ion substitues for calcium in either the aragonite or calcite lattice, and calcite is a common associate of barite and celestite in the hydrothermal environment (Deer et al., 1962). The ratio $a_{Ca^{++}}/a_{Sr^{++}}$ in ore solutions is probably smaller than 10 which is the value of the ratio K_{CaCO_3}/K_{SrCO_3} at 25° C, and is the maximum value for this ratio at any temperature in the range of hydrothermal deposition (Barton, 1957). Because Ca^{++} activity is much higher than Sr^{++} in the ore-solution and the equilibrium constants of the two carbonates are close in value for a wide range of temperatures, strontium is more likely to co-precipitate with calcium to form $(Ca,Sr)CO_3$ in the hydrothermal environment than to form a separate deposit of strontianite.

Another possible mechanism for the formation of hydrothermal $(Ca,Sr)CO_3$ is the metathesis of limestone. Whenever an ore-solution containing high activities of $SrSO_4$ permeates a limestone host rock, the following reaction should take place:

$$\underset{\text{(solid)}}{2\ CaCO_3} + \underset{\text{(aq.)}}{SrSO_4} \longrightarrow \underset{\text{(solid)}}{(Ca,Sr)CO_3} + \underset{\text{(aq.)}}{CaSO_4}$$

The value of the ratio of equilibrium constants at 25° C is $K_{CaSO_4} / K_{SrSO_4} = 10^2$ using the values given in Holland (1967).

Mineralogical controls on Ba^{++}, Sr^{++}, and $SO_4^{=}$ in natural waters

The probability of forming a $BaSO_4$-$SrSO_4$ solid solution in a sedimentary environment depends on the activities of Ba^{++}, Sr^{++}, and $SO_4^{=}$ in natural waters. The activities of these ions are controlled by the equilibrium relationships between natural waters and several minerals which include barite and celestite.

It is possible that either sulfate or carbonate ion controls the activity of barium ion in natural waters, and the following calculations using the data in Table IV show that $SO_4^=$ probably governs the Ba^{++} concentration in seawater:

$$a_{Ba^{++}} \times a_{SO_4^=} = m_{Ba^{++}} \times m_{SO_4^=} \times \gamma_{Ba^{++}} \times \gamma_{SO_4^=}$$

$$1.5 \times 10^{-7} \times 2.8 \times 10^{-2} \times 0.28 \times 0.12 = 1.4 \times 10^{-10}$$

$$a_{Ba^{++}} \times a_{SO_4^=} = 1.4 \times 10^{-10} \simeq K_{BaSO_4} = 1.0 \times 10^{-10}$$

$$a_{Ba^{++}} \times a_{CO_3^=} = m_{Ba^{++}} \times m_{CO_3^=} \times \gamma_{Ba^{++}} \times \gamma_{CO_3^=}$$

$$1.5 \times 10^{-7} \times 2.7 \times 10^{-4} \times 0.28 \times 0.20 = 2.3 \times 10^{-12}$$

$$a_{Ba^{++}} \times a_{CO_3^=} = 2.3 \times 10^{-12} < K_{BaCO_3} = 10^{-8.8}$$

where the value for K_{BaCO_3} is given by Hogness and Johnson (1954).

The product of the $Ba^{++} \times SO_4^=$ ionic activities based on measured values of molar concentrations is approximately the same as the equilibrium constant, therefore, sea water is saturated with respect to $BaSO_4$. Any increase in the activity of Ba^{++} caused by weathering or biological activity is prevented by precipitation with $SO_4^=$, thus sulfate ion controls the activity of Ba^{++} in sea water.

The product of $Ba^{++} \times CO_3^=$ ionic activities based on observed molar concentrations is less than the $BaSO_3$ equilibrium constant, therefore, seawater is undersaturated with respect to $BaCO_3$ and carbonate ion is probably not a control on Ba^{++} activity in seawater.

TABLE IV

s of observed molar solubilities in sea water and activity coefficients

Solubility (m)	Source of data	Single ion activity coefficient I = 0.7	Source
1.5×10^{-7}	Turekian and Johnson (1966)	0.28	Garrels and Christ (1965)
8.6×10^{-5}	Hanor (1969)	0.28	Garrels and Christ (1965)
2.8×10^{-2}	Garrels and Christ (1965)	0.12	Garrels and Christ (1965)
2.7×10^{-4}	Garrels and Christ (1965)	0.20	Garrels and Christ (1965)

The following calculation for determining the mineralogical control of Sr^{++} activity in sea water using the data in Table IV shows that either carbonate or sulfate ion may control Sr^{++} activity:

$$a_{Sr^{++}} \times a_{SO_4^{=}} = m_{Sr^{++}} \times m_{SO_4^{=}} \times \gamma_{Sr^{++}} \times \gamma_{SO_4^{=}}$$

$$8.6 \times 10^{-5} \times 2.8 \times 10^{-2} \times 0.28 \times 0.2 = 8.1 \times 10^{-8}$$

$$a_{Sr^{++}} \times a_{SO_4^{=}} = 8.1 \times 10^{-8} < K_{SrSO_4} = 4.7 \times 10^{-7}$$

$$a_{Sr^{++}} \times a_{CO_3^{=}} = m_{Sr^{++}} \times m_{CO_3^{=}} \times \gamma_{Sr^{++}} \times \gamma_{CO_3^{=}}$$

$$8.6 \times 10^{-5} \times 2.7 \times 10^{-4} \times 0.28 \times 0.20 = 1.3 \times 10^{-9}$$

$$a_{Sr^{++}} \times a_{CO_3^{=}} = 1.3 \times 10^{-9} > K_{SrCO_3} = 7 \times 10^{-10}$$

where the value for K_{SrCO_3} is given by Hogness and Johnson (1954).

The $Sr^{++} \times SO_4^{=}$ product is smaller than K_{SrSO_4} by a factor of 6 and the $Sr^{++} \times CO_3^{=}$ product larger than K_{SrCO_3} by a factor of 2. Thus sea water is slightly undersaturated with respect to celestite and nearly saturated with respect to strontianite. It seems most likely that carbonate ion controls the activity of Sr^{++} in sea water although it is possible that Sr^{++} is in equilibrium with a $(Ba,Sr)SO_4$ of approximately 20 mole% $SrSO_4$. The barite in pelagic sediments contain about 5 mole% $SrSO_4$ (Arrhenius, 1963).

Kramer (1965) has suggested that Sr^{++} in the oceans is controlled by carbonate concentration and that $SO_4^{=}$ is a function of Sr^{++} concentration.

Sedimentary environments

Separation of barium and strontium sulfates in sedimentary deposits is consistent with the ideality of the $(Ba,Sr)SO_4$ series. Because of the large differences in the solubilities of barite and celestite, each mineral is formed and stabilized in a different sedimentary environment.

Formation of a sedimentary deposit of celestite is possible whenever the product $a_{Sr^{++}} \times a_{SO_4^=}$ exceeds K_{SrSO_4} and the ratio $a_{SO_4^=}/a_{CO_3^=}$ exceeds the value of K_{SrSO_4}/K_{SrCO_3} which is $10^{2.8}$ at 25° C. Strontianite should be precipitated from sea water before celestite because the activity ratio $a_{SO_4^=}/a_{CO_3^=}$ is approximately 10^2.

Celestite is commonly associated with gypsum, gypsum-bearing rocks, dolomite, dolomitic-limestone, marls, and other lagoonal deposits of high salinity (Teodorovich, 1961; Berry and Mason, 1959). Thus the source of strontium in this sedimentary environment includes Sr^{++} contained in sea water, the Sr^{++} rejected from the crystal lattice of aragonite during conversion to calcite (equation 22), or from limestone being converted to dolomite (equation 23).

$$\underset{\text{(aragonite)}}{Ca,Sr(CO_3)_2} + Ca^{++} \longrightarrow \underset{\text{(calcite)}}{2\ CaCO_3} + Sr^{++} \quad (22)$$

$$\underset{\text{(limestone)}}{Ca_{2-x},Sr_x(CO_3)_2} + Mg^{++} \longrightarrow \underset{\text{(dolomite)}}{Ca,Mg(CO_3)_2} + (1-x)Ca^{++} + xSr^{++} \quad (23)$$

The source of sulfate for celestite deposition in this environment is probably $SO_4^=$ contained in sea water although another possibility is the oxidation of H_2S or sulfide from sulfide minerals.

The ratio of $a_{SO_4^=}/a_{CO_3^=}$ can be increased by increasing the acidity of the solution so that carbonate ion is converted to bicarbonate. A change in 1 pH unit will change the $a_{CO_3^=}/a_{HCO_3^-}$ by a factor of 10 as can be calculated from the following equilibrium relationship:

$$\frac{(H^+)(CO_3^=)}{(HCO_3^-)} = 10^{-10.3}$$

Oxidation of H_2S or a sulfide mineral will increase the acidity of the solution in addition to increasing $a_{SO_4^=}$ as shown in (24) and (25).

$$H_2S \quad + \quad 2\ O_2 \longrightarrow SO_4^= \quad + \quad 2\ H^+ \qquad (24)$$

$$S^= \quad + \quad 4\ H_2O \longrightarrow SO_4^= \quad + \quad 4\ H^+ \qquad (25)$$

Whenever limestone or dolomite is formed, carbonate is consumed and sulfate not. The ratio of $a_{SO_4^=}/a_{CO_3^=}$ contained in the solution is increased because of this process.

The ratio $a_{SO_4^=}/a_{CO_3^=}$ is increased by evaporation of sea water because carbonate minerals are first to precipitate in an evaporite deposit. Evaporation may be the most important mechanism for increasing the sulfate/ carbonate ratio. Because the ratio $a_{Ca^{++}}/a_{Sr^{++}} \approx 100$ and $K_{CaSO_4}/K_{SrSO_4} \approx 100$, calcium and strontium sulfate are likely to co-precipitate during the evaporation of sea water. Celestite is commonly associated with gypsum in evaporite deposits either interbedded with gypsum as independent crystals or grains or in separate beds (Harness,1949). Recrystallization of a gypsum-celestite deposit from a solution of much lower sulfate activity than the original evaporite solution should separate celestite and gypsum because of the large difference in equilibrium constants.

Some geologists have suggested that many celestite deposits are of secondary origin (Kraus, 1905). Primary celestite may form as independent grains in the pores of sedimentary rocks, and secondary celestite is later deposited from ground water that percolates through the rock and transports the $SrSO_4$. The most common occurence of celestite is in dolomite or dolomitic limestones throughout which the mineral grains are disseminated (Deer et al., 1962; Mudd, 1949; Rankama, 1950; and Stewart, 1963).

Barite occurs in sedimentary environments either as a residual deposit formed by the weathering of bedrock or by direct chemical precipitation. Because barite is extremely insoluble, it frequently occurs in residual clay deposits formed during the weathering of limestone (Brobst, 1958; Bateman, 1950). Nearly all the barite produced in the United States is associated with weathered limestone.

Chemically precipitated barite is distributed throughout sedimentary rocks, often as concretions and sometimes as cement in sandstones and in sedimentary iron and manganese ores. Sedimentary barite also occurs in large high-grade bedded deposits (Shawe et al, 1969).

Sedimentary barite is probably precipitated by mixing a barium-rich solution with either sea water or other natural water containing a high concentration of sulfate ion. Barium-rich solutions could be derived from the weathering of igneous rocks, volcanic emanations, or hot springs.

Celestite and barite formed at low temperatures in sedimentary environments should be well separated because of the large difference in their solubilities. The weathering process preferentially leaches $SrSO_4$ from rocks and concentrates Sr^{++} in the ocean (Horn and Adams, 1966) whereas $BaSO_4$ is resistant to weathering and forms residual sedimentary deposits. The evaporation of sea water cannot yield sizeable barite deposits or deposits of $(Ba,Sr)SO_4$ of intermediate composition because of the low concentration of Ba^{++}.

Whenever sedimentary barite is formed by direct precipitation, celestite may co-precipitate if the original barium-rich solution is also strontium-rich. Because sedimentary barite is precipitated at a relatively low temperature, it may recrystallize slowly and be fine-grained. A fine-grained solid solution of intermediate composition would probably re-equilibrate rapidly to form a barium-rich solid solution because most natural waters are undersaturated with respect to $SrSO_4$.

Conclusions

The nearly-ideal behavior of the barite-celestite solid solution is consistent with the geochemical separation of barium and strontium sulfates in both hydrothermal and sedimentary environments.

The common occurence of sulfide minerals with hydrothermal deposits of barite suggests that the oxygen fugacity is low at the time of barite deposition and the sulfate activity too low to form sizable deposits of celestite and $(Ba_{N_B},Sr_{N_S})SO_4$ of intermediate composition, $N_B \approx N_S$. Another reason for the scarcity of hydrothermal celestite and intermediate $(Ba_{N_B},Sr_{N_S})SO_4$ may be the precipitation of Sr^{++} by $CO_3^{=}$.

Selective leaching of $SrSO_4$ contributes to the separation of barium and strontium sulfates in the sedimentary environment and to the concentration of Sr^{++}

in the ocean and $BaSO_4$ in residual deposits. The low concentration of Ba^{++} in sea water probably prevents the formation of large intermediate $(Ba,Sr)SO_4$ deposits by the evaporation of water. Recrystallization of chemically precipitated $(Ba,Sr)SO_4$ in sedimentary environments should yield a barium-rich solid and strontium-rich solution.

SUMMARY AND INTERPRETATION

Summary

The following factors influence the occurence and composition of barite and celestite:

(1) A high $a_{Sr^{++}}/a_{Ba^{++}}$ ratio in the ore-forming solution favors the formation of (Ba,Sr)SO_4 of intermediate composition.

(2) A high value of P_{O_2} and $a_{SO_4^=}$ favors the formation of intermediate (Ba,Sr)SO_4; low values of $a_{SO_4^=}$ causes barium sulfate to precipitate preferentially because $K_{SrSO_4} \gg K_{BaSO_4}$ at all temperatures.

(3) An increase in salinity of an ore-forming solution increases the solubility of both strontium and barium sulfates although the solubility of barium sulfate is more affected.

(4) Recrystallization of (Ba,Sr)SO_4 in solutions of low sulfate activity preferentially removes $SrSO_4$. Most surface waters are undersaturated with respect to $SrSO_4$; therefore, equilibration of (Ba,Sr)SO_4 with surface waters should enrich the original mineral with respect to barium.

(5) An increase in the $a_{CO_3^=}/a_{SO_4^=}$ ratio of the ore-forming solution increases the amount of strontium precipitated as carbonate, either in solid solution with calcium or as strontianite, and decreases the amount of strontium precipitated as sulfate, either in solid solution with barium or as celestite.

(6) Cooling below 100° C causes K_{BaSO_4} to decrease and K_{SrSO_4} to increase; consequently, barite will incorporate smaller amounts of strontium if formed by cooling a hydrothermal solution below 100° C.

Interpretation of geological observations

Because there are so many factors that influence the composition of a natural $(Ba,Sr)SO_4$ deposit, the composition of the ore-solution and the conditions at which a particular mineral was formed cannot be determined from the composition of a particular specimen. Consider two hydrothermal barite deposits, A and B. If the strontium concentration of the barite in deposit A is 10 times greater than in B, any of the following may be implicated: (1) the $a_{Sr^{++}}/a_{Ba^{++}}$ ratio in ore solution A was greater than in B, (2) the temperature for deposition of A was higher than for B (assuming $T \quad 125^{\circ}C$), (3) the values of P_{O_2} and $a_{SO_4^{=}}$ were greater during deposition of A than B, (4) B has either recrystallized or weathered to a barium-enriched solid solution following deposition, and (5) the ratio of $a_{CO_3^{=}}/a_{SO_4^{=}}$ was higher during the formation of B than A so that more strontium was partitioned into the carbonate phase in B than in A.

The composition of barite or celestite can be used, however, as a diagnostic tool for estimating the conditions of deposition in conjuction with other geological information. The temperature of deposition can be estimated from fluid inclusion data, and it may be possible also to estimate $a_{Sr^{++}}/a_{Ba^{++}}$ ratios in the ore-solution from fluid inclusion analyses. Whenever sulfide minerals are associated with the deposit, the values of P_{O_2} and $a_{SO_4^=}$ can be estimated; and their absence might be indicative of a high value of the oxygen fugacity and $a_{SO_4^=}/a_{S^=}$ ratio during deposition.

Because the molar solubilities of $SrCO_3$ and $CaCO_3$ are very close, $K_{SrCO_3}/K_{CaCO_3} \approx 1/10$ at 25° C, the Sr^{++}/Ca^{++} ratio in the calcite should be indicative of the $a_{Sr^{++}}/a_{Ca^{++}}$ ratio in the ore-solution. Recrystallization of calcite in fresh water should cause only a slight enrichment of Sr in the solid. Calcium carbonate should leach selectively from $(Ca,Sr)CO_3$ at 25° C for solid solutions in equilibrium with fresh water because $K_{CaCO_3} \approx K_{SrCO_3}$. If the strontium concentration is known for both barite and calcite in two hydrothermal deposits of approximately the same depositional temperature and containing the same sulfide minerals, the deposits might be compared in the following way: the Sr concentration in calcite of deposit A is higher than in B, but the Sr concentration in barite A is lower than in B. Two possible explanations are (1) deposit A has recrystallized in fresh water so that the calcite has become enriched in Sr and the barite enriched in barium, or (2) the $a_{CO_3^=}/a_{SO_4^=}$ ratio was higher during deposition of A than B. In order to choose between (1) and (2) we need to know more about the occurence and abundance of other sulfate and carbonate minerals in the deposit. If celestite, gypsum, or anhydrite, are also found in deposit B but not in A, we might infer that the $a_{CO_3^=}/a_{SO_4^=}$ ratio in ore-solution A was much higher than in B. This inference would be strengthened by finding strontianite in deposit A but not in B.

Another clue for estimating the Sr concentration of the ore-forming solution might be the Sr concentration in fluorite in conjunction with barite and calcite. If the barite, calcite, and fluorite of deposit A are all strontium-rich compared to the same minerals in deposit B, this should indicate a strontium-enrichment of ore-solution A relative to ore-solution B.

A clue for estimating $a_{SO_4^=}/a_{S^=}$ and P_{O_2} in the ore-solution might be the comparison of the amount of strontium and lead contained in solid solution in barite. The ratio $K_{PbSO_4}/K_{BaSO_4} = 10$ according to values given by Hogness and Johnson (1954) for T=25° C. If the values of strontium and lead increase from one section of a barite deposit to another in a comparable way, the increase might indicate increasing sulfate activity in the ore-solution at the time of deposition.

Conclusions

Because there are many factors that influence the composition of a natural $(Ba,Sr)SO_4$ specimen, the composition of a single specimen can be related to the conditions of deposition only by careful observation, analysis, and interpretation of the entire mineral assemblage. However, if such information can be obtained, an understanding of the depositional process would be greatly enhanced. Such understanding might lead to better exploration for ore deposits.

APPENDIX

Heat of precipitation data

Temp. °C	Mole% Ba	ΔH measured cal/mole	ΔH dilution cal/mole	ΔH precip. cal/mole	average value
61	0	+2570	-366	+2936	+3061
61	0	+2820	-366	+3186	
61	9.6	+1925	-366	+2291	
61	22.6	+2135	-366	+2510	
61	30.3	+1030	-366	+1396	
61	40.0	+ 841	-366	+1207	
61	50.0	+ 255	-366	+ 628	
61	60.0	- 253	-366	+ 113	
61	70.0	- 551	-366	- 185	
61	80.0	-1055	-366	- 689	
61	90.0	-1700	-366	-1334	
61	100.0	-2185	-366	-1819	-1986
61	100.0	-2520	-366	-2154	
25	0	+1523	+875	+ 648	
25	0	+1596	+875	+ 721	
25	10	+ 948	+875	+ 73	
25	20	+ 934	+875	+ 59	
25	33	- 62	+875	- 937	
25	50	- 945	+875	-1820	-1865
25	50	- 745	+875	-1620	
25	50	-1280	+875	-2155	
25	60	-1390	+875	-2265	

Temp. °C	Mole% Ba	ΔH measured cal/mole	ΔH dilution cal/mole	ΔH precip. cal/mole	average value
25	70	-1984	+875	-2859	
25	80	-2500	+875	-3375	
25	90	-2440	+875	-3315	
25	95	-2460	+875	-3335	
25	100	-2600	+875	-3475	
25	100	-2793	+875	-3668	-3668
25	100	-2800	+875	-3675	
25	100	-2980	+875	-3855	

REFERENCES

Arrhenius, G., 1963, Pelagic Sediments, <u>in</u> Hill, M.N. (ed.), The Sea, v. 3: New York, Interscience Publishers, p. 655-727.

Ballman, A.A. and Laudise, R.A., 1963, Hydrothermal growth, <u>in</u> Gilman, J.J. (ed.), The art and science of growing crystals: New York, John Wiley and Sons Inc. , p. 231-251.

Barnes, H.L. and Czamanske, C.K., 1967, Solubilities and transport of ore minerals, <u>in</u> Barnes, H.L. (ed.), Geochemistry of hydrothermal ore deposits: New York, Holt, Rinehart, and Winston, Inc., p. 334-381.

Barnes, H.L. and Kullerud, G., 1961, Equilibria in sulfur-containing aqueous solutions: Econ. Geol. v. 56, p. 648-688.

Barton, Jr., P.B., 1957, Some limitations on the possible composition of the ore-forming fluid: Econ. Geol. v. 52, p.333-353.

Bateman, A.M., 1950, Economic mineral deposits: New York, John Wiley and Sons, p.761-763.

Berry, L.G. and Mason, Brian, 1959, Mineralogy: San Francisco , W.H. Freeman and Co., p. 426-430.

Bostrom, K., Frazer, J., and Blankenburg, J., 1968, Subsolidus phase relations and lattice constants in the system $BaSO_4$-$SrSO_4$-$PbSO_4$: Arkiv Mineralogi och Geologi, v. 4, p. 477-485.

Brobst, D.A., 1958, Barite resources of the United States: Geol. Surv. Bull., 1072-B, p. 67-130.

Brower, H.E. and Bhappu, R.B., 1969, Recovery of barium and strontium from Mountain Pass tailings: unpublished report to Molybdenum Corp. of America by New Mexico Bureau of Mines and Mineral Resources, 18 p.

Brower, K.R., Peslak, John Jr., and Elrod, James, 1969, A correlation of molecular flexibility with volume and heat of mixing of organic solutes with water and glycol-water mixture: J. Phys. Chem., v. 73, p. 207-211.

Buckley, H.E., 1951, Crystal growth: New York, John Wiley and Sons Inc., p. 1-104.

Cohen, A.I., and Gordon, Louis, 1961, Co-precipitation in some binary sulphate systems: Talanta, v. 7, p. 195-211.

Czamanske, G.K., 1959, Sulfide solubility in aqueous solution: Econ. Geol., v. 54, p. 57-63.

Deer, W.A., Howie, R.A., and Zussman, J., 1962, Rock-forming minerals, v. 5, Non-silicates: New York, John Wiley and Sons Inc., p. 186-201.

Emmons. W.H., 1940, Principles of economic geology; 2nd edition: New York, McGraw Hill, p. 507-508.

Garrels, R.M. and Christ, C.L., 1965, Solutions, minerals, and equilibria: New York, Harper and Row, 450 p.

Gordon, Louis, Reimer, C.C., Burtt, B.P., 1954, Distribution of strontium with barium sulfate precipitated from homogeneous solution: Anal. Chem., v. 26, p. 842-846.

Grawe, O.R. and Nackowski, M.P., 1949, Strontianite and witherite associated with Southern Illinois fluorite: Science, v. 110, p. 331.

Hanor, J.S., 1968, Barite saturation in sea water: Geochim. Cosmochim. Acta, v. 33, p. 894-898.

Hanor, J.S., 1968, Frequency distribution of compositions in the barite-celestite series: Am. Mineral., v. 53, p. 1215-1222.

Hanor, J.S., 1966, The origin of barite, Ph.D. Thesis, Harvard University, Cambridge, Mass., 257 p.

Harness, C.L., 1949, Strontium minerals, in Mudd, S.W. (ed.), Industrial minerals and rocks: Amer. Inst. Met. Eng., 2nd edition, p. 980-988.

Helgeson, H.C., 1969, Thermodynamics of hydrothermal systems at elevated temperatures and pressures: Am. J. Sci., v. 267, p. 729-801.

Helz, G.R. and Holland, H.D., 1965, The solubility and geologic occurence of strontianite: Geochim. Cosmochim, Acta, v. 29, p. 1303-1315.

Heyl, A.V., 1968, Minor epigenetic, diagenetic, and syngenetic sulfide, fluorite, and barite occurences in the central United States: Econ. Geol., v. 63, p. 585-594.

Hildebrand, J.H. and Scott, R.L., 1950, The solubility of non-electrolytes: New York, Dover Publications Inc., 488 p.

Hogness, T.R. and Johnson, W.C., 1954, Ionic equilibrium as applied to qualitative analysis, 3rd edition: New York, Holt, Rinehart, and Winston, 381 p.

Holland, H.D., 1967, Gangue minerals in hydrothermal deposits, in Barnes, H.L. (ed.), Geochemistry of hydrothermal ore deposits: New York, Holt, Rinehart, and Winston, Inc., p. 382-436.

Horn, M.K. and Adams, J.A., 1966, Computer-derived geochemical balances and element abundances: Geochim. Cosmochim. Acta, v. 30, p. 279-297.

Kohman, G.T., 1963, Precipitation of crystals from solution, in Gilman, J.J. (ed.), The art and science of growing crystals: New York, John Wiley and Sons Inc., p. 152-162.

Kramer, J.R., 1965, History of sea water: Geochim. Cosmochim. Acta, v. 29, p. 921-945.

Kraus, E.H., 1905, Occurence and distribution of celestite-bearing rocks: Am. J. Sci., v. 19, p. 286-293.

Latimer, W.M., 1952, The oxidation states of the elements and their potentials in aqueous solutions, 2nd edition: New York, Prentice-Hall Inc., 392 p.

Ludd, M.F.C. and Lee, W.H., 1961, Lattice energies and associated thermodynamic properties of some crystalline sulphates and of silver selenate: J. Inorg. Nucl. Chem., v. 21, p. 216-220.

Mason, Brian, 1966, Principles of geochemistry: New York, John Wiley and Sons Inc., p. 45-46.

Mosebach, R. and Strubel, G., 1962, Landolt-Bornstein part 2, section b, 3-326 and 3-327; Losungsgleichgewichte I.

O'Hara, W.F., Wu, Ching-Hsien, and Helper, L.G., 1961, Temperature and power measurement in precision solution calorimetry: J. Chem. Educ., v. 38, p. 512-515.

Palache, C.H., Berman, H., and Frondel, C., 1951, Dana's system of mineralogy, 7th edition, v. 2: New York, John Wiley and Sons, p. 407-420.

Rankama, Kalervo, and Sahama, Th.G., 1950, Geochemistry: Chicago, Ill., The University of Chicago Press, p. 457-484.

Renault, Jacques and Brower, Elise, 1971, X-ray line broadening in the barium sulfate-strontium sulfate series: Am. Mineral., in press.

Roedder, Edwin, Heyl, A.V., and Creel, J.P., 1968, Environment of ore deposition at the Mex.-Tex. deposits, Hansonberg district, New Mexico, from studies of fluid inclusions: Econ. Geol., v. 63, p. 336-348.

Schraut, Joseph, 1951, Special mineral and rock collecting in the Rosiclare fluorite district of southeastern Illinois: Rocks and Minerals, v. 26, p. 375-377.

Seidell, Atherton, 1940, Solubilities of Inorganic and metal organic compounds; 3rd edition, v.1, New York, D. Van Nostrand Co., 1698 p.

Shawe, D.R., Poole, F.G., and Brobst, D.A., 1969, Newly discovered bedded barite deposits in East Northumberland Canyon, Nye County, Nevada: Econ. Geol., v. 64, p. 245-254.

Starke, R., 1962, Die Strontiumgehalte der Baryte; Freiberger Forschungshefte. C 150. 85 p.

Steinbach, O.F. and King, C.V., 1950, Experiments in physical chemistry: New York, American Book Co., p. 147-150.

Stewart, F.H., 1963, Marine evaporites, Chapt. Y, Data of geochemistry, 6th edition, Geol. Surv. Prof. Paper, 440-Y.

Turekian, K.K. and Johnson, D.G., 1966, The barium distribution in seawater: Geochim. Cosmochim. Acta, v. 30, p. 1153-1174.

This thesis is accepted on behalf of the faculty of the Institute by the following committee:

Gale K. Billings

Richard B. Hallett

Kent C. Condie

Date May 13, 1971