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FREQUENCY DISTRIBUTION OF COMPOSITIONS IN THE BARITE-CELESTITE SERIES

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ABSTRACT

Complete solid solution exists between $BaSO_4$ and $SrSO_4$, but intermediate compositions are rare in nature. During precipitation from aqueous solution, $(Ba,Sr)SO_4$ does not re-equilibrate in response to changes in the composition of the parent liquid. Frequency distributions of compositions calculated for precipitation models that assume this inert behavior, complete solid solution, and a wide range of initial liquid compositions agree closely with the observed frequency distribution of barite-celestite compositions. Inert behavior results in a geochemical separation of Ba and Sr and can account for the paucity of intermediate sulfate compositions.

INTRODUCTION

Experimental work has demonstrated that complete solid solution exists between $BaSO_4$ and $SrSO_4$ (Grahman, 1920; Starke, 1964; Boström *et al.*, 1967). It has been recognized for some time, however, that natural occurrences of $(Ba, Sr)SO_4$ of intermediate composition are rare (*e.g.*, Palache *et al.*, 1951, p. 407). Analyses show most barite contains only a few mole percent $SrSO_4$ and most celestite only a few mole percent $BaSO_4$ (Starke, 1964; Hintze, 1921; and Miropolski, 1943).

In this paper, it will be shown that the tendency for $(Ba,Sr)SO_4$ to behave as an inert or unreactive precipitate can account for the bimodal distribution of compositions in the barite-celestite series. Distributions calculated from precipitation models which assume inert behavior will be compared with the observed distribution of compositions. An analytical study of regional and local variations in barite composition will be presented in another paper.

BARITE-CELESTITE ANALYSES

Starke (1964) compiled 2293 analyses of barite from various epigenetic vein deposits and diagenetic and submarine hydrothermal occurrences. Fewer analyses of celestite have been published. The 77 analyses used here are from Hintze (1929) and Miropolski (1941). Although the barite and celestite analyses are of material from all over the world, quite obviously not all occurrences have been sampled to the same extent. Further, some of the barite and celestite analyses are of composite samples, others are of small portions of single crystals or aggregates. It seems reasonable, however, that the analyses as a group represent an ap-

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proximation, at least in form, of the actual distribution of compositions which exists in nature. Although barite is probably somewhat more common than celestite, their relative abundance is difficult to evaluate quantitatively. To facilitate comparison between the two sets of analyses, the number of barite and celestite analyses have been normalized so that each set of data represents 50 percent of the total. The analyses have been recalculated so that mole fraction $SrSO_4$ plus mole fraction $BaSO_4$ equals one.

The frequency distribution of observed barite-celestite compositions is shown by the histogram in Figure 2. As may be seen most of the barite contains less than 7 mole percent $SrSO_4$. The average composition range for celestite appears to be more limited. Most of the celestite contains less than 4 mole percent $BaSO_4$. Although compositions intermediate to these values are represented, they are relatively uncommon.

Precipitation of $(Ba,Sr)SO_4$

Nearly all barite and celestite appear to have been precipitated directly from aqueous solution. The distribution of Ba and Sr between a homogeneous aqueous solution and an infinitesmal amount of sulfate precipitated in equilibrium with the solution may be described by the relation:

$$\frac{Sr_f}{Ba_f} = \lambda \frac{N_{SrSO_4}}{N_{BaSO_4}} \qquad 1)$$

where λ is a partition coefficient, N is mole fraction in the solid, and the subscript f denotes final molal concentration of the species in aqueous solution.

Experimental work (Gordon *et al.*, 1954; Cohen and Gordon, 1961; and Starke, 1964) has shown that during precipitation of $(Ba,Sr)SO_4$ from homogeneous aqueous solution, Ba is preferentially partitioned over Sr into the sulfate phase. Precipitation of $(Ba,Sr)SO_4$ therefore tends to remove Ba from aqueous solution at a faster rate than it removes Sr. If the reservior of Ba plus Sr in the liquid is finite, both the aqueous phase and coexisting sulfate will become progressively enriched in Sr relative to Ba as precipitation proceeds.

Further laboratory study (Gordon *et al.*, 1954; Cohen and Gordon, 1961) has shown that $(Ba,Sr)SO_4$ is generally unreactive. During precipitation, the solid does not reequilibrate in response to changes in the composition of the liquid, and chemical equilibrium is maintained only between liquid and last-formed increment of precipitate, rather than between liquid and total precipitate. It can thus be shown that the parti-

tion coefficient, λ, will tend to obey the logarithmic distribution law, or Doerner-Hoskins relation (Doerner and Hoskins, 1925; McIntire, 1963; Holland *et al.*, 1963):

$$(Ba_i/Ba_f) = (Sr_i/Sr_f)^{\lambda} \qquad 2)$$

where the subscripts i and f denote the initial and final concentrations of the species in aqueous solution. Equation (1) thus represents equilibrium between liquid and last-formed increment of sulfate rather than equilibrium between liquid and total precipitate.

Significant compositional variations over small distances in barite crystals and aggregates are common (Starke, 1964; Hanor, 1966). Apparently barite is unreactive in terms of Ba-Sr exchange in most sedimentary and hydrothermal environments. Therefore, relation (2) is reasonable for the precipitation of natural Ba-Sr sulfates.

According to equations (1) and (2) the inertness of $(Ba,Sr)SO_4$ has a significant influence on composition during precipitation. As we shall see later in the discussion, it is useful to relate solid composition to the fraction of Ba plus Sr removed from aqueous solution.

From (2), and assuming λ constant,

$$Sr_f/Ba_f = [(Sr_i)^{\lambda}(Sr_f)^{1-\lambda}]/(Ba_i) \qquad 3)$$

From relations (1) and (3), the mole ratio of $SrSO_4$ to $BaSO_4$ in the final increment of mineral precipitated is:

$$N_{SrSO_4}/N_{BaSO_4} = [(Sr_i)^{\lambda}(Sr_f)^{1-\lambda}]/\lambda(Ba_i) \qquad 4)$$

The quantity (Sr_f) is related to the fraction of Ba plus Sr which has been precipitated out, Q, by the expression

$$Q = 1 - \frac{Ba_f + Sr_f}{Ba_i + Sr_i}$$

or

$$Q = 1 - \frac{[(Ba_i)/(Sr_i)^{\lambda}](Sr_f)^{\lambda} + (Sr_f)}{Ba_i + Sr_i} \qquad 5)$$

Relations (4) and (5) are complicated by the fact that at a given temperature and pressure, λ is not constant, but tends to increase with increasing N_{SrSO_4}. A recalculation of Starke's (1964) partitioning data for Ba-Sr sulfates (Hanor, 1966) indicates that $(Ba,Sr)SO_4$ behaves as a non-ideal, regular solid solution, and that λ is related to the composition of the solid by an equation of the form

$$\lambda = (K_{ex}) \exp\left(\frac{B}{RT} - \frac{2B}{RT} N_{SrSO_4}\right) \qquad 6)$$

where K_{ex} is the thermodynamic equilibrium constant for the reaction

$$SrSO_4 + Ba^{2+} = BaSO_4 + Sr^{2+}$$

and B is a constant (see Garrels and Christ, 1965, p. 44).

In the model calculations which follow, the difficulties arising from non-ideality of the solid solution will be avoided by assuming an average, constant value for λ, to cover the temperature and composition ranges of interest.

In practice, the composition of last-formed increment of sulfate can be related to the fraction of Ba plus Sr precipitated by assuming that small, homogeneous increments of $(Ba,Sr)SO_4$ are successively removed from the liquid and by calculating the resultant succession of coexisting liquid and solid compositions. If the increments are made small enough, a very satisfactory approximation to the continuous function can be obtained.

Model Calculations

To test the effect of inert behavior on the frequency distribution of sulfate compositions, a series of model calculations were made. The models were deliberately kept simple to ascertain the general applicability of the precipitation mechanism. It would be desirable, of course, to constuct a less simple but more real model. A major difficulty here, however, is the lack of information regarding the distribution of Ba and Sr in natural waters, particularly those waters involved in the formation of epigenetic mineral deposits. The purpose of the model calculations is not to reconstruct the average environment of barite-celestite deposition, but to show that barite-celestite compositions as a whole can be explained as a simple consequence of inert behavior.

An Olivetti-Underwood Programma 101 was programmed to compute the composition of sulfate increments as a function of the mole fraction of Ba plus Sr precipitated out, assuming values for Ba_i, Sr_i, and λ. Results of calculations for a series of different initial liquid compositions and a constant λ are shown by the curves in Figure 1. From such curves, model frequency distributions of compositions are calculated.

Model I. In Model I, it was assumed that all initial aqueous solution compositions between $Ba_{90}Sr_{10}$ and $Ba_{10}Sr_{90}$ occur with equal frequency. It was furthermore assumed that all of the waters initially contained the same number of moles of Ba plus Sr and that all of the Ba and Sr was

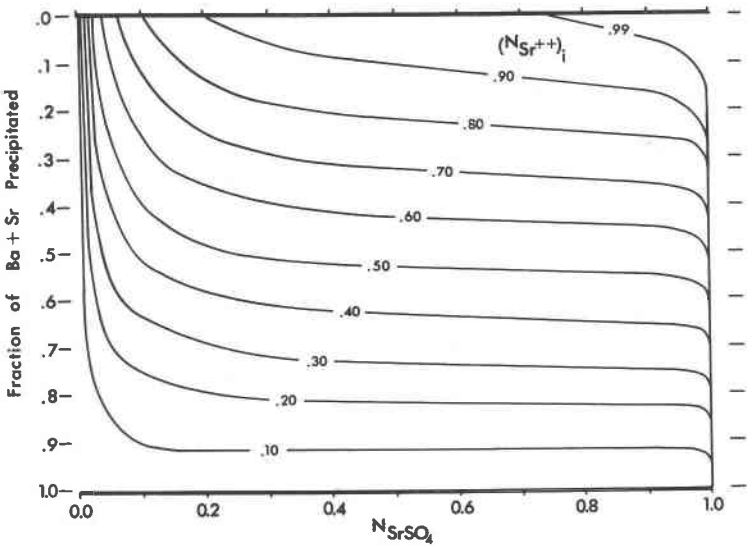

FIG. 1. Composition of the last-formed increment of $(Ba,Sr)SO_4$ as a function of the mole fraction of Ba plus Sr precipitated, for a series of initial aqueous solution compositions. The calculations assume inert behavior of the precipitate and $\lambda=33$. The solid and liquid compositions are expressed as mole fractions, where N_{Sr} plus N_{Ba} equals one.

eventually precipitated out by the addition of sulfate or removal of H_2O. A value of $\lambda=33$ was used. This represents an average value for temperatures between 20° and 80°C and the complete range of solid solution composition (Starke, 1964). Experimental work (Cohen and Gordon, 1961; Starke, 1964) has shown that variations in temperature, rate of precipitation, and bulk aqueous solution composition can affect the value of λ. In natural systems, λ may deviate from the value chosen here by up to a factor of two. Any value of λ within this range, however, will give results very similar to those obtained here.

Model II. Model II is similar to Model I with the exception that it was assumed that initial aqueous solution compositions between $Ba_{70}Sr_{20}$ and $Ba_{60}Sr_{40}$ are twice as frequent as the other initial compositions. This model was constructed to show the effect of having a somewhat different distribution of inital water compositions.

RESULTS

Results of the model calculations are shown in Figures 2 and 3. Figure 2 shows the frequency distribution of $(Ba,Sr)SO_4$ compositions, assuming conditions of Model I. It can be seen that even with a uniform

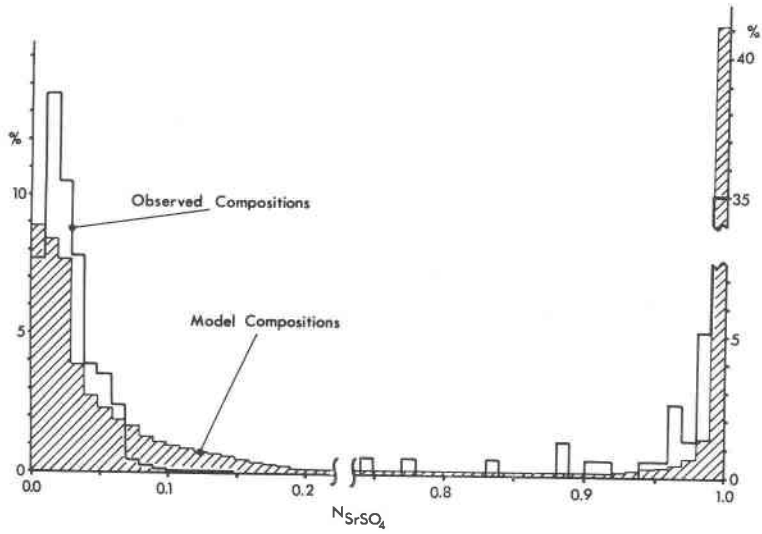

FIG. 2. Comparison of the frequency distribution of observed barite-celestite compositions (normalized) and the frequency distribution of Model I compositions. Note that there are breaks in the vertical and horizontal axes.

distribution of initial liquid compositions and complete solid solution, the sulfates precipitated under model conditions tend to be either Sr-rich or Ba-rich. Only about 15 mole percent of the model sulfates have compositions between $Ba_{90}Sr_{10}$ and $Ba_{10}Sr_{90}$. In general form, the frequency distribution of model compositions closely resembles that of observed compositions, even to celesite having a somewhat more restricted average composition range than barite. If the Model I calculations had assumed that the entire precipitate continuously reequilibrates with the parent liquid, then, instead of a bimodal distribution, all model sulfate compositions would be limited to the range $Ba_{90}Sr_{10}$ to $Ba_{10}Sr_{90}$ and would occur with equal frequency.

Figure 3 shows a more detailed comparison between observed barite compositions and Model I and Model II compositions, normalized to represent 2293 analyses each. Model I, and particularly Model II correspond fairly closely to the observed frequency distribution of barite compositions. Similar model distributions can be obtained by suitably varying at the same time λ and the frequency distribution of initial water compositions. The similarity in form between observed and model distributions strongly suggests that on a grand scale, barite-celestite compositions are controlled by precipitation of an unreactive phase.

If the non-ideality of the solid solution were taken into account in the

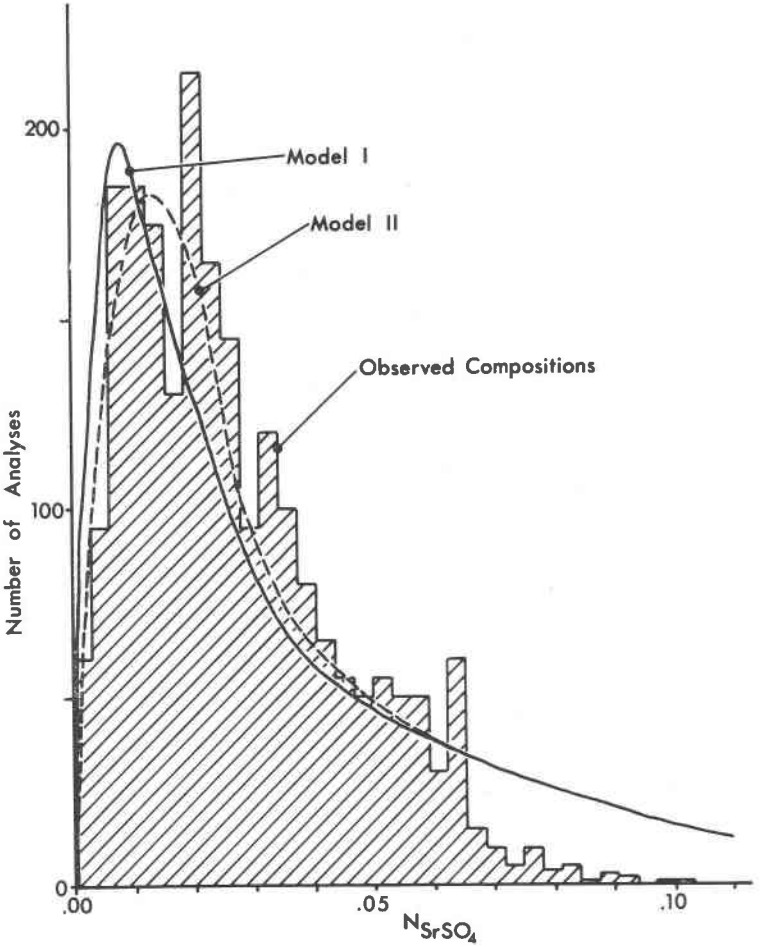

FIG. 3. Comparison of Model I and Model II compositions and 2293 barite analyses compiled by Starke (1964).

model calculations, λ would increase with increasing N_{SrSO_4}, and the model curves shown in Figure 3 tend to drop off more quickly in the direction of increasing $SrSO_4$.

CONCLUSIONS

1. Laboratory studies and analyses of natural material indicate that $(Ba,Sr)SO_4$ is an inert phase in terms of Ba-Sr exchange.

2. The correspondence between the frequency distribution of observed barite-celestite compositions and calculated model compositions

shows that inert behavior can account for the paucity of intermediate compositions in the barite-celestite series.

3. Despite complete solid solution between $BaSO_4$ and $SrSO_4$, inert precipitation results in a geochemical separation of Ba and Sr and produces a bimodal distribution of solid compositions, simulating immiscibility.

4. In the absence of more complex phase relations, a similar control of composition is expected in other natural solid solutions which behave inertly. In general, the frequency of intermediate compositions will decrease as λ deviates from unity.

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