LARGE-SCALE BACTERIOGENIC
FRACTIONATION OF SULPHUR ISOTOPES†

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INTRODUCTION

The economic geologist is principally interested in the genesis of mineral deposits which entails essentially a study of the processes by which specific minerals are concentrated in certain locales. Many of the base metal deposits, for example, consist of these specific metals in the form of sulphides. If evidence can be obtained that indicate the source of the sulphur in sulphide minerals, this evidence may aid in determining the processes by which certain base metal deposits have formed.

The possibility of determining, with the aid of sulphur isotopes, whether sulphur has been derived from an inorganic source or from a biogenic source has provided some hope that more diagnostic evidence might be provided to better determine which of two vastly different processes has resulted in the formation of certain mineral deposits.

It has become evident, not only from the thousands of sulphur isotopic measurements made, but also from theoretical considerations, that sulphur of biogenic origin exhibits a much greater spread in $\delta^{34}S$ values than does sulphur of inorganic origin. The greater fractionation of sulphur isotopes by biogenic processes results from oxidation–reduction mechanisms, whereby, for example, sulphate ($SO_4^{2-}$) is reduced to sulphide ($S^{2-}$) by sulphate-reducing anaerobes. This is a resulting change in valence of the sulphur from $+6$ to $-2$ respectively, a significant energy change. The sole process by which this reduction occurs in nature at temperatures of several hundred degrees C and less is by sulphate-reducing bacteria.

Beijerinck gave the name of Spirillum desulphuricans to the first fresh-water sulphate-reducing anaerobes that he managed to isolate. Van Delden managed to obtain a pure culture of sulphate reducers active in salt water, to which species he gave the name of Sp. estuarii. The generic name of sulphate reducers has at various times been Spirillum, Microspirra, Sporovibrio,

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$$\delta^{34}S_{\%o} = \frac{^{34}S/^{32}S (\text{standard}) - 1}{^{32}S/^{32}S (\text{sample})} \times 1000$$

The "standard" used by sulphur isotope investigators is troilite from the Cañon Diablo meteorite which is assumed to have a $^{34}S/^{32}S$ value of 22.220.
DISCUSSION OF RESULTS

Magmatic hydrothermal deposits

In order to emphasize the differences in $\delta^{34}$S compositions and extent of variations from the average value, graphical representations of the $\delta^{34}$S values of sulphide minerals from several magmatic hydrothermal deposits are shown in comparison to the same information obtained from several sandstone-type uranium deposits and "red beds" copper deposits. This information is shown on Figure 1 where the $\delta^{34}$S and $^{32}$S/$^{34}$S composition of

<table>
<thead>
<tr>
<th>BIOTHEMATIC DEPOSITS</th>
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<tbody>
<tr>
<td>RED-BEDS COPPER DEPOSITS:</td>
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<tr>
<td>Dorchester Mine, N.B.</td>
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<tr>
<td>Happy Jack Mine, Utah</td>
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<tr>
<th>SANDSTONE-TYPE URANIUM DEPOSITS:</th>
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</thead>
<tbody>
<tr>
<td>Woodrow Mine, N.M.</td>
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<tr>
<td>Mi Vida Mine, Utah</td>
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<tr>
<td>Jackpile Mine, New Mexico</td>
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<tr>
<td>Schwartzwalder (Supergene)</td>
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<tr>
<td>(Hypogene)</td>
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</tbody>
</table>

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<tr>
<th>MAGMATIC HYDROTHERMAL DEPOSITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marysvale, Utah</td>
</tr>
<tr>
<td>Central City, Colo.</td>
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<tr>
<td>Tintic Dist., Utah</td>
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<tr>
<td>Butte, Montana</td>
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<table>
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<tr>
<th>Buchans, Nfld.</th>
<th>$^{34}$S</th>
<th>$^{32}$S/$^{34}$S</th>
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<tbody>
<tr>
<td>45.5</td>
<td>0.40</td>
<td>0.60</td>
</tr>
<tr>
<td>36.5</td>
<td>0.80</td>
<td>2.02</td>
</tr>
<tr>
<td>27.5</td>
<td>0.20</td>
<td>0.40</td>
</tr>
<tr>
<td>18.5</td>
<td>0.20</td>
<td>0.60</td>
</tr>
<tr>
<td>9.5</td>
<td>0.80</td>
<td>23.00</td>
</tr>
</tbody>
</table>

Figure 1. $\delta^{34}$S values of organic and inorganic sulphur-bearing mineral deposits

each analysis is plotted along the abscissa as a short vertical line opposite the deposit from which the sulphide specimen was collected and, of course, at the appropriate isotopic compositional value. If more than one specimen has the same composition, the length of the vertical line is doubled, for three identical analyses it is tripled in length, and so on for additional identical $\delta^{34}$S values.

Even though only seven sulphide samples were analysed from the Buchan’s Newfoundland, Canada, deposit, all are closely grouped together. With

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more than three times as many sulphides isotopically analysed from all three vein systems of the Butte, Montana, district, the spread in values is only slightly greater than the Buchan’s spread.

The results of almost 100 isotopic analyses of sulphides from the Tintic district, Juab County, Utah, exhibit the characteristic closely grouped δ²⁴S values for sulphates of magmatic hydrothermal origin—sulphides intimately related to the intrusive bodies from which it is inferred the isotopically homogenized, sulphur bearing, mineralizing solutions were derived.

The Tintic samples were collected from numerous mines over a distance of more than 7 miles. Yet there is little difference in the δ²⁴S values, which indicates the lack of extensive fractionation of sulphur isotopes by diffusion or differential mobility (of ³²S and ³⁴S) during migration of the sulphur-bearing solutions.

Isotopic analyses of sulphides from Central City, Colorado, and from Marysvale, Utah, are included because of the presence of uranium in both districts, in order to contrast with the δ²⁴S compositions of the sandstone-type uranium deposits (Figure 1). Marysvale is located on the western edge of the Colorado Plateau and Central City near the eastern edge of the Plateau. Each is intimately associated with the intrusive stock from which the magmatic hydrothermal solutions are inferred to have been derived, and each exhibits a relatively narrow spread in δ²⁴S compositions.

Biogenic deposits

In contrast, however, the δ²⁴S compositions of sulphides from several typical sandstone-type uranium deposits and two representative “red beds” copper deposits exhibit two distinct differences from the magmatic hydrothermal deposits†. The first and most important difference is the much greater spread in δ²⁴S values compared to the magmatic hydrothermal deposits. The second difference is the enrichment in the lighter isotope, i.e. ³²S (with the exception of the Woodrow deposit, the results of which are believed to be caused by a limited sulphate supply). Fortunately, the cause of both of these features is believed to be understood; it is the result of the variable enrichment of ³²S in the hydrogen sulphide produced during the reduction of sulphate by sulphate-reducing bacteria. Reduction of sulphate to hydrogen sulphide results in an enrichment of ³²S in the hydrogen sulphide produced. The method by which this reduction occurs in nature, at normal earth surface temperatures, is through the rôle of anaerobic bacteria.

The importance of sulphate-reducing bacteria in producing hydrogen sulphide is indicated by their wide distribution in streams, swamps, lakes, soil, sulphate connate waters, and oil at depths of several kilometres, and not only along the extensive shelf areas of the oceans but even in the ocean depths. In fact, they have been recovered from the bottom of the Philippine Trench. And neither the great pressure at that depth nor its release by

† The δ²⁴S analyses of the Schwartzwalder samples originally suggested a biogenic origin until it was noticed that the sulphur enriched in δ²⁴S were all from one vein in which oxidation had occurred and these sulphides were all marcasite. Apparently, anaerobes existed in the supergene zone and generated hydrogen sulphide that formed the secondary sulphides. The isotopic distinction between the hypogene and supergene sulphides, therefore, is indicated in Figure 1.

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bringing the anaerobes to the surface affects the viability of these barophilic bacteria. The sulphur in sour crude oils, in syngenetic sulphides, in marsh gases, and the organic sulphur in coal, oil, and organisms is derived from biogenically produced hydrogen sulphide.

**Laboratory raw culture experiments**

In addition to the isotopic evidence obtained from the study of sandstone-type uranium deposits, "red beds" copper deposits, and syngenetic sulphides\(^7-^9\), all of which indicate the spread in \(\delta^{34}\)S values of even juxtaposed sulphides which is caused by the variable enrichment in the lighter isotope, corroborative isotopic data have also been obtained from raw culture experiments with anaerobic bacteria of the *Desulfocibrio* genus in the laboratory\(^10\). We have been endeavouring, by collecting the gas produced by the anaerobes from raw culture cells, to determine what factors have a bearing on the yield and extent of isotopic fractionation of hydrogen sulphide. Through these studies it is apparent that the metabolic behaviour of the anaerobes can be varied considerably by different factors.

In one of these studies 80 g (wet weight) of the mud and 450 ml of the sea water, both from Long Island Sound, Connecticut, with no nutrient, were used in order to closely approximate isotopic behaviour as it occurs in nature. The results of one experiment are shown in *Figure 2*. In this experi-

![Graph](image)

*Figure 2. Bacterial reduction of sea-water sulphate and resulting isotopic fractionation*

ment, however, only sulphate was collected for isotopic analyses because the hydrogen sulphide yields were too low for sufficient samples to be collected. Furthermore, as sea water was removed from the cylinder for sulphate analyses at proper intervals, the ratio of sea water to mud gradually changed, nevertheless, hydrogen sulphide enriched in \(^{32}\)S must have formed because the sulphate \(\delta^{34}\)S isotopic composition changed from +20.2 to +27.7 per mil. It is believed that most of the hydrogen sulphide produced
reacted with iron in the mud to form ferrous sulphide according to the reaction, Fe₂O₃ + 4H₂S → 2FeS₂ + H₂ + 3H₂O.

In order to produce enough hydrogen sulphide to be precipitated for isotopic analysis, a second cell was prepared containing 80 g of (wet) mud from Long Island Sound which was placed in a glass cylinder and covered with 450 ml of sea-water. The sea-water initially contained 725·0 mg of sulphur (in the form of sulphate) per litre of sea water and had a δ³⁴S composition of +20·2 per mil. The hydrogen sulphide that escaped from the mud and water was bubbled through a solution of cadmium acetate, and the sulphur was precipitated as cadmium sulphide. In order to increase the rate of reduction, 2 ml of 60 per cent sodium lactate solution was added to the culture as an energy source; the anaerobes in the mud then produced hydrogen sulphide so rapidly that the concentration of sulphate in the sea-water decreased from 725 mg to 62·5 mg of sulphur per litre in 5 days, and the δ³⁴S composition of the remaining sulphate changed from +20·2 to +35·0 per mil because of evolution of hydrogen sulphide enriched in ³²S. The hydrogen sulphide produced was enriched to a variable extent in ³²S, as shown by Figure 3, which varies between about 4 to 16 per mil.

![Figure 3](image)

**Figure 3.** Bacterial reduction of sea-water sulphate with nutrient added and resulting isotopic composition

The actual amount of hydrogen sulphide that was collected, however, was surprisingly low, but still enriched in ³²S. The dashed curve in Figure 3, labelled S²⁻, shows the actual amount of sulphur that must have been produced by the anaerobes since this quantity must be equal to the amount by which the sulphate was reduced. Yet, as indicated by the curve labelled H₂S, only a very small amount of hydrogen sulphide escaped from the cell to be collected.

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Much of the hydrogen sulphide reacted so rapidly with ferric iron in the mud to form sulphide that it did not have an opportunity to escape! Proof of this inference is that the original content of sulphur as sulphide in the mud before the experiment was 0.51 mg/g of wet mud, which, following the experiment, had increased to 1.62 mg/g of wet mud. The change, moreover, in isotopic composition of sulphide in the mud from −9.8 to +3.6 per mil, respectively, is added proof that a significant quantity of sulphur with a $\delta^{34}S$ composition less than +3.6 per mil was added to the mud where it formed sulphides.

In order to collect a larger proportion of the hydrogen sulphide produced by bacterial reduction of sulphate, two raw culture cells containing only 1 g of mud were used, and both sulphate and the produced hydrogen sulphide were collected from the cells.

The data obtained from these experiments are shown in Figure 4. Three days after beginning the experiments, the hydrogen sulphide production rate increased ten-fold during a period of a few hours, and the $\delta^{34}S$ compositions changed from +4.5 to +17.4 per mil in one cell, and from +3.2 to +16.5 per mil in the other cell. After this peak, the production of hydrogen sulphide decreased just as rapidly, and the $\delta^{34}S$ compositions changed from +17.4 to +10.5 per mil and from +16.5 to +12.8 per mil. After ten days the production rate had increased again, but only about one-fifth as much as the initial rise and with an increase in $^{34}S$ content. Following this peak, the production rate decreased again and the isotopic
composition underwent an increase in $^{32}\text{S}$. As the production rate of hydrogen sulphide increased, the viability of the bacteria decreased, presumably because of the toxic effect of hydrogen sulphide on these bacteria. Thus, the curve for the production rate of hydrogen sulphide indicates alternating maxima and minima which correlate inversely with the changes in isotopic composition, i.e., increased production resulted in decreased isotopic fractionation, while low production resulted in greater isotopic fractionation. As both the reduction rate and the $\delta^{34}\text{S}$ composition of hydrogen sulphide indicate alternately maxima and minima, the remaining sulphate residue became enriched in $^{34}\text{S}$, and as a result, the hydrogen sulphide produced from this also became enriched in $^{34}\text{S}$.

Be this as it may, none of these laboratory raw culture experiments indicate the total $\delta^{34}\text{S}$ variation measured for some specific mineral deposits as, for example, the sulphides in sandstone-type uranium deposits, the results for which are shown on Figure 1. Furthermore, based on calculations for the partition function ratios of the isotopic exchange reaction, $\text{H}_2^{34}\text{S} + ^{32}\text{SO}_4^{2-} \rightleftharpoons \text{H}_2^{32}\text{S} + ^{34}\text{SO}_4^{2-}$, at $25^\circ$ under equilibrium conditions, $K_{25} = 1.073$, which means there should be an enrichment of $^{32}\text{S}$ in the hydrogen sulphide of 73 per mil. For a unidirectional reaction, the hydrogen sulphide should be enriched in $^{32}\text{S}$ by 88 per mil.

In the latest work, by Nakai, several culture flasks were used in order to have one entire flask for each of the analyses at specific times. In addition, 65 g of wet mud and 30 ml of sea-water were used in each cell. The results obtained from these experiments are shown in Figure 5. During a period of 65 days, the sulphate in the sea-water decreased continuously, as shown in

![Figure 5. Biochemical reduction of sulphate to sulphide](image-url)
Figure 5, from an average rate of 30·4 to 8·8 mg of S/flask, or at about 0·3 mg of S/day, while the $\delta^{34}S$ values varied from $+30·7$ to $+56·6$ per mil. The produced sulphide, however, increased from 46·9 to 66·2 mg of S/flask, during which time the $\delta^{34}S$ value changed from $-12·0$ to $-5·3$ per mil.

The original sulphate in this experiment (sulphate in sea-water + sulphate in interstitial water of the mud) had an isotopic composition of $+30·7$ per mil, although the sea-water sulphate used had a $\delta^{34}S$ value of $+20·5$ per mil. This suggests, presumably, that the sulphate in the interstitial water of the mud had been undergoing bacterial reduction while the mud samples had been stored in the laboratory.

The fractionation factors between sulphate and sulphide obtained from these experiments are plotted on Figure 6. The fractionation factor appears to increase the longer the experiment lasted—in fact, from 1·043 to 1·062.

![Figure 6. Variation of isotopic fractionation between SO$_4^{2-}$ and S$_2^-$.](image)

From the fractionation factors observed from the experiments and calculated from isotopic exchange equilibrium, it seems that the fractionation factors in the experiments approach the theoretical values by allowing greater reaction time. In order to attempt to analyse the mechanism of the isotopic fractionation in the processes of biochemical reduction, a further examination of the results obtained should be made.

If the reduction reaction is assumed to be a first-order reaction, the quantitative relation of reactant and product may be indicated by the following equation:

\[
\ln \frac{[SO_4^{2-}]}{[SO_4^{2-}] - [S^{2-}]} = kt
\]  

(1)
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\[ [\text{SO}_4^{2-}] = \text{initial concentration of sulphate (mg of S/flask)} \]

\[ [\text{S}^{2-}] = \text{amount of the sulphide produced in time } t \text{ (mg of S/flask)} \]

\[ t = \text{time (days)} \]

\[ k = \text{rate constant} \]

Furthermore, \([\text{SO}_4^{2-}] - [\text{S}^{2-}] = [\text{SO}_4^{2-}]\), where \([\text{SO}_4^{2-}]\) is the concentration of the remaining sulphate at time \(t\).

Therefore,

\[
\ln \left( \frac{[\text{SO}_4^{2-}]}{[\text{SO}_4^{2-}]} \right) = kt \tag{2}
\]

From the ratios of \([\text{SO}_4^{2-}]/[\text{SO}_4^{2-}]\) observed, rate constants \(k\), can be calculated by equation (2), resulting in the following:

Rate constants calculated by observed values

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
<th>(D)</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(t \text{ (days)})</td>
<td>7</td>
<td>14</td>
<td>44</td>
<td>47</td>
<td>65</td>
</tr>
<tr>
<td>(k \text{ at } 32^\circ)</td>
<td>(1.909 \times 10^{-2})</td>
<td>(1.929 \times 10^{-2})</td>
<td>(2.395 \times 10^{-2})</td>
<td>(2.262 \times 10^{-2})</td>
<td>(1.907 \times 10^{-2})</td>
</tr>
</tbody>
</table>

The \(k\) values are reasonably constant throughout the reduction experiment. Since \(k\) is constant in equations (1) and (2), it is suggested that the reduction reaction of sulphate to sulphide is evidently of the first order and the average rate constant at \(32^\circ\) in this experiment is \(2.08 \times 10^{-2}\).

The kinetic isotopic effect in the chemical reduction (unidirectional reaction) of sulphate to sulphide was studied by Harrison and Thode12. They found that \(^{32}\text{SO}_4^{2-}\) reacts 2.2 per cent faster than \(^{34}\text{SO}_4^{2-}\), which is in agreement with the theoretical values calculated by statistical mechanics. They calculated the two extreme limits of the ratio of rate constants by assuming two activated complexes. They assumed that one of the activated complexes is identical with the reactant, sulphate, and one with sulphite. In the former case, the ratio was calculated to be 1.010, and in the latter case the ratio was calculated to be 1.035, both at \(25^\circ\). As the isotopic fractionation obtained by their chemical reduction experiments was almost intermediate between the two values theoretically calculated as the two extreme limits, they postulated a two-step, rate-controlling process for the bacteriogenic reduction of sulphate.

As the reactions in the raw cultures of this work are believed to be of the first order, the reduction of sulphate to sulphide for the two isotopic species may be represented by the following equations:

\[ ^{32}\text{SO}_4^{2-} \xrightarrow{k_1} \text{H}_2^{32}\text{S} \tag{3} \]

\[ ^{34}\text{SO}_4^{2-} \xrightarrow{k_2} \text{H}_2^{34}\text{S} \tag{4} \]

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For these two equations, equation (2) can be applied separately, resulting in

\[ \ln \left( \frac{[32\text{SO}_4^{2-}]}{[32\text{SO}_4^{2-}]} \right) = k_1 t \]  
(5)

\[ \ln \left( \frac{[34\text{SO}_4^{2-}]}{[34\text{SO}_4^{2-}]} \right) = k_2 t \]  
(6)

Where \([32\text{SO}_4^{2-}]\) and \([34\text{SO}_4^{2-}]\) are the initial concentrations of \(32\text{SO}_4^{2-}\) and \(34\text{SO}_4^{2-}\) respectively, and \([32\text{SO}_4^{2-}]\) and \([34\text{SO}_4^{2-}]\) are the concentrations of \(32\text{SO}_4^{2-}\) and \(34\text{SO}_4^{2-}\) at time \(t\). From equations (5) and (6), the relationships between the isotopic ratios of \(\text{SO}_4^{2-}\) at time 0 and time \(t\) are given as:

\[ R_{\text{SO}_4^{2-}} = R_{\text{SO}_4^{2-}}^0 - F^{1-(k_2/k_1)} \]  
(7)

where \(R_{\text{SO}_4^{2-}}\) and \(R_{\text{SO}_4^{2-}}^0\) are the \(33\text{S}/34\text{S}\) ratios of sulphate at time \(t\) and time 0 respectively, and \(F\) is the ratio of the amount of residual sulphate at time \(t\) to initial sulphate at time 0, i.e., \([\text{SO}_4^{2-}]/[\text{SO}_4^{2-}]\). Using equation (7), \(k_1/k_2\) ratios can be calculated through the reduction process. During this experiment, the \(k_1/k_2\) ratios were rather constant and averaged about 1.020. It is suggested that the sulphur isotopes of sulphate are reduced unidirectionally to sulphide, and the lighter isotope reacts 2.0 per cent faster than the heavier isotope.

In the calculations above, the residual concentration amount was measured at time \(t\) and the initial concentration of the sulphate was measured at the beginning of the experiment (time 0); their \(\delta^{34}\text{S}\) values were used to examine the experimental results. If at the beginning of the reduction experiment, no sulphide is contained in the culture flask, the fractionation factors expected between sulphate and sulphide at certain times during the process of the reduction are given by using equations (5) and (6) as follows:

\[ r = \left( \frac{R'_{\text{S}^{2-}}}{R_{\text{SO}_4^{2-}}} \right) = \frac{F(k_2/k_1)-1}{1 - F} \]  
(8)

\(R'_{\text{S}^{2-}}\) and \(R_{\text{SO}_4^{2-}}\) = \(\delta^{34}\text{S}\) of produced sulphide and residual sulphate at time \(t\) respectively

\(F\) = the same as in equation (7)

\(k_1\) and \(k_2\) = the rate constants in the reduction reaction for light and heavy isotopes respectively

The fractionation factors \((r)\) expected from equation (8) are calculated with different \(F\) values. In this case, \(k_1/k_2 = 1.020\), which is an average constant value obtained from the fermentation experiments even though \(k_1/k_2\) is constant throughout the experiments.

In practice, however, both the sulphide and the sulphate existed originally in the mud used for the fermentation experiment, and at the beginning of the experiment additional sea-water was added to the mud. We cannot, therefore, apply equation (8) directly to this experiment. In order to obtain the correct equation to be used for this experiment, some correction factors
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must be introduced, and by converting equations (5) and (6), the following
equation is derived:

$$ r = \frac{R_{82^-}^{2-}}{R_{SO_4^{2-}}} = \frac{F(k_2/k_1)^{-1}(AB + 1) - F}{A + (1 - F)} \quad (9) $$

- $R_{82^-}$ = $\delta^{34}S$ of sulphide observed at time $t$, i.e., $\delta^{34}S$ value of the mixture of sulphides originally contained in the mud and produced in this fermentation experiment
- $R_{SO_4^{2-}}$ = $\delta^{34}S$ value of sulphate remaining at time $t$
- $k_1$ and $k_2$ = rate constants (the same as equations (7) and (8))
- $F$ = the same as equations (7) and (8)
- $A$ = ratio of sulphide to sulphate contents at the beginning of this experiment (time 0)
- $B$ = fractionation factor between sulphate and sulphide at time 0

Using $k_1/k_2 = 1.020$ as obtained in this experiment, the fractionation factor expected in different degrees of sulphate reduction can be calculated by equation (9). $A$ and $B$ in this equation are the values at time 0. The fractionation factors calculated by equation (9) are plotted on Figure 6 as is also the relationship between the fractionation factors expected and the degree of reduction.

As shown in Figure 6, the fractionation factor expected theoretically from the unidirectional reaction between residual sulphate and produced sulphide increases during the process of reduction. The values observed in the reduction experiment as plotted on Figure 6, approach the theoretical curve derived from equation (9). This indicates, therefore, that the bacterial reduction of sulphate is of the first order and is completely unidirectional, showing no isotopic exchange, because the $k_1/k_2$ ratios are constant throughout the reduction process. It is concluded, therefore, that in the case of a limited sulphate supply, the fractionation factor does exceed the value of 1.020 obtained for inorganic reduction of sulphate experiments.

CONCLUSION

These experimental results are, therefore, most helpful in understanding the very large variations found in $\delta^{34}S$ values in nature for many biogenic sulphide deposits, especially the results obtained from sandstone-type uranium deposits. It is not at all unusual, therefore, that $\delta^{34}S$ values in nature vary by considerable amounts.

References