DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

SULFUR AND CARBON ISOTOPES IN
PHOSPHORITES OF THE RETORT PHOSPHATIC SHALE MEMBER
OF THE PHOSPHORIA FORMATION, HAWLEY CREEK AREA, IDAHO

by
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Abstract

In carbonate-fluorapatite of the Retort Phosphatic Shale Member of the Permian Phosphoria Formation in the Hawley Creek area, east-central Idaho, $\text{SO}_4$ partially substitutes for $\text{PO}_4$ and $\text{Na}$ partially substitutes for $\text{Ca}$. The average composition of the apatite on the basis of the chemical analysis of 9 phosphorites is $(\text{Ca}^{9.69}\text{Na}^{0.31})[(\text{PO}_4)^{5.44}(\text{CO}_3)^{0.36}(\text{SO}_4)^{0.20}]^{F^{2.35}}$.

The phosphorites are characterized by heavy sulfur and light carbon isotope ratios ($\delta^{34}\text{S} = +18$ to $+27^\circ/oo$; $\delta^{13}\text{C} = -7$ to $-9^\circ/oo$) in comparison to Permian evaporites and carbonates. The isotopic characteristics are caused by bacterial reduction of sulfate in interstitial waters and the concomitant decomposition of organic matter in sediments; marine apatites are formed diagenetically in the organic-rich sediments under anoxic conditions.

The sulfate content and the sulfur isotope ratio ($\delta^{34}\text{S}$) are inversely related in phosphorites of the Phosphoria Formation. The phosphorites of the Meade Peak Phosphatic Shale Member of the Phosphoria Formation contain more sulfate and less $\delta^{34}\text{S}$ than the phosphorite of the Retort Phosphatic Shale Member. The sulfate content and the $\delta^{34}\text{S}$ value in phosphorites are related in part to the extent of the bacterial sulfate reduction in sediments. Greater bacterial activities promote the formation of phosphorites with less $\text{SO}_4$ and more $\delta^{34}\text{S}$. 
Introduction

Previously, apatite of marine phosphorites was thought to precipitate directly from nutrient-rich, upwelling waters onto the sea bottom. Modern opinion predominantly favors the belief that apatite diagenetically replaces carbonate fragments or nucleates and precipitates from interstitial waters within the organic-rich sediments and that phosphorus for apatite is supplied from the decomposition of organic matter in reducing environments (Baturin, 1972; Calvert, 1976; Price, 1976; Burnett, 1977; Manheim and Gulbrandsen, 1979). Evidence supporting the modern opinion includes the high concentration of dissolved phosphate in interstitial waters in the organic-rich shelf-sediments, up to 100 times higher than the bottom water (Bushinskii, 1966; Baturin, 1972), and the discoveries of phosphatized Recent foraminifera and contemporary formation of apatite within sediments in the inner shelves off Chile and Peru (Manheim and others, 1975; Burnett, 1977) and southwest Africa (Baturin, 1970; Parker and Siessen, 1972; Price and Calvert, 1978). The isotopic composition of sulfur and carbon in phosphorites can yield additional information on the environments and processes of phosphorite formation. However, only a few studies on sulfur and carbon isotopes of phosphorites have been made thus far.
Kolodny and Kaplan (1970) and Al-Bassam (1980) have shown that the lighter isotope of carbon is significantly enriched in apatite of phosphorites relative to marine carbonates and relative to coexisting calcite. Bliskovskiy and others (1977) have determined the sulfur isotope composition of apatite in 21 phosphorites from Precambrian to Recent ages and concluded that in general the sulfur isotope composition in many apatites is similar to that of contemporaneous evaporites and that weathering enriches the light sulfur isotope in some apatites. But, they have noted that Permian phosphorites from the Rocky Mountains, USA, and Seleuk, USSR, and Eocene phosphorite from Guliob, USSR, are unusually enriched in the heavy sulfur isotope. Nathan and Nielsen (1980) have determined the sulfur isotope ratio in phosphorites of Permian (Phosphoria Formation, USA), Campanian (Israel), Ypresian (Morocco), and Eocene (Tunisia) ages, and found that the apatites have $\delta^{34}$S values equal to or above the coeval sea water values in contrast to associated gypsum that is distinctively depleted in $\delta^{34}$S. In particular, 8 phosphorites of the Phosphoria Formation are highly enriched in $\delta^{34}$S as compared to Permian evaporites. Nathan and Nielsen (1980) believe that the high concentration of $\delta^{34}$S in phosphorites is caused by bacterial reduction of sulfate in interstitial waters.

In this report we present additional data on the isotope composition of Permian phosphorites from Idaho and compare them with the published data in the hope of advancing our knowledge of the environments and processes of phosphorite formation.
Acknowledgements

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Samples and Analysis

The phosphorite samples reported here are from the bulldozer trench (USGS CP-71) in the Hawley Creek area, about 13 km east of Leadore, east-central Idaho, near the Idaho-Montana border (fig. 1). The samples are part of the Retort Phosphatic Shale Member of the Permian Phosphoria Formation. The Phosphoria Formation occurs over wide areas in Idaho, Montana, Wyoming, and Utah, and forms the Western Phosphate Field of the United States (McKelvey and others, 1959; Gulbransen, 1960). Large phosphate resources exist in the Meade Peak Phosphatic Shale Member of the Phosphoria Formation in southeastern Idaho and western Wyoming (Mansfield, 1927; Cressman and Gulbransen, 1955; Gulbransen and others, 1956; Gulbransen, 1960; Sheldon, 1963; Cressman, 1964; Montgomery and Cheney, 1967; Gulbransen and Krier, 1980). Phosphate resources in the Retort Phosphatic Shale Member in east-central Idaho are not large and have been only briefly described by Cressman and Swanson (1964) and Swanson (1970).
Oberlindacher and Hovland (1979) mapped the Retort Phosphatic Shale Member, and sampled and described phosphate rocks from the trench in the Hawley Creek area. There, the Retort Phosphatic Shale Member is 22.3 m in average thickness and is generally composed of phosphorite, phosphatic mudstone, and dolomitic mudstone that contain various proportions of apatite, carbonates, quartz and silicates. The phosphorite occurs as oolites, pellets, nodules, and laminar cementing materials. The phosphate rocks having 24 to 31 percent $P_2O_5$ total 2.7 m in cumulative thickness and those having 16 to 24 percent $P_2O_5$ constitute 10.2 m in cumulative thickness.

Channel samples of 24 phosphate rocks of the lower and middle Retort Phosphatic Shale Member were taken from the freshly exposed trench and were analyzed for major and trace elements at the U.S. Geological Survey laboratories. Major-element analyses of 9 phosphorites having $P_2O_5$ greater than 21.3 percent are shown in Table 1. Sulfur and carbon isotope compositions (Table 2) of 5 phosphorites were determined at the Institute for Thermal Spring Research, Japan, by the "Kiba solution" method (Sakai and others, 1978; Ueda and Sakai, 1983) developed for simultaneous analysis of sulfate-sulfur, sulfide-sulfur, and carbonate-carbon in geological materials.
Powdered samples are decomposed in vacuum at 280°C by phosphoric acid containing Sn++ ions. Sulfate-sulfur is extracted as SO₂, sulfide-sulfur as H₂S, and carbonate-carbon as CO₂. The gases are then purified by successive vacuum distillation. H₂S is converted to SO₂. The sulfur and carbon isotope ratios in the SO₂ and CO₂ are then determined mass-spectrometrically. No appreciable amount of sulfide sulfur exists in the phosphorites (Table 2). The sulfate and carbonate concentrations determined using the "Kiba solution" compare well with those using standard chemical methods within the error of analysis (Table 2).

Composition of Apatite

The composition of carbonate-fluorapatite that constitutes sedimentary phosphate deposits has not been well established, partly due to the difficulty in obtaining pure samples of the apatite, which is usually a micron-size fine admixture of apatite and other minerals. Carbonate-fluorapatite is a variety of fluorapatite, Ca₅(PO₄)₃F, and various substitutional schemes have been proposed. Although partial substitutions of CO₃ for PO₄ and Na for Ca and the increased F content for compensating change imbalance have been widely accepted, other potential substitutions, SO₄ and SiO₄ for PO₄, Mg and Sr for Ca, are not universally accepted.
McClellan and Lehr (1969) consider sulfate substitution too small to be significant. Price and Calvert (1978) also question sulfate substitution in apatite of Recent phosphorites from the Namibian Shelf off southwest Africa. On the other hand, Gulbrandsen (1966) finds Na:S atomic ratio of 1:1 in phosphorites of the Phosphoria Formations and suggests the coupled substitution, \( \text{Na} + \text{SO}_4 \ \text{Ca} + \text{PO}_4 \), and a \( \text{SO}_3 \) content of 0.3 to 3.1 percent in the apatite. Bliskovskiy and others (1977) report a \( \text{SO}_3 \) content as high as 3.8 percent in Eocene apatite and suggest a high paleosalinity of the water. McArthur (1978) claims that all sea-floor apatites have a constant composition of 2.9 percent \( \text{SO}_4 \) upon precipitation and that weathering reduces the "impurities," \( \text{SO}_4 \), \( \text{CO}_3 \), Na and Sr, toward the pure fluorapatite composition. This view conflicts with Gulbrandsen's (1970) suggestion that the composition of carbonate-fluorapatite, particularly the \( \text{CO}_2 \) content, reflects the temperatures of deposition. Gulbrandsen and Krier (1980) have shown, from the study of underground and surface samples of phosphate rocks, that weathering dissolves and leaches out carbonates (dolomite and calcite) and organic matter from phosphate rocks; weathering does not affect the composition of apatite.

We propose here that \( \text{SO}_4 \) is a significant substitution for \( \text{PO}_4 \) in the apatite of the Retort Phosphatic Shale Member in the Hawley Creek area. The compositions of 9 phosphorites shown in Table 1 were used to calculate the average composition of the carbonate-fluorapatite. First, the mineral composition of the phosphorites was calculated from the chemical analysis.
We modified and used here Gulbrandsen's (1960) method of mineral-norm calculation, as follows: All P$_2$O$_5$ is assigned to apatite. Apatite is assumed to contain 38.5 percent P$_2$O$_5$, and thus the apatite content is obtained by multiplying the P$_2$O$_5$ percentage by 100/38.5. All MgO is assumed to be in dolomite. Dolomite contains 21.86 percent MgO, and thus the dolomite content is obtained by multiplying the MgO percentage by 100/21.86. CO$_2$ is contained in calcite, dolomite, and apatite. Calcite contains 43.965 percent CO$_2$, and dolomite 47.73 percent CO$_2$. On the basis of the X-ray diffraction method of Gulbrandsen (1970), the apatite in 15 phosphate rocks of the Hawley Creek area was found to contain 1.58 percent CO$_2$ (standard deviation = 0.35 percent CO$_2$). Thus, the calcite content is obtained by multiplying the CO$_2$ that is not contained in dolomite and apatite by 100/43.965: calcite = 2.2745 (CO$_2$ - 0.4773 dolomite - 0.0158 apatite). If the calcite value is negative, dolomite calculated from MgO is modified for the CO$_2$ deficiency. In this case, all CO$_2$ not used in apatite is assigned to dolomite. The average SiO$_2$/Al$_2$O$_3$ ratio of silicate minerals in the phosphorites is assumed to be 2.5. Thus, the quartz is SiO$_2$ not used in silicate minerals: quartz = SiO$_2$ - 2.5 Al$_2$O$_3$. The silicate mineral content equals 100 minus apatite, dolomite, calcite, and quartz contents.
The calculated mineral composition is given in Table 3. The chemical composition of apatite in the phosphorites is shown in Table 4, in which Na\textsubscript{2}O, P\textsubscript{2}O\textsubscript{5}, SO\textsubscript{3}, and F are unadjusted rock compositions, and CaO and CO\textsubscript{2} are rock compositions adjusted for those contained in dolomite and calcite.

The average chemical composition was then used to calculate the average formula of the apatite, according to the method of Manheim and Gulbrandsen (1979). We obtained:

$$(\text{Ca}_{9.69} \text{Na}_{0.31}) [(\text{P}O_4)_{5.44} (\text{SO}_4)_{0.20} (\text{CO}_3)_{0.36}] F_{2.35}.$$ 

In this formula, 9.3 percent of the PO\textsubscript{4} site is substituted by SO\textsubscript{4} (3.3%) and CO\textsubscript{3} (6%), and the positive charge totals 19.69 and the negative charge 19.79 in a close charge balance. In terms of oxides and fluorine, the apatite contains CaO, 53.67%; Na\textsubscript{2}O, 0.95%; P\textsubscript{2}O\textsubscript{5}, 38.06%; SO\textsubscript{3}, 1.58%; CO\textsubscript{2}, 1.57%; and F, 4.17%. The substitution in the Hawley Creek apatite is within the substitutional range proposed by Gulbrandsen (1966) for the apatite of the Phosphoria Formation.
Sulfur Isotope Composition

The phosphorites of the Retort Phosphatic Shale Member are significantly enriched in the heavy sulfur isotope in comparison to Permian evaporites. The $^{34}$S values of apatite from 5 Retort phosphorites range from +18.2 to +27.3 and averages +24.3‰ (Table 2), whereas $^{34}$S values of Permian marine evaporites of the United States range from +9 to +13 (Holser and Kaplan, 1966; Claypool and others, 1980) in accordance with the worldwide average of +10.4 ± 0.2‰ (Veizer and others, 1980), representing the normal value for the Permian sea. Nathan and Nielsen (1980) also reported high $^{34}$S values for apatites of the Phosphoria Formation $^{34}$S values of 8 samples range from +14.2 to +19.8 and averages +17.7‰. Bliskovskiy and others (1977) reported $^{34}$S value of +23.3‰ for one apatite sample from the Rocky Mountains, United States (most likely Phosphoria Formation). Sulfur in phosphorites of other ages is also generally enriched in the heavy isotope relative to contemporaneous evaporites (Nathan and Nielsen, 1980).

The enrichment of the heavy sulfur isotope in phosphorites is caused by bacterial reduction of sulfate in interstitial waters of sediments, as postulated by Nathan and Nielsen (1980). Carbonate-fluorapatite diagenetically precipitates or replaces carbonate fragments within the organic-rich sediments on a shelf, embayment or basin of high biologic productivity.
The decomposition of organic matter progresses effectively by dissimilatory sulfate reduction by sulfate-reducing bacteria under anaerobic conditions (Goldhaber and Kaplan, 1974). The generalized reaction describing the decomposition of organisms may be written (Filipek and Owen, 1980):

\[ 2 \left( \text{CH}_2\text{O} \right)_c \left( \text{NH}_3 \right)_n \left( \text{H}_3\text{PO}_4 \right)_p + \left( \text{SO}_4^{2-} \right)_c \rightarrow 2\left( \text{CO}_2 \right)_c + \\text{average carbon: nitrogen: phosphorus ratio of decomposing organisms.} \]

Decomposed organisms release phosphate and carbonate to be fixed in apatite, and the interstitial reservoir becomes increasingly depleted in sulfate. Reduced sulfur may combine with iron, if available, to form pyrite, or escape as \( \text{H}_2\text{S} \) gas. Since bacteria prefer \( \delta^{32}\text{SO}_4 \), over \( \delta^{34}\text{SO}_4 \), sulfate in the interstitial reservoir becomes enriched in \( \delta^{34}\text{SO}_4 \) relative to the original interstitial sulfate. Thus, only \( \delta^{34}\text{S} \)-enriched sulfate is available for precipitating apatite in the reservoir. Sulfide, if formed, would be depleted in \( \delta^{34}\text{S} \). In fact, in 3 samples of the Retort phosphorites, \( \delta^{34}\text{S} \) values in sulfide sulfur are -26.2, -4.9, and +4.8°/oo (Table 2).

The depletion of sulfate in the reservoir by bacterial reduction is correlated with the sulfur isotope composition of apatite, as noted by Nathan and Nielsen (1980). As the sulfate reduction progresses, the total sulfate in the reservoir decreases and at the same time becomes \( \delta^{34}\text{S} \)-enriched. Thus, apatite precipitated at equilibrium with the reservoir in a closed system must retain the \( \text{SO}_4 \) content and \( \delta^{34}\text{S} \) value reflecting the condition of the reservoir; apatite containing more \( \text{SO}_4 \) has less \( \delta^{34}\text{S} \), and vice versa.
Increasing $\delta^{34}S$ with decreasing $SO_4$ in apatite can be described by the Rayleigh distillation equation (Goldhaber and Kaplan, 1974, p.632):

$$R_t = R_0 \frac{C_t}{C_0} \left(1 - \frac{1}{\alpha}\right)$$  \hspace{1cm} (1)

Where $R_t = (S^{32}/S^{34})$ in apatite at time $t$

$R_0 = (S^{32}/S^{34})$ in apatite at start

$C_t = \text{Concentration of } SO_4 \text{ in apatite at time } t$

$C_0 = \text{Concentration of } SO_4 \text{ in apatite at start}$

$$\alpha = \frac{K_1}{K_2}$$

$K_1 = \text{rate of } S^{32}SO_4 \text{ reduction}$

$K_2 = \text{rate of } S^{34}SO_4 \text{ reduction}$

Equation (1) is rewritten in a natural log form:

$$\ln R_t = \ln R_0 + \left(1 - \frac{1}{\alpha}\right) \ln \frac{C_t}{C_0}$$  \hspace{1cm} (2)

On the other hand, by definition

$$\delta^{34}S = \left(\frac{(S^{34}/S^{32})_{\text{sample}}}{(S^{34}/S^{32})_{\text{standard}}} - 1\right) \times 1000$$

$$= \left(\frac{(S^{32}/S^{34})_{\text{standard}}}{(S^{32}/S^{34})_{\text{sample}}} - 1\right) \times 1000$$

$$= \left(\frac{R_{\text{standard}}}{R_{\text{sample}}} - 1\right) \times 1000$$  \hspace{1cm} (3)

Equation (3) is rewritten:

$$\ln R_{\text{sample}} = R_{\text{standard}} - \ln \left(1 + \frac{\delta^{34}S}{1000}\right)$$  \hspace{1cm} (4)

Since $|\delta^{34}S| \ll 1$, $\ln \left(1 + \frac{\delta^{34}S}{1000}\right) \approx \frac{\delta^{34}S}{1000}$

Thus, equation (4) becomes:

$$\ln R_{\text{sample}} = \ln R_{\text{standard}} - \frac{\delta^{34}S}{1000}$$  \hspace{1cm} (5)
Substituting equation (5) in equation (2), we obtain:

\[ s^{34}S_t = s^{34}S_0 - 1000 \left(1 - \frac{t}{\infty}\right) \ln \frac{C_t}{C_0} \]

(6)

or

\[ s^{34}S_t = s^{34}S_0 - 2302.6 \left(1 - \frac{t}{\infty}\right) \log \frac{C_t}{C_0} \]

(7)

Equation (7) expresses the relationship between \( s^{34}S \) and \( \log C_t \) in the form of \( y = ax + b \), and when \( s^{34}S_0 \), \( a \), and \( b \) are known, \( \alpha \) and \( C_0 \) can be obtained.

Figure 2 shows the relationship between \( s^{34}S \) and \( \log (SO_3/P_{2O_5}) \) for 6 Retort phosphorites (5 from this study, 1 from Nathan and Nielsen, 1980) and 6 Meade Peak phosphorites (Nathan and Nielsen, 1980). \( (SO_3/P_{2O_4}) \) instead of \( SO_3 \) is used here because the \( SO_3 \) analysis was made of apatite-bearing phosphorites, not of pure apatites; \( (SO_3/P_{2O_4}) \) shows the relative concentration of \( SO_4 \) in apatite better. It is obvious from the figure that the phosphorites of the Phosphoria Formation follow generally the Rayleigh distillation equation and that sulfur isotope fractionation occurs in a closed-system reservoir, with which precipitating apatite maintains equilibrium.
The Retort Phosphatic Shale Member is more enriched in the heavy sulfur isotope than the Meade Peak Phosphatic Shale Member. The greater enrichment may have been caused by a greater extent of bacterial reduction of sulfate, a greater kinetic isotope effect, or a combination of both. If we assume that both the Retort and the Meade Peak had the same sulfate concentration in the original interstitial reservoir, the greater $^{34}$SO$_4$ enrichment in the Retort was probably due mainly to the greater extent of sulfate reduction in the Retort, which must have accumulated more organic debris. An alternative explanation assumes that the Retort and the Meade Peak had different sulfate concentrations in the original reservoir and underwent different kinetic isotope effects. As shown in Figure 2, the Retort appears to have undergone a greater kinetic fractionation (fractionation factor $\alpha C = 1.022$, line (1)) than the Meade Peak (fractionation factor $\alpha C = 1.008$, line (2)). On the average, the Retort contains 1.07 percent SO$_3$ and the Meade Peak 2.17 percent SO$_3$ (Gulbrandsen, 1966). The different SO$_3$ content suggests that the two members were deposited in environments of different salinity. The difference in the kinetic isotope effect may be due to different depth and temperature of deposition, different species of bacteria involved, or some unknown factors. The isotopic variation within the Retort Member of the Hawley Creek area suggests that the extent of bacterial sulfate reduction was variable locally, for example, from one bed to another.
Carbon Isotope Composition

The $^{13}$C values of carbonates from 5 Retort phosphorites range from -9.1 to -6.6 and averages -8.5\(^\circ\)/oo. The ratio is intermediate between the values for Permian inorganic carbonate ($^{13}$C = + 2.00 ± 0.16\(^\circ\)/oo, Veizer and others, 1980) and Permian organic carbon ($^{13}$C = -26\(^\circ\)/oo, Degens, 1969).

Carbonate in the phosphorite is mostly in apatite (the dolomite and calcite content averages 5.4 percent in the analyzed samples). The light-carbon enrichment in phosphorites indicates that carbonate in apatite was not entirely from the entrapped sea water within sediments but also from the $^{13}$C-depleted biogenic bicarbonate released by the organic decomposition. The interstitial water of sediments becomes a "closed system" reservoir and exchanges no material with the overlying sea water, as burial increases with sediment accumulation. The decomposition of organic matter by sulfate reducing bacteria releases bicarbonate enriched in light carbon into the reservoir. Thus, the entrapped original sea water with the normal $^{13}$C value becomes increasingly contaminated with biogenic carbonate. The carbon isotope ratio in phosphorites must reflect the state of the contaminated reservoir. Increasing bacterial sulfate reduction increases the amount of heavy sulfur and at the same time increases light carbon in precipitating apatite. This hypothesis could be tested if the carbon isotope ratios in Meade Peak phosphorites were known.
Murata and others (1972) report that dolomites of the Phosphoria Formation are characterized by light-carbon carbonate ($^{13}\text{C} = -6.8^0/oo$, average of 9) derived from the decomposition of organic matter. Phosphoria dolomites are not as high in light carbon as Phosphoria (Retort) phosphorites; the diagenetic dolomitization of primary carbonate and the isotopic exchange probably occurred in the interstitial environments where the organic decomposition was not as extensive as for phosphorite formation. Also, Al-Bassam (1980) reports that Pliocene phosphorites of Iraq have more light carbon than underlying and overlying limestones ($^{13}\text{C} = -5.8^0/oo$ in phosphorites, $^{13}\text{C} = -2$ to $-3^0/oo$ in limestone). The differences in $^{13}\text{C}$ must reflect the diagenetic environment of different microbiologic activities.

Kolodny and Kaplan (1970) report that apatite has more light carbon than coexisting calcite in many phosphorites from offshore as well as onshore environments and consider that the difference was caused by isotope fractionation (removal of light carbon) of primary calcite with increasing phosphatization of limestone. In this view, apatite can accommodate more light carbon than coexisting calcite, due to some crystal-structural difference.
Alternatively, calcite with less light carbon than coexisting apatite may represent either primary calcite slightly contaminated with biogenic carbonate, or secondary calcite contaminated with meteoric-water carbon. The abundant occurrence of carbonate veins and cements in phosphorites of the Retort Phosphatic Shale Member suggests the latter possibility. However, the carbon isotope composition of coexisting apatite and carbonate minerals in the Phosphoria Formation needs to be investigated further in order to clarify this issue.

Conclusion

The sulfur and carbon isotope data support the idea that phosphorites are formed diagenetically in organic-rich sediments under reducing conditions; marine apatites do not precipitate directly from sea water. The relative enrichment of heavy sulfur and light carbon isotopes in phosphorites is caused by bacterial reduction of sulfate in interstitial waters.

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Figure 1  LOCATION OF HAWLEY CREEK AREA
Figure 2. Relationship between \( ^{34}S \) and sulfate content (expressed as \( SO_3/P_2O_5 \)) in phosphorite of the Phosphoria Formation. \( P_2O_5 \) and \( SO_3 \) analyses by the U.S. Geological Survey (this study, and Gulbrandsen, 1966). \( ^{34}S \) values for 6 Meade Peak phosphorites and 1 Retort phosphorite from Nathan and Nielsen (1980). Line (1) shows the trend of Retort phosphorites and from the Reyleigh equation (see text) \( \alpha = 1.008 \) and \( C_\circ = 0.07 \) are derived at \( SS_\circ = 10.4 \). Line (2) shows the trend of Meade Peak phosphorites and \( \alpha = 1.008 \) and \( C_\circ = 0.165 \) are derived at \( SS_\circ = 10.4 \).
Table 1. Chemical analyses of phosphorites from the Retort Phosphatic Shale Member in the Hawley Creek area, Idaho (Results in Percent)

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>H₂O⁺</th>
<th>H₂O⁻</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>MnO</th>
<th>CO₂</th>
<th>F</th>
<th>SO₃</th>
<th>S</th>
<th>Organic Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rt-2</td>
<td>22.5</td>
<td>3.1</td>
<td>0.53</td>
<td>0.04</td>
<td>1.6</td>
<td>36.3</td>
<td>0.63</td>
<td>0.84</td>
<td>1.4</td>
<td>0.65</td>
<td>0.13</td>
<td>23.5</td>
<td>-</td>
<td>4.0</td>
<td>2.88</td>
<td>1.17</td>
<td>0.09</td>
<td>0.33</td>
</tr>
<tr>
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<td>2.0</td>
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<td>0.04</td>
<td>4.7</td>
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<td>0.63</td>
<td>0.59</td>
<td>1.1</td>
<td>0.58</td>
<td>0.13</td>
<td>21.6</td>
<td>-</td>
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<td>2.80</td>
<td>1.02</td>
<td>0.13</td>
<td>0.26</td>
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<tr>
<td>Rt-5</td>
<td>28.1</td>
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<td>1.5</td>
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<td>30.3</td>
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</tr>
<tr>
<td>Rt-7</td>
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<td>0.54</td>
<td>0.04</td>
<td>1.5</td>
<td>40.0</td>
<td>0.73</td>
<td>0.56</td>
<td>1.2</td>
<td>0.56</td>
<td>0.13</td>
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<td>-</td>
<td>4.5</td>
<td>3.21</td>
<td>1.20</td>
<td>0.12</td>
<td>0.74</td>
</tr>
<tr>
<td>Rt-12</td>
<td>22.6</td>
<td>1.8</td>
<td>0.76</td>
<td>0.04</td>
<td>0.18</td>
<td>38.9</td>
<td>0.60</td>
<td>0.51</td>
<td>0.97</td>
<td>0.51</td>
<td>0.16</td>
<td>26.2</td>
<td>-</td>
<td>3.0</td>
<td>2.99</td>
<td>1.02</td>
<td>0.11</td>
<td>0.38</td>
</tr>
<tr>
<td>Rt-19</td>
<td>16.0</td>
<td>1.3</td>
<td>0.99</td>
<td>0.04</td>
<td>0.14</td>
<td>42.6</td>
<td>0.62</td>
<td>0.28</td>
<td>1.1</td>
<td>0.53</td>
<td>0.08</td>
<td>28.4</td>
<td>0.01</td>
<td>2.9</td>
<td>3.14</td>
<td>1.04</td>
<td>0.05</td>
<td>0.39</td>
</tr>
<tr>
<td>Rt-20</td>
<td>16.1</td>
<td>2.3</td>
<td>1.1</td>
<td>0.04</td>
<td>0.30</td>
<td>39.2</td>
<td>0.67</td>
<td>0.71</td>
<td>1.3</td>
<td>0.67</td>
<td>0.15</td>
<td>29.7</td>
<td>0.01</td>
<td>1.2</td>
<td>3.32</td>
<td>1.10</td>
<td>0.11</td>
<td>0.37</td>
</tr>
<tr>
<td>Rt-21</td>
<td>23.3</td>
<td>4.3</td>
<td>1.5</td>
<td>0.05</td>
<td>0.67</td>
<td>35.6</td>
<td>0.58</td>
<td>1.5</td>
<td>1.7</td>
<td>0.94</td>
<td>0.25</td>
<td>24.1</td>
<td>-</td>
<td>1.3</td>
<td>2.77</td>
<td>0.77</td>
<td>0.09</td>
<td>0.34</td>
</tr>
<tr>
<td>Rt-23</td>
<td>11.5</td>
<td>1.9</td>
<td>0.82</td>
<td>0</td>
<td>0.35</td>
<td>45.3</td>
<td>0.72</td>
<td>0.44</td>
<td>1.2</td>
<td>0.76</td>
<td>0.10</td>
<td>30.9</td>
<td>0.01</td>
<td>2.3</td>
<td>3.38</td>
<td>1.17</td>
<td>0.11</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Table 2. Concentrations and isotope ratios of sulfur and carbon in phosphorites of the Retort Phosphatic Shale Member.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$S^=$</th>
<th>$SO_4^-$</th>
<th>$\delta S$</th>
<th>$CO_3^-$</th>
<th>$\delta S^=$</th>
<th>$\delta SO_4^-$</th>
<th>$\delta S**^=$</th>
<th>$\delta CO_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rt- 2</td>
<td>168</td>
<td>4800</td>
<td>4970</td>
<td>523</td>
<td>-4.9</td>
<td>18.2</td>
<td>17.4</td>
<td>-9.1</td>
</tr>
<tr>
<td>Rt-12</td>
<td>0</td>
<td>3760</td>
<td>3760</td>
<td>26900</td>
<td>-</td>
<td>22.9</td>
<td>22.9</td>
<td>-9.0</td>
</tr>
<tr>
<td>Rt-19</td>
<td>112</td>
<td>4780</td>
<td>4890</td>
<td>30400</td>
<td>-26.2</td>
<td>26.8</td>
<td>25.6</td>
<td>-9.1</td>
</tr>
<tr>
<td>Rt-23</td>
<td>0</td>
<td>4760</td>
<td>4760</td>
<td>23900</td>
<td>-</td>
<td>26.1</td>
<td>26.1</td>
<td>-8.8</td>
</tr>
<tr>
<td>Rt-20</td>
<td>523</td>
<td>4560</td>
<td>5090</td>
<td>16100</td>
<td>+4.8</td>
<td>+27.3</td>
<td>+25.0</td>
<td>-6.6</td>
</tr>
</tbody>
</table>

** weighted average of $S^=$ and $SO^=$

*** not determined

Analysis by H. Sakai
Table 3. Calculated mineral composition of the analyzed phosphorites °/o.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Apatite</th>
<th>Dolomite</th>
<th>Calcite</th>
<th>Quartz</th>
<th>Silicate Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rt-2</td>
<td>61.10</td>
<td>6.36</td>
<td>0</td>
<td>14.75</td>
<td>17.79</td>
</tr>
<tr>
<td>Rt-4</td>
<td>56.16</td>
<td>21.53</td>
<td>0.31</td>
<td>9.00</td>
<td>13.00</td>
</tr>
<tr>
<td>Rt-5</td>
<td>55.38</td>
<td>2.36</td>
<td>0</td>
<td>16.35</td>
<td>25.91</td>
</tr>
<tr>
<td>Rt-7</td>
<td>71.50</td>
<td>6.87</td>
<td>0.21</td>
<td>11.05</td>
<td>10.37</td>
</tr>
<tr>
<td>Rt-12</td>
<td>68.12</td>
<td>0.82</td>
<td>3.47</td>
<td>18.10</td>
<td>9.49</td>
</tr>
<tr>
<td>Rt-19</td>
<td>73.84</td>
<td>0.64</td>
<td>3.24</td>
<td>12.75</td>
<td>9.53</td>
</tr>
<tr>
<td>Rt-20</td>
<td>77.22</td>
<td>0</td>
<td>0</td>
<td>10.35</td>
<td>12.43</td>
</tr>
<tr>
<td>Rt-21</td>
<td>62.66</td>
<td>0.65</td>
<td>0</td>
<td>12.55</td>
<td>24.14</td>
</tr>
<tr>
<td>Rt-23</td>
<td>80.34</td>
<td>1.60</td>
<td>0.60</td>
<td>6.75</td>
<td>10.71</td>
</tr>
</tbody>
</table>
Table 4. Chemical composition of the apatite in the phosphorites.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>P$_2$O$_5$</th>
<th>CO$_2$</th>
<th>SO$_3$</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rt-2</td>
<td>34.4</td>
<td>0.63</td>
<td>23.5</td>
<td>0.96</td>
<td>1.17</td>
<td>2.88</td>
</tr>
<tr>
<td>Rt-4</td>
<td>31.2</td>
<td>0.63</td>
<td>21.6</td>
<td>0.88</td>
<td>1.02</td>
<td>2.80</td>
</tr>
<tr>
<td>Rt-5</td>
<td>29.6</td>
<td>0.62</td>
<td>21.3</td>
<td>0.87</td>
<td>0.97</td>
<td>2.48</td>
</tr>
<tr>
<td>Rt-7</td>
<td>37.8</td>
<td>0.73</td>
<td>27.5</td>
<td>1.13</td>
<td>1.20</td>
<td>3.21</td>
</tr>
<tr>
<td>Rt-12</td>
<td>36.7</td>
<td>0.60</td>
<td>26.2</td>
<td>1.08</td>
<td>1.02</td>
<td>2.99</td>
</tr>
<tr>
<td>Rt-19</td>
<td>40.6</td>
<td>0.62</td>
<td>28.4</td>
<td>1.17</td>
<td>1.04</td>
<td>3.17</td>
</tr>
<tr>
<td>Rt-20</td>
<td>39.2</td>
<td>0.67</td>
<td>29.7</td>
<td>1.2</td>
<td>1.10</td>
<td>3.32</td>
</tr>
<tr>
<td>Rt-21</td>
<td>35.4</td>
<td>0.58</td>
<td>24.1</td>
<td>0.99</td>
<td>0.77</td>
<td>2.77</td>
</tr>
<tr>
<td>Rt-23</td>
<td>44.5</td>
<td>0.72</td>
<td>30.9</td>
<td>1.28</td>
<td>1.17</td>
<td>3.38</td>
</tr>
<tr>
<td>Average</td>
<td>36.6</td>
<td>0.64</td>
<td>25.9</td>
<td>1.06</td>
<td>1.05</td>
<td>3.00</td>
</tr>
</tbody>
</table>

Note: Na$_2$O, P$_2$O$_5$, SO$_3$, and F are unadjusted rock compositions; CaO and CO$_2$ are adjusted rock compositions for those contained in dolomite and calcite.