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

Shingi Kuniyoshi [1]

and

Hitoshi Sakai [2]

OPEN-FILE REPORT 87-100

1987

[1] Bureau of Land Management
California Desert District
1695 Spruce Street
Riverside, CA 92507

[2] Ocean Research Institute
University of Tokyo
15-1, 1-Chome, Minamidai,
Nakano-Ku, Tokyo, 164 Japan

CONTENTS

ILLUSTRATIONS

TABLES

Abstract

In carbonate-fluorapatite of the Retort Phosphatic Shale Member of the Permian Phosphoria Formation in the Hawley Creek area, east-central Idaho, SO_4 partially substitutes for PO_4 and Na partially substitutes for Ca. The average composition of the apatite on the basis of the chemical analysis of 9 phosphorites is $(Ca_{9.69}Na_{0.31})[(PO_4)_{5.44}(CO_3)_{0.36}(SO_4)_{0.20}]F_{2.35}$.

The phosphorites are characterized by heavy sulfur and light carbon isotope ratios ($\delta^{34}S$ = +18 to +27°/oo; $\delta^{13}C$ = -7 to -9°/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 ($\delta^{34}S$) 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 $\delta^{34}S$ than the phosphorite of the Retort Phosphatic Shale Member. The sulfate content and the $\delta^{34}S$ 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 SO_4 and more $\delta^{34}S$.

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

The authors thank Robert A. Gulbrandsen, Peter Oberlindacher, and R. David Hovland for review of this manuscript. Peter Oberlindacher was kind enough to prepare the report for publication.

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; Gulbrandsen, 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 Gulbrandsen, 1955; Gulbrandsen and others, 1956; Gulbrandsen, 1960; Sheldon, 1963; Cressman, 1964; Montgomery and Cheney, 1967; Gulbrandsen and Krier, 1980). Phosphate resources in the Retort Phospatic 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 2.7m 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 SO_2, sulfide-sulfur as H_2S, and carbonate-carbon as CO_2. The gases are then purified by successive vacuum distillation. H_2S is converted to SO_2. The sulfur and carbon isotope ratios in the SO_2 and CO_2 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, $Ca_5(PO_4)_3F$, and various substitutional schemes have been proposed. Although partial substitutions of CO_3 for PO_4 and Na for Ca and the increased F content for compensating change imbalance have been widely accepted, other potential substitutions, SO_4 and SiO_4 for PO_4, 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, $Na + SO_4 \quad Ca + PO_4$, and a SO_3 content of 0.3 to 3.1 percent in the apatite. Bliskovskiy and others (1977) report a 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 SO_4 upon precipitation and that weathering reduces the "impurities," SO_4, 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 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 SO_4 is a significant substitution for 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_2O_5 is assigned to apatite. Apatite is assumed to contain 38.5 percent P_2O_5, and thus the apatite content is obtained by multiplying the P_2O_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_2O_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_2O_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_2O, P_2O_5, SO_3, and F are unadjusted rock compositions, and CaO and CO_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:

$(Ca_{9.69}\ Na_{0.31})\ [(PO_4)_{5.44}\ (SO_4)_{0.20}\ (CO_3)_{0.36}]\ F_{2.35}$.

In this formula, 9.3 percent of the PO_4 site is substituted by SO_4 (3.3%) and CO_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_2O, 0.95%; P_2O_5, 38.06%; SO_3, 1.58%; CO_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 $\delta^{34}S$ values of apatite from 5 Retort phosphorites range from +18.2 to +27.3 and averages +24.3^{o}/oo (Table 2), whereas $\delta^{34}S$ 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^{o}/oo (Veizer and others, 1980), representing the normal value for the Permian sea. Nathan and Nielsen (1980) also reported high $\delta^{34}S$ values for apatites of the Phosphoria Formation $\delta^{34}S$ values of 8 samples range from +14.2 to +19.8 and averages +17.7^{o}/oo. Bliskovskiy and others (1977) reported $\delta^{34}S$ value of +23.3^{o}/oo 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):

$$2\ (CH_2O)_c\ (NH_3)_n\ (H_3PO_4)_p + (SO_4^{2-})_c \quad 2(CO_2)_c$$

$$+ (S^{2-})_c + 2\ (NH_3)_n + 2(H_2O)_c + 2\ (H_3PO_4)_p, \text{ where, } c,\ n,\ p$$

= 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 H_2S gas. Since bacteria prefer $\delta^{32}SO_4$, over $\delta^{34}SO_4$, sulfate in the interstitial reservoir becomes enriched in $\delta^{34}SO_4$ relative to the original interstitial sulfate. Thus, only $\delta^{34}S$-enriched sulfate is available for precipitating apatite in the reservoir. Sulfide, if formed, would be depleted in $\delta^{34}S$. In fact, in 3 samples of the Retort phosphorites, $\delta^{34}S$ 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 $\delta^{34}S$-enriched. Thus, apatite precipitated at equilibrium with the reservoir in a closed system must retain the SO_4 content and $\delta^{34}S$ value reflecting the condition of the reservoir; apatite containing more SO_4 has less $\delta^{34}S$, 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):

$$R_t = R_o \frac{Ct}{Co} \quad 1-1/\alpha \qquad (1)$$

Where R_t = (S^{32}/S^{34}) in apatite at time t
R_o = (S^{32}/S^{34}) in apatite at start
C_t = Concentration of SO_4 in apatite at time t
C_o = Concentration of SO_4 in apatite at start

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

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

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

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

$$\ln R_t = \ln R_o + (1 - 1/\alpha) \ln \frac{Ct}{Co} \qquad (2)$$

On the other hand, by definition

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

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

$$= \left(\frac{R\ \text{standard}}{R\ \text{sample}} - 1 \right) \times 1000 \qquad (3)$$

Equation (3) is rewritten:

$$\ln R\ \text{sample} = R\ \text{standard} \qquad -\ln 1 + \frac{\delta^{34}S}{1000} \qquad (4)$$

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

Thus, equation (4) becomes:

$$\ln R\ \text{sample} = \ln R\ \text{standard} - \frac{\delta^{34}S}{1000} \qquad (5)$$

Substituting equation (5) in equation (2), we obtain:

$$\delta^{34}S_t = \delta^{34}S_o - 1000\ (1 - \frac{1}{\alpha})\ \ln \frac{Ct}{Co} \qquad (6)$$

or

$$\delta^{34}S_t = \delta^{34}S_o - 2302.6\ (1 - \frac{1}{\alpha})\ \log \frac{Ct}{Co} \qquad (7)$$

Equation (7) expresses the relationship between $\delta^{34}S$ and log C_t in the form of $y = ax + b$, and when $\delta^{34}S_o$, a, and b are known, α and C_o can be obtained.

Figure 2 shows the relationship between $\delta^{34}S$ 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/PO_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/PO_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 $\delta^{34}SO_4$ 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 $\alpha = 1.022$, line (1)) than the Meade Peak (fractionation factor $\alpha = 1.008$, 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 a 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 $\delta^{13}C$ values of carbonates from 5 Retort phosphorites range from -9.1 to -6.6 and averages $-8.5^{o}/oo$. The ratio is intermediate between the values for Permian inorganic carbonate ($\delta^{13}C = + 2.00 \pm 0.16^{o}/oo$, Veizer and others, 1980) and Permian organic carbon ($\delta^{13}C = -26^{o}/oo$, 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 $\delta^{13}C$-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 $\delta^{13}C$ 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 ($\delta^{13}C = -6.8^{o}$/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 ($\delta^{13}C = -5.8^{o}$/oo in phosphorites, $\delta^{13}C = -2$ to -3^{o}/oo in limestone). The differences in $\delta^{13}C$ 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 meteroric-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.

References Cited

Al-Bassam, K.S., 1980, Carbon and oxygen isotopic composition of some marine sedimentary apatites from Iraq: Economic Geology, v. 75, p. 1231 -1233.

Baturin, G. N., 1970, Authigenic phosphate concretions in Recent sediments of the southwest African shelf: Doklady of the Academy of Sciences, USSR, Earth Sciences Section, v. 189, p. 227 - 230.

_____________ 1972, Phosphorus in interstitial waters of sediments of the southeastern Atlantic: Oceanology; v. 12, p. 849 - 855.

Bliskovskiy, V. Z., Grinenko, V. A., Migdisov, A. A., and Savina, L. I., 1977, Sulfur isotope composition of the minerals of phosphorites: Geochemistry International, v. 14, p. 148 - 155.

Burnett, W. C., 1977, Geochemistry and origin of phosphorite deposits from off Peru and Chile: Geological Society of America Bulletin, v. 88, p. 813 - 823.

Bushinskii, G. I., 1966, The origin of marine phosphorites: Lithology and Mineral Resources, No. 3, p. 292 - 311

Calvert, S. E., 1976, The mineralogy and geochemistry of near-shore sediments, _in_ Riley, J. P., and Chester, R., eds., Chemical oceanography, v. 6 (2nd ed.): London, Academic Press, p. 187 - 280.

Claypool, G. E., Holser, W T., Kaplan, I. R., Sakai, H., and Zak, I., 1980, The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretations: Chemical Geology, v. 28, P. 199 - 260

Cressman, E. R., 1964, Geology of the Georgetown Canyon-Snowdrift Mountain area, southeastern Idaho: U. S. Geological Survey Bulletin 1153, 105 p.

Cressman, E. R., and Gulbrandsen, R.A., 1955, Geology of the Dry Valley quadrangle, Idaho: U. S. Geological Survey Bulletin 1015-I, p. 1257-1270.

Cressman, E. R., and Swanson, R. W., 1964, Stratigraphy and petrology of the Permian rocks of southwestern Montana: U. S. Geological Survey Professional Paper 313-C, p. C275 - C569.

Degens, E. T., 1969, Biogeochemistry of stable isotopes _in_ Eglinton, G., and Murphy M. T. J., eds., Organic geochemistry: New York, Springer-Verlag, p. 304 - 329.

Filipek, L. H., and Owen, R. M., 1980, Early diagenesis of organic carbon and sulfur in outer shelf sediments from the Gulf of Mexico: American Journal of Science, v. 280, p. 1097 - 1112.

Goldhaber, M. B., and Kaplan, I. R., 1974, The suflur cycle, in Goldberg, E. D., ed., The sea, v. 5, Marine chemistry: New York, John Wiley, P. 569 - 655.

Gulbrandsen, R. A., 1960, Petrology of the Meade Peak Phosphatic Shale Member of the Phosphoria Formation at Coal Canyon, Wyoming: U. S. Geological Survey Bulletin 1111-C, p. C71-C146.

__________, 1966, Chemical composition of phosphorites of the Phosphoria Formation: Geochemica et Cosmochimica Acta, v. 30, p. 769 - 778.

__________, 1970, Relation of carbon dioxide content of apatite of the Phosphoria Formation to regional facies: U. S. Geological Survey Professional Paper 700-B, p. B9-B13.

Gulbrandsen, R. A., McLaughlin, K. P., Honkala, F. S., and Clabaugh, S. E., 1956, Geology of the Johnson Creek quadrangle, Caribou County, Idaho: U. S. Geological Survey Bulletin 1042-A, p. A1-A21.

Gulbrandsen, R. A., and Krier, D. J., 1980, Large and rich phosphorus resources in the Phosphoria Formation in the Soda Springs area, southeastern Idaho: U. S. Geological Survey Bulletin 1496, 25 p.

Holser, W. T., and Kaplan, I. R., 1966, Isotope geochemistry of sedimentary sulfates: Chemical Geology, v. 1. p. 93 - 135.

Kolodny, Y., and Kaplan, I. R., 1970, Carbon and oxygen isotopes in apatite CO_2 and coexisting calcite from sedimentary phosphorite: Journal of Sedimentary Petrology, v. 40, p. 954 - 959.

McArthur, J. M., 1978, Systematic variations in the contents of Na, Sr, CO_3 and SO_4 in marine carbonate-fluorapatite and their relation to weathering: Chemical Geology, v. 21, p. 89 -112.

McClellan, G. H., and Lehr, J. R. 1969, Crystal-chemical investigation of natural apatites: American Mineralogist, v. 54, p. 1374 - 1391.

McKelvey, V. E., and others, 1959, The Phosphoria, Park City, and Shedhorn Formations in the western phosphate field: U. S. Geological Survey Professional Paper 313-A, p. A1-A47.

Manheim, F. T., and Gulbrandsen, R. A., 1979, Marine phosphorites, in Burns, R. G., ed., Marine minerals: Mineralogical Society of America Short Course Notes, v. 6, p. 151 - 173.

Manheim, F. T., Rowe, G. T., and Vipa, D., 1975, Marine phosphorite formation off Peru: Journal of Sedimentary Petrology, v. 45, p. 243 - 251.

Mansfield,G. R., 1927, Geography, geology, and mineral resources of part of southeastern Idaho: U. S. Geological Survey Professional Paper 152, 453 p.

Montgomery, K. M., and Cheney, T. M., 1967, Geology of the Stewart Flat quadrangle, Caribou County, Idaho: U. S Geological Survey Bulletin 1217, 63 p.

Murata, K. J., Friedman, I., and Gulbrandsen, R. A., 1972, Geochemistry of carbonate rocks in Phosphoria and related formations of the western phosphate fiels: U. S. Geological Survey Professional Paper 800 - D, p. D103 - D110.

Nathan, Y., and Nielsen, M., 1980, Sulphur isotopes in phosphorites, in Bentor Y. K., ed., Maine phosphorites - geochemistry, occurrence, genesis: Society of Economic Paleontologists and Mineralogists Special Publication No. 29, p. 73 - 78.

Oberlindacher, P., and Hovland, R. D., 1979, Geology and phosphate resources of the Hawley Creek area, Lemhi County, Idaho: U. S. Geological Survey Open-file Report 79-1283, 18p.

Parker, R. J., and Siesser, W. G., 1972, Petrology and origin of some phosphorites from the South African continental margin: Journal of Sedimentary Petrology, v. 42, p. 434 - 440.

Price, N. B., 1976, Chemical diagenesis in sediments, in Riley, J. P., and Chester R., eds., Chemical oceanography, v. 6 (2nd ed.): London, Academic Press, p.1 - 58.

Price, N. B., and Calvert, S. E., 1978, The geochemistry of phosphorites from the Namibian shelf: Chemical Geology, V. 23, p. 151 - 170.

Sakai, H., Ueda, A., and Field C. W., 1978, $S^{34}S$ and concentration of sulfide and sulfate sulfurs in some ocean-floor basalts and serpentinites in Zartman, R. E., ed., Fourth International Conference on Geochronology, Cosmochronology, and Isotope Geology: U. S. Geological Survey Open-file Report 78-701, p. 372 - 374

Sheldon, R. P., 1963, Physical stratigraphy and mineral resources of Permian rocks in western Wyoming: U. S. Geological Survey Professional Paper 313-B, p. B49 - B273.

Swanson, R. W., 1970, Mineral resources in Permian rocks of southwest Montana: U. S. Geological Survey Professional Paper 313-E, p. E661-E777.

Veizer, J., Holser, W. T., and Wilgus, C. K., 1980, Correlation of $^{13}C/^{12}C$ and $^{34}S/^{32}S$ secular variations: Geochimica et Cosmochimica Acta, v. 44, p. 579 - 587.

Ueda, A. and Sakai, H., 1983, Simultaneous determinations of the concentration and isotope ratio of sulfate - and sulfide - sulfur and carbonate - carbon in geological samples: Geochem, J., V. 17, p. 185 - 198

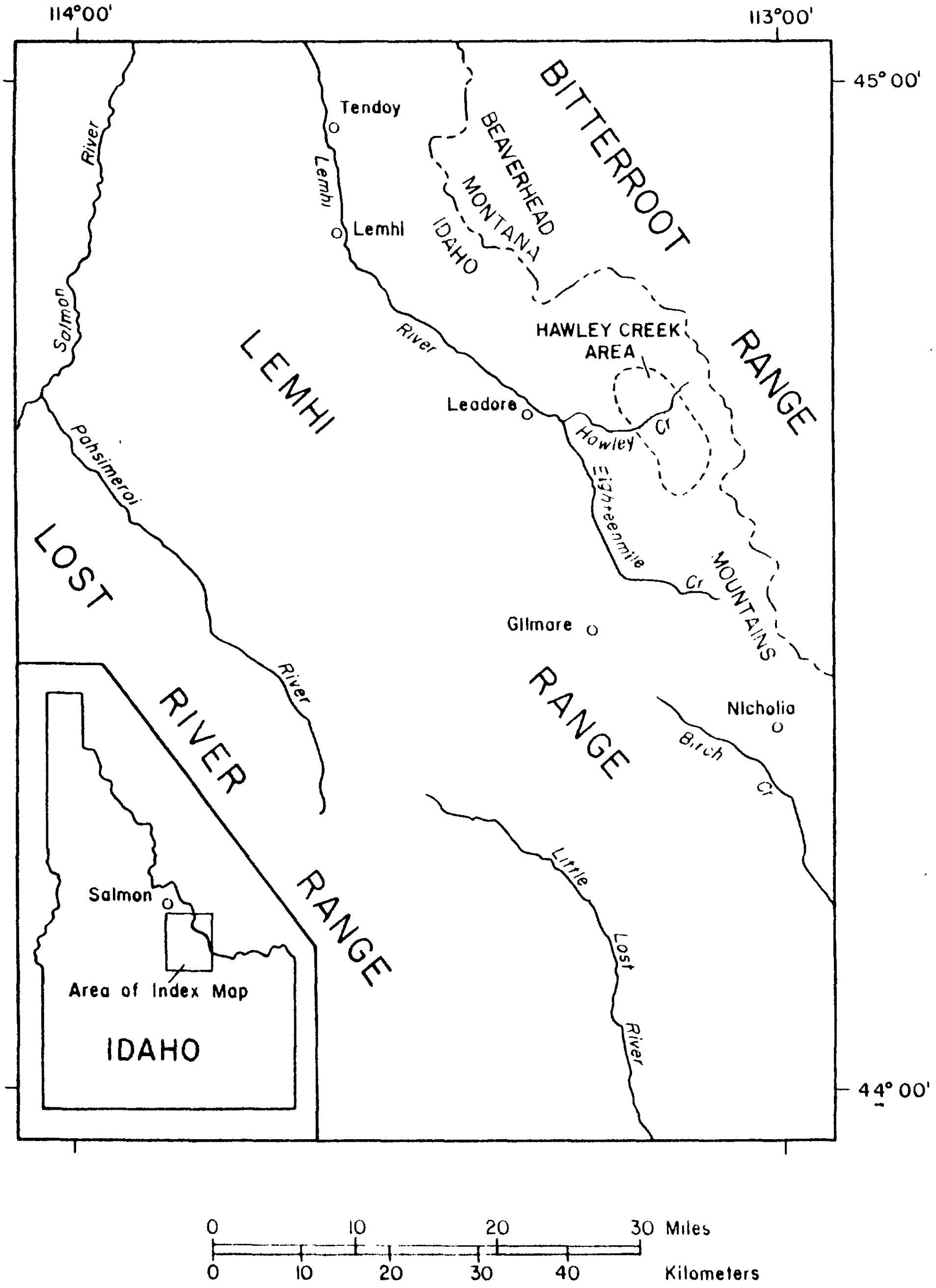

Figure 1 LOCATION OF HAWLEY CREEK AREA

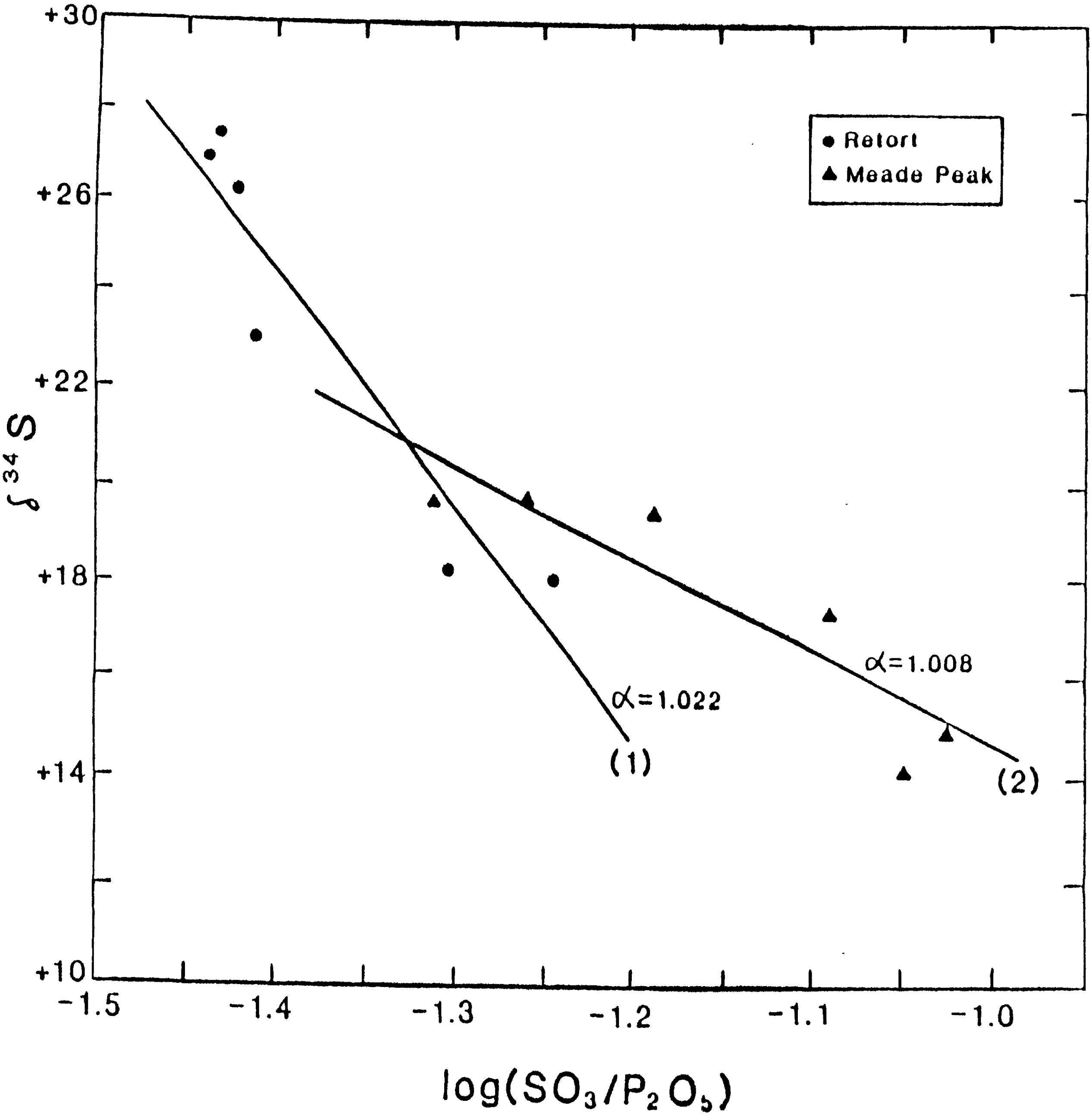

Figure 2. Relationship between $\delta^{34}S$ and sulfate content (expressed as SO_3/P_2O_5) in phosphorite of the Phosphoria Formation. P_2O_5 and SO_3 analyses by the U.S. Geological Survey (this study, and Gulbrandsen, 1966). $\delta^{34}S$ values for 6 Mead Peak phosphorites and 1 Retort phosphorite from Nathan and Nielsen (1980). Line (1) shows the trend of Retort phosphorites and from the Reyleigh equation (see text) $\alpha = 1.008$ and $C_o = 0.07$ are derived at $SS_o = 10.4$. Line (2) shows the trend of Meade Peak phosphorites and $\alpha = 1.008$ and $C_o = 0.165$ are derived at $SS_o = 10.4$.

Table 1. Chemical analyses of phosphorites from the Retort Phosphatic Shale Member in the Hawley Creek area, Idaho (Results in Percent)

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	H_2O+	H_2O-	TiO_2	P_2O_5	MnO	CO_2	F	SO_3	S	Organic Carbon
Rt-2	22.5	3.1	0.53	0.04	1.6	36.3	0.63	0.84	1.4	0.65	0.13	23.5	-	4.0	2.88	1.17	0.09	0.33
Rt-4	14.0	2.0	0.59	0.04	4.7	37.9	0.63	0.59	1.1	0.58	0.13	21.6	-	11.3	2.80	1.02	0.13	0.26
Rt-5	28.1	4.7	1.5	0.06	0.98	30.3	0.62	1.6	2.0	1.1	0.31	21.3	0.01	2.0	2.48	0.97	0.12	0.55
Rt-7	15.8	1.9	0.54	0.04	1.5	40.0	0.73	0.56	1.2	0.56	0.13	27.5	-	4.5	3.21	1.20	0.12	0.74
Rt-12	22.6	1.8	0.76	0.04	0.18	38.9	0.60	0.51	0.97	0.51	0.16	26.2	-	3.0	2.99	1.02	0.11	0.38
Rt-19	16.0	1.3	0.99	0.04	0.14	42.6	0.62	0.28	1.1	0.53	0.08	28.4	0.01	2.9	3.14	1.04	0.05	0.39
Rt-20	16.1	2.3	1.1	0.04	0.30	39.2	0.67	0.71	1.3	0.67	0.15	29.7	0.01	1.2	3.32	1.10	0.11	0.37
Rt-21	23.3	4.3	1.5	0.05	0.67	35.6	0.58	1.5	1.7	0.94	0.25	24.1	-	1.3	2.77	0.77	0.09	0.34
Rt-23	11.5	1.9	0.82	0	0.35	45.3	0.72	0.44	1.2	0.76	0.10	30.9	0.01	2.3	3.38	1.17	0.11	0.37

Analyzed by U. S., Geological Survey Laboratories, Reston, Virginia, and Menlo Park, California.

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

	Concentration (ppm)				Isotopic ratios (°/oo)			
Sample No.	$S^=$	$SO_4^=$	ΣS	$CO_3^=$	$\delta S^=$	$\delta SO_4^=$	$\delta \Sigma S$**	$\delta CO_3^=$
Rt- 2	168	4800	4970	***	-4.9	+18.2	+17.4	-9.1
Rt-12	0	3760	3760	26900	-	+22.9	+22.9	-9.0
Rt-19	112	4780	4890	30400	-26.2	+26.8	+25.6	-9.1
Rt-23	0	4760	4760	23900	-	+26.1	+26.1	-8.8
Rt-20	523	4560	5090	16100	+4.8	+27.3	+25.0	-6.6

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

*** not determined

Analysis by H. Sakai

Table 3. Calculated mineral composition of the analyzed phosphorites °/o.

Sample No.	Apatite	Dolomite	Calcite	Quartz	Silicate Minerals
Rt-2	61.10	6.36	0	14.75	17.79
Rt-4	56.16	21.53	0.31	9.00	13.00
Rt-5	55.38	2.36	0	16.35	25.91
Rt-7	71.50	6.87	0.21	11.05	10.37
Rt-12	68.12	0.82	3.47	18.10	9.49
Rt-19	73.84	0.64	3.24	12.75	9.53
Rt-20	77.22	0	0	10.35	12.43
Rt-21	62.66	0.65	0	12.55	24.14
Rt-23	80.34	1.60	0.60	6.75	10.71

Table 4. Chemical composition of the apatite in the phosphorites.

Sample No.	CaO	Na_2O	P_2O_5	CO_2	SO_3	F
Rt-2	34.4	0.63	23.5	0.96	1.17	2.88
Rt-4	31.2	0.63	21.6	0.88	1.02	2.80
Rt-5	29.6	0.62	21.3	0.87	0.97	2.48
Rt-7	37.8	0.73	27.5	1.13	1.20	3.21
Rt-12	36.7	0.60	26.2	1.08	1.02	2.99
Rt-19	40.6	0.62	28.4	1.17	1.04	3.17
Rt-20	39.2	0.67	29.7	1.2	1.10	3.32
Rt-21	35.4	0.58	24.1	0.99	0.77	2.77
Rt-23	44.5	0.72	30.9	1.28	1.17	3.38
Average	36.6	0.64	25.9	1.06	1.05	3.00

Note: Na_2O, P_2O_5, SO_3, and F are unadjusted rock compositions; CaO and CO_2 are adjusted rock compositions for those contained in dolomite and calcite.