

SULFUR ISOTOPE COMPOSITION OF SOME SULFIDE AND SULFATE MINERALS IN OHIO^{1, 2}

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Abstract. The isotopic compositions of sulfur in sulfide and sulfate minerals from northwestern Ohio vary by more than five percent. Sulfides (pyrite, sphalerite, and galena) from Gibsonburg and Clay Center have $\delta^{34}\text{S}$ values that are closely clustered about zero. Differences in the $\delta^{34}\text{S}$ values of coexisting sphalerite and galena suggest isotopic equilibration temperatures ranging from 43° to 63°C. Pyrite and marcasite from Pugh Quarry at Custar are strongly enriched in ^{32}S , but have significantly different $\delta^{34}\text{S}$ values. The sulfur of these minerals appears to have been fractionated by bacteria in marked contrast to the sulfur of pyrite, sphalerite and galena from Clay Center. The sulfur of marcasite is less enriched in ^{32}S compared to coexisting pyrite, perhaps because marcasite is a secondary mineral formed from H_2S produced by bacteria working on sulfate enriched in ^{34}S compared to normal marine sulfate. The $\delta^{34}\text{S}$ of anhydrite from the Tymochtee Formation is 24.9 per mil, which is in good agreement with values for marine sulfate of Silurian age. The celestite from vugs in the Greenfield Formation is enriched in ^{34}S relative to Silurian sulfate, indicating bacterial activity during or after dolomitization.

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Sulfide and sulfate minerals are widely distributed throughout the Paleozoic sedimentary rocks which form the bedrock of Ohio. The sulfides consist primarily of pyrite and marcasite, FeS_2 , but include also sphalerite, $(\text{Fe}, \text{Zn})\text{S}$, and galena, PbS . Notable occurrences of sphalerite have been described from the Serpent Mound structure in Adams County (Reidel, 1972, 1970; Stryker, 1971; Jacobs, 1971; Heyl and Brock, 1962). Other occurrences of sphalerite and galena have been reported from the area of the Findlay Arch in northwestern Ohio (Howard, 1959; Morrison, 1935; Botoman, 1975). Pyrite and marcasite occur in black shales and carbonate rocks. In addition, these minerals, as well as sphalerite and galena, are found as linings in cavities of dolomitic carbonates and as fillings of fractures and in brecciated rocks together with calcite, CaCO_3 , fluo-

rite, CaF_2 , celestite, SrSO_4 , anhydrite, CaSO_4 , and gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Although the sulfide minerals are widely distributed and fairly common, no economic concentrations have been found.

It is well known that sulfate minerals (anhydrite and gypsum) occur in the evaporite sequences of the Tymochtee Formation of the Salina Series of Upper Silurian age. In northern Ohio gypsum and anhydrite are currently being recovered from the Tymochtee Formation in a quarry operated by the Celotex Corporation in Portage Township of Ottawa County near Sandusky Bay. Celestite occurs primarily in the form of cavity fillings in dolomitic carbonate rocks and may have formed as a result of the exsolution of strontium during dolomitization of marine limestones. Some celestite also occurs in the marine evaporite rocks of the Tymochtee Formation.

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ISOTOPE GEOLOGY OF SULFUR

The isotopic composition (^{32}S , ^{33}S , ^{34}S , and ^{36}S) of sulfur in nature is subject to fractionation by a variety of physico-

chemical and biologic processes, including precipitation of sulfur-bearing compounds from aqueous solutions and bacterial reduction of sulfate to sulfide ions. The isotope geochemistry of this element has been described by Hoefs (1973). The isotopic composition of a sample of sulfur is expressed in terms of a parameter, $\delta^{34}\text{S}$, defined as:

$$(1) \quad \delta^{34}\text{S} = \left[\frac{(^{34}\text{S}/^{32}\text{S})_{\text{spl}} - (^{34}\text{S}/^{32}\text{S})_{\text{std}}}{(^{34}\text{S}/^{32}\text{S})_{\text{std}}} \right] \times 10^3$$

where $(^{34}\text{S}/^{32}\text{S})_{\text{spl}}$ is the ratio of these isotopes in the sample and $(^{34}\text{S}/^{32}\text{S})_{\text{std}}$ is the ratio in troilite (FeS) of the iron meteorite Canyon Diablo. A positive value of $\delta^{34}\text{S}$ implies enrichment in ^{34}S relative to the standard; a negative value indicates enrichment in ^{32}S .

It is well known that bacteria of the species *Desulfovibrio desulfuricans* reduce sulfate to hydrogen sulfide and in so doing enrich the sulfide phase in ^{32}S . Consequently, the $\delta^{34}\text{S}$ values of sulfide minerals which contain biogenic sulfur are generally negative and variable. This property has been used to distinguish sulfide minerals of sedimentary origin from those deposited by hydrothermal solutions of magmatic origin; in the latter case $\delta^{34}\text{S}$ values are close to zero. The preferential removal of ^{32}S by bacteria has caused a strong enrichment of marine sulfate in ^{34}S . Therefore, sulfate minerals in marine evaporite rocks have positive $\delta^{34}\text{S}$ values ranging from +10‰ to +30‰.

In addition, isotopic fractionation occurs during the precipitation of sulfide minerals from aqueous solutions. The extent of fractionation depends on the temperature and on the nature of the precipitating phases. Therefore, when two sulfide minerals form at the same temperature from the same solution they generally incorporate sulfur of differing isotopic composition. The difference, expressed as the difference between their respective $\delta^{34}\text{S}$ values, is inversely related to the square of the absolute temperature. The fractionation of sulfur isotopes between sphalerite and galena has been studied experimentally by Grootenboer and Schwarcz (1969), Kajiwaru and

Krouse (1971), and Czamanske and Rye (1974). The last two workers obtained a temperature dependence of the form:

$$(2) \quad \Delta_{\text{s-g}} = 7.0 \times 10^5 \text{T}^{-2}$$

where $\Delta_{\text{s-g}} = \delta^{34}\text{S}$ (sphalerite) - $\delta^{34}\text{S}$ (galena) and T is degrees Kelvin. This relationship was subsequently confirmed by Rye (1974) on the basis of comparisons

between filling temperatures of fluid inclusions in sphalerite and isotopic temperatures in a suite of sphalerite-galena pairs from Providencia, Mexico. The temperature dependence of isotope fractionation between pyrite and galena and between pyrite and sphalerite is given by:

$$(3) \quad \Delta_{\text{p-g}} = 11.0 \times 10^5 \text{T}^{-2}$$

$$(4) \quad \Delta_{\text{p-s}} = 3.0 \times 10^5 \text{T}^{-2}$$

(Kajiwaru and Krouse, 1971). These relationships make possible the determination of isotopic equilibration temperatures, provided the sulfide minerals formed at the same temperature from the same fluid under conditions of isotopic equilibrium.

The objective of this study is to report measurements of the isotopic compositions of sulfur in sulfide and sulfate minerals collected from five quarries in northwestern Ohio (figure 1) and to interpret the results in terms of the origin of the sulfur and the temperature of equilibration of the sulfide minerals.

RESULTS AND DISCUSSION

Sulfide minerals, including pyrite, marcasite, sphalerite, and galena, were collected from the working faces of three quarries identified in table 1. In addition, specimens of anhydrite and celestite were taken from two other quarries (table 1). The sulfide minerals were handpicked and their purity was checked by x-ray diffraction. The sulfate minerals required no purification. The isotope analyses were carried out by Geochron Laboratories, Inc., and are expressed in terms of the $\delta^{34}\text{S}$ notation relative to the meteorite sulfur standard.

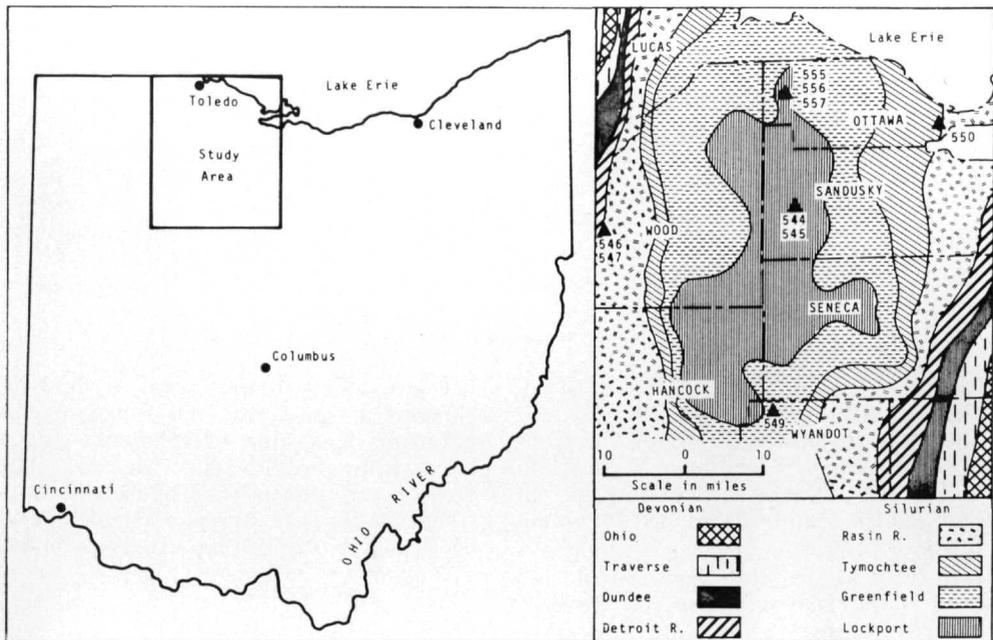


FIGURE 1. Maps showing location of the study area in northwestern Ohio (left) and the general geology of the collection sites (right). (Adapted from Janssens, 1970).

The analytical precision of $\delta^{34}\text{S}$ values is $\pm 0.1\text{‰}$ (table 1).

The $\delta^{34}\text{S}$ values of pyrite, sphalerite, and galena from Gibsonburg and Clay Center, Ohio, range from -3.3‰ to $+7.0\text{‰}$. The enrichment of these minerals in ^{34}S decreases in the order pyrite > sphalerite > galena; this is typical for these minerals in ore deposits elsewhere. Their $\delta^{34}\text{S}$ values are closely clustered about zero, suggesting, but not proving, that the sulfur had a magmatic origin. The temperatures of isotope equilibration for mineral pairs from each locality have been calculated by means of equations 2, 3, and 4. The results are compiled in table 2.

The temperatures indicated by the isotope composition of sulfur in these minerals are uniformly low and range from an unlikely value of zero to 63°C . The sphalerite-galena isotope thermometer is more reliable than those of the other mineral pairs because it has been tested by comparison with filling temperatures of fluid inclusions. Consequently, the best estimates of the isotope equilibration temperatures indicated by these data range from 43° to 63°C .

The validity of these temperatures cannot be demonstrated directly because no filling temperatures of fluid inclusions in sphalerite from Ohio have been reported. However, a comparison is possible with lead-zinc deposits in the upper Mississippi Valley of Wisconsin, Iowa, and Illinois. The ore in this district occurs primarily in fractures and solution cavities in limestone and dolomite of Ordovician age. Pinckney and Rafter (1972) reported $\delta^{34}\text{S}$ values for sphalerite and galena from the Booty mine, New Diggings, Wisconsin. The $\Delta^{34}\text{S}$ values of these minerals range from 7.3 to 2.6‰ , corresponding to temperatures from 36° to 235°C , based on equation 2. Pinckney and Rafter were able to distinguish bands of mineralization formed at high temperature (150° – 260°C) from later bands formed at lower temperatures (50° – 100°C). Recalculation of their data for the low-temperature band by means of equation 2 results in a temperature range of 36° to 87°C . These values are in reasonably good agreement with filling temperatures ranging from 75° to 121°C reported by Baily and Cameron (1951) for fluid inclusions from this district. Therefore, tempera-

TABLE 1
Isotopic Compositions of Sulfide and Sulfate Minerals from Northwestern Ohio.

Sample #	Mineral	Formation	Description	$\delta^{34}\text{S}\%$
Charles Pfizer and Co., Gibsonburg, Madison Twp., Sandusky County				
544	Galena	Lockport Group Middle Silurian	Crystals of 1-5 mm in vein with fluorite	- 2.2
545	Sphalerite	same	Crystals of 2-8 mm in vein with fluorite and in vugs in dolomite	+ 4.8
Edward Kramer and Sons, Inc., Clay Center, Allen Twp., Ottawa County				
555	Galena	Lockport Group	Crystals of 1-10 mm in vein with fluorite and in vugs in dolomite	- 3.3
556	Sphalerite	same	Crystals of 1-20 mm in vein with fluorite	+ 2.9
557	Pyrite	same	Horizontal veinlet, 1-3 cm thick about 3 m long in dolomite	+ 7.0
Pugh Quarry Co., Custar, Milton Twp., Wood County				
546	Pyrite	Detroit River Lower Devonian	Massive aggregate in brecciated dolomite	-21.9
547	Marcasite	same	Massive aggregate in brecciated dolomite	-15.4
Celotex Corp., Gypsum, Portage Twp., Ottawa County				
550	Anhydrite	Tymochtee Upper Silurian	Interbedded with dolomite	+24.9
National Lime and Stone Co., Findlay, Crawford Twp., Wyandot County				
549	Celestite	Greenfield Upper Silurian	Vug filling in dolomite	+32.4

tures ranging from 43° to 63°C for sphalerite-galena pairs in northwestern Ohio are not unreasonable. Nevertheless, isotopic equilibration is a slow process at low temperatures and the possibility cannot be ruled out that the sulfide minerals from Gibsonburg and Clay Center are not in isotopic equilibrium.

The $\delta^{34}\text{S}$ values of pyrite and marcasite

from Pugh Quarry in Custar, Ohio, are -21.9 and -15.4‰, respectively. These values contrast strongly with the $\delta^{34}\text{S}$ value of +7.0‰ of the pyrite from Clay Center. The strong enrichment in ^{32}S of the pyrite and marcasite from Pugh Quarry suggests that the sulfur in these minerals is of biogenic origin. These data indicate the presence of two suites

TABLE 2
*Isotopic Equilibration Temperature for Sulfide Minerals from
 Gibsonburg and Clay Center, Ohio.¹*

Locality	Minerals	$\Delta^{34}\text{S}\%$	Temperature °C
Gibsonburg	sphalerite-galena	7.0	43
Clay Center	sphalerite-galena	6.2	63
Clay Center	pyrite-sphalerite	4.1	~0
Clay Center	pyrite-galena	10.3	54

¹The temperatures are based on equations 2, 3 and 4 given in the text.

of sulfide minerals containing sulfur having quite different histories. The pyrite that is associated with sphalerite and galena at Clay Center could have an igneous-hydrothermal origin, whereas the pyrite and marcasite at Pugh Quarry appear to be sedimentary in origin.

The anhydrite and celestite are strongly enriched in ^{34}S compared to the sulfide minerals. The $\delta^{34}\text{S}$ value of the anhydrite from the Tymochtee Formation is +24.9‰. This value is in good agreement with the isotopic composition of marine sulfate of Silurian age which had a $\delta^{34}\text{S}$ value of +24.2‰ (Sangster, 1968). The celestite, on the other hand, has a $\delta^{34}\text{S}$ value of +32.4‰ and is therefore significantly enriched in ^{34}S compared to normal Silurian sulfates. The occurrence of the celestite as a vug filling in dolomite of the Greenfield Formation indicates that it was formed some time after deposition of this formation, perhaps during dolomitization. It is possible, therefore, that the sulfate of the celestite was acted upon by bacteria which partially reduced sulfate of Silurian age to sulfide and thereby enriched the residual sulfate in ^{34}S . The enrichment of the celestite in ^{34}S compared to anhydrite of Silurian age is therefore compatible with the secondary origin of this mineral. The H_2S produced from the sulfate may have been precipitated locally as either pyrite or marcasite. The isotopic composition of sulfur in such secondary sulfide minerals should differ from that formed at the time for deposition of the rocks because of the limited supply of sulfate ion and different living conditions for the bacteria. The marked difference in the $\delta^{34}\text{S}$ values of pyrite and marcasite from Pugh Quarry may be due to this cause.

The isotopic composition of sulfur in sphalerite and galena from northwestern Ohio, suggests, but does not prove, that the sulfur, and perhaps the metals as well, had a magmatic source located presumably in the underlying Precambrian basement. The difference in $\delta^{34}\text{S}$ values between coexisting sphalerite and galena indicates temperatures of formation ranging from 43° to 63°C. Such low temperatures are not unreasonable, but should be confirmed by work with fluid

inclusions. Temperatures indicated by pyrite-sphalerite and pyrite-galena are discordant either because of the unreliability of the experimentally determined calibration equations or because isotopic equilibrium was not established, or both.

The $\delta^{34}\text{S}$ of anhydrite from the Tymochtee Formation is in good agreement with the isotope composition of marine sulfate from other evaporite basins of Silurian age. This suggests that the Silurian evaporite rocks of Ohio were deposited in a basin which interacted with the open ocean. The celestite of the Greenfield Formation is significantly enriched in ^{34}S , presumably because of bacterial fractionation that took place during or after dolomitization of the rocks.

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