

ISOTOPIC STUDY OF A SIDERITE CONCRETION, TUSCARAWAS COUNTY, OHIO¹

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ABSTRACT. A carbonate concretion from the shale bed overlying the No. 5 coal of Pennsylvanian age in Tuscarawas County is composed of siderite and contains pyrite, barite, sphalerite and traces of calcite in its interior and in fractures. The siderite has $\delta^{13}\text{C} = +0.65\%$, $\text{Sr} = 289$ ppm and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7110 \pm 0.0009$. These results indicate that the siderite was deposited from brackish water in the pore spaces of the sediment and discredit the hypothesis that the carbonate ions originated by oxidation of peat or organic material. The barite has $\delta^{34}\text{S} = -4.6\%$, indicating that it was not precipitated from sea water. Pyrite and sphalerite have $\delta^{34}\text{S} = -10.8\%$ and -4.6% , respectively, and were not deposited in isotopic equilibrium with each other. The sulfur in all three minerals is enriched in ^{32}S as a result of bacterial reduction of sulfate to sulfide.

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INTRODUCTION

Carbonate concretions exist in many shale formations in the Paleozoic bedrock of Ohio. Clifton (1957) summarized their occurrence in the Ohio Shale of Upper Devonian age. Olson (1975) reported average concentrations for $\text{FeO} = 2.39 \pm 0.11\%$ and $\text{Sr} = 75.3 \pm 1.6\%$ ppm in a profile across a ferroan dolomite concretion from the Olentangy Shale in Delaware County. A complete chemical analysis of a concretion from the Olentangy Shale was published by Westgate (1926).

The concretions apparently formed by precipitation of minerals from aqueous so-

lutions after deposition of the sediment. They are composed not only of carbonate minerals but also may contain layers of pyrite or marcasite. Therefore, the geochemical process by which they formed must be capable of producing both carbonate and sulfide minerals. Barth (1975) proposed that concretions in the lower section of the Ohio Shale north of Columbus were formed by the action of bacteria reducing sulfate ions to H_2S and oxidizing organic compounds to CO_2 . These gases dissolved in the pore water of the sediment and caused precipitation of iron sulfide and carbonate minerals, respectively.

Concretions also are found in the shale units between the coal seams of Pennsylvanian age in Tuscarawas County. In this

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case, the presence of peat and organic material in the shale may have provided an abundant food source for bacteria. The CO_2 released by their metabolic activity may have contributed to the growth of carbonate concretions in the overlying shale units. We have attempted to test this hypothesis by a study of one concretion collected from a shale unit just above the No. 5 coal seam exposed at the strip mine of the Eberhart Coal Co. in Tuscarawas County, Ohio.

MINERAL COMPOSITION

The concretion was about 30 x 18 x 13 cm in size. The bulk of it was composed of siderite (FeCO_3) identified by x-ray diffraction and we detected small amounts of quartz and kaolinite or chlorite in the insoluble residue of the siderite. The interior contained a veinlet of pyrite (FeS_2) covered by a layer of barite (BaSO_4). A few tabular crystals of dark brown sphalerite (Zn, Fe)S, up to 2 cm in diameter, were embedded in the barite. Both pyrite and barite occurred in fractures that extended from the outside of the concretion into the interior. Pyrite appears to have formed first followed by barite and sphalerite. The presence of a small amount of calcite (CaCO_3) in the interior of the concretion was detected by the reaction with HCl.

CARBON AND STRONTIUM

The isotopic composition of carbon in the siderite (table 1) indicates the source of carbon in this mineral. Studies of the isotope composition of carbon in nature, re-

viewed by Faure (1977), have revealed that plants are enriched in ^{12}C as a result of photosynthesis. Since coal, petroleum, and natural gas formed from plant tissue, they are enriched in ^{12}C and have $\delta^{13}\text{C}$ values that are commonly in excess of -25% relative to the PDB standard. By contrast, calcite in marine limestones has $\delta^{13}\text{C}$ values close to zero. The use of carbon isotopic compositions to determine the environment of deposition of siderite concretions and to identify the source of the carbon is described in detail by Weber *et al* (1964). The siderite of the concretion from Tuscarawas County has a $\delta^{13}\text{C}$ value of $+0.65\%$. According to the criteria of Weber *et al* (1964), this value indicates a restricted marine (brackish) environment and thereby discredits the hypothesis that this concretion formed from CO_2 derived from bacterial oxidation of peat or coal.

The siderite has a Sr concentration of 289 ppm, determined by x-ray fluorescence. Its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is 0.7110 ± 0.0009 . The variation of the isotopic composition of Sr in the oceans during the past 600 million years has been reviewed by Faure and Powell (1972) and by Faure (1977). A study by Mukhopadhyay and Brookins (1976) indicates that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of limestones in the Madera Formation (Pennsylvanian) of New Mexico varied from 0.7066 to 0.7118. The value obtained for the concretion from Tuscarawas County is near the high end of this spectrum and confirms a brackish near-shore environment of deposition.

SULFUR

The isotopic composition of sulfur in marine sulfate deposits varies widely depending on their geologic age. The variation is the result of isotope fractionation during the reduction of sulfate to sulfide ion by the bacterium *Desulfovibrio desulfuricans*. This process enriches the sulfide in ^{32}S and concentrates ^{34}S in the residual sulfate. The systematics of sulfur isotope fractionation have been reviewed by Faure (1977). According to Claypool *et al* (1980),

TABLE 1

Analytical Data for Concretion from Eberhart Coal Co., Tuscarawas County, Ohio.*

	$\delta^{34}\text{S}$ (‰)	$\delta^{13}\text{C}$ (‰)	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$
Siderite	—	+0.65	289	0.7110 ± 0.0009
Barite	-4.6	—	—	—
Sphalerite	-4.6	—	—	—
Pyrite	-10.8	—	—	—

*The isotopic compositions of sulfur and carbon were determined by Geochron Laboratories. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was measured by the authors and was corrected for isotope fractionation to a value of 0.1194 for the $^{86}\text{Sr}/^{88}\text{Sr}$ ratio.

sulfate deposits of Pennsylvanian age have $\delta^{34}\text{S} = +15.5\%$, relative to sulfur in the iron meteorite Canyon Diablo. During the past 600 million years, the $\delta^{34}\text{S}$ values of marine sulfate have varied between limits of $+10\%$ and $+30\%$, indicating varying enrichment in ^{34}S .

The $\delta^{34}\text{S}$ of the barite in the concretion (table 1) is -4.6% , indicating that the sulfate was *not* derived from sea water. The negative value is characteristic of sulfide produced by bacteria and suggests that the sulfate may have formed by oxidation of sulfide minerals in adjacent shale units. Since oxidation of sulfide to sulfate does not cause isotope fractionation (Claypool *et al* 1980), these sulfide minerals should have had a similar isotopic composition as the barite.

The $\delta\text{S}^{34}\text{S}$ values of the pyrite and sphalerite in the concretion are -10.8% and -4.6% , respectively (table 1). The enrichment in ^{32}S of both minerals is compatible with bacterial fractionation of marine sulfate discussed above. The difference between the $\delta^{34}\text{S}$ values corresponds to an isotope equilibration temperature of -33.4°C (Orr 1980). This result is not sensible and indicates that pyrite and sphalerite in the concretion did not form in isotopic equilibrium with a common reservoir. The large difference in the $\delta^{34}\text{S}$ values probably indicates that pyrite and sphalerite formed at different times from solutions containing sulfide of different isotopic composition. This conclusion is supported by the evidence that pyrite was deposited first, followed by barite and sphalerite. A more extensive discussion of sulfur-isotope equilibration temperatures for pyrite, sphalerite and galena in Ohio is given by Botoman and Faure (1976).

The results of this study indicate that the concretion formed by precipitation of siderite from brackish water and that very little, if any, carbonate ion originated by oxida-

tion of organic material. The concretion was subsequently fractured, and pyrite, followed by barite and sphalerite, was deposited in its interior. The sulfur in the barite is not of marine origin but may have formed by oxidation of sulfide previously enriched in ^{32}S by sulfur-reducing bacteria. The pyrite and sphalerite were not in isotopic equilibrium at the time of deposition.

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