

A NEW PARAGENESIS AND NEW LOCALITIES FOR WITHERITE

STEVEN C. CHAMBERLAIN AND WILLIAM P. DOSSERT

Institute for Sensory Research, Syracuse University, Syracuse, New York 13210, U.S.A.

DONALD I. SIEGEL

Department of Geology, Syracuse University, Syracuse, New York 13210, U.S.A.

ABSTRACT

Witherite BaCO_3 occurs in the mineralized septarian fractures of concretions in the Chittenango Member of the Marcellus Formation of the Middle Devonian Hamilton Group at three occurrences in Onondaga County, New York. The minerals occurring in the septarian fractures, in order of formation, are, pyrite I and calcite I $[(\text{Ca}_{0.96}\text{Mg}_{0.02}\text{Fe}_{0.02})\text{CO}_3]$, calcite II $[(\text{Ca}_{0.96}\text{Mg}_{0.02}\text{Fe}_{0.02})\text{CO}_3]$ and barite, pyrite II, ferroan dolomite $[\text{Ca}(\text{Mg}_{0.57}\text{Fe}_{0.43})(\text{CO}_3)_2]$ and calcite III, quartz, calcite IV $[(\text{Ca}_{0.98}\text{Mg}_{0.01}\text{Fe}_{0.01})\text{CO}_3]$, strontianite, witherite, calcite V. Both the calcite matrix $[(\text{Ca}_{0.97}\text{Mg}_{0.02}\text{Fe}_{0.01})\text{CO}_3]$ of the concretions and the mineralization in the septarian fractures contain abundant hydrocarbon. Like other witherite, this witherite formed from the alteration of barite. The geological setting, however, precludes the normal alteration of barite by hydrothermal solutions rich in carbonate. The composition of the stable isotopes of carbon, in witherite from the septarian concretions, is significantly enriched in the heavy isotope ^{13}C ($+2.11\% \leq \delta^{13}\text{C} \leq +14.77\%$ PDB) compared to witherite from 26 other worldwide localities ($-29.41\% \leq \delta^{13}\text{C} \leq +1.16\%$ PDB). These data suggest that this witherite formed as the result of sulfate reduction and methane fermentation by bacteria in anoxic groundwaters. This represents both a new mode of occurrence for witherite and a new mechanism for its formation from barite.

Keywords: witherite, barite, carbonates, sulfate reduction, methane fermentation, stable isotopes, New York.

SOMMAIRE

La withérite se trouve dans les fractures septariennes minéralisées de concrétions du membre Chittenango de la formation Marcellus du groupe Hamilton (Dévonien moyen). Trois gîtes ont été trouvés dans le comté d'Onondaga, état de New-York, aux États-Unis. Les minéraux qui cristallisent dans ces fractures sont les suivants (dans l'ordre de leur formation): pyrite I et calcite I $[(\text{Ca}_{0.96}\text{Mg}_{0.02}\text{Fe}_{0.02})\text{CO}_3]$, calcite II $[(\text{Ca}_{0.96}\text{Mg}_{0.02}\text{Fe}_{0.02})\text{CO}_3]$ et barytine, pyrite II, dolomite à Fe^{2+} $[\text{Ca}(\text{Mg}_{0.57}\text{Fe}_{0.43})(\text{CO}_3)_2]$ et calcite III, quartz, calcite IV $[(\text{Ca}_{0.98}\text{Mg}_{0.01}\text{Fe}_{0.01})\text{CO}_3]$, strontianite, withérite, calcite V. Tant la pâte (matrix) des concrétions, constituée de calcite $[(\text{Ca}_{0.97}\text{Mg}_{0.02}\text{Fe}_{0.01})\text{CO}_3]$, que la minéralisation des fractures septariennes contient des hydrocarbures en abondance. Ici comme ailleurs, la withérite s'est formée par alté-

ration de la barytine, mais les données géologiques excluent la possibilité de l'altération normale de la barytine par solutions hydrothermales carbonatées. La composition des isotopes stables du carbone, dans la withérite des concrétions, est notablement plus riche en isotope lourd ^{13}C ($+2.11\% \leq \delta^{13}\text{C} \leq +14.77\%$ PDB) que dans la withérite de 26 autres localités ($-29.41\% \leq \delta^{13}\text{C} \leq +1.16\%$ PDB). Ces résultats portent à croire que la withérite d'Onondaga s'est formée par réduction du sulfate et fermentation du méthane par bactéries dans des eaux souterraines anoxiques. Ce serait là, à la fois, un nouveau type de gisement pour la withérite et un nouveau mécanisme pour sa formation à partir de la barytine.

(Traduit par la Rédaction)

Mots-clés: withérite, barytine, carbonates, réduction des sulfates, fermentation du méthane, isotopes stables, New-York.

INTRODUCTION

Although the orthorhombic barium carbonate witherite is the second most common barium mineral, it is not of widespread occurrence (Palache *et al.* 1951, Deer *et al.* 1962). Witherite usually occurs as a product of late-stage alteration of barite in low-temperature hydrothermal veins (*e.g.*, Hancox 1934, Sidorenko 1947, Weller *et al.* 1952). In this paragenesis, the witherite forms from the action of carbonated waters on pre-existing barite as the solubility of witherite decreases and the solubility of barite increases with increasing temperature (Holland 1967, Lydon *et al.* 1979). Recently, one of us discovered an occurrence of witherite in fracture fillings in septarian concretions in Devonian shales near Syracuse, New York (Dossert *et al.* 1984). Subsequently, we have discovered several other occurrences in the same geological setting. These occurrences represent a new paragenesis for witherite, one quite different from any previously described. Here we describe the location and geology of the occurrences, the mineral assemblage in the septarian fracture-fillings, the paragenesis, and the carbon and oxygen stable-isotope compositions of this witherite and that from many other localities.

METHODS

The identity of each witherite specimen was verified by testing for effervescence in dilute HCl, by flame testing for the presence of barium, and by standard X-ray-diffraction methods using a General Electric X-ray diffractometer and $\text{CuK}\alpha$ radiation. Samples of witherite were powdered, then half the sample was tested as above and half was used for determination of stable-isotope compositions. The stable-isotope compositions for both carbon and oxygen in witherite were made by mass spectrometry by the Global Geochemistry Corporation and are reported relative to the PDB standard. The identification of other carbonate species was made by a combination of chemical analysis and X-ray diffraction. For chemical analysis, samples of carbonate minerals were dissolved in dilute nitric acid. The supernatant liquid was then analyzed for calcium, magnesium, iron, barium and strontium by direct-current plasma-emission spectroscopy using a Beckman Spectrospan V spectrometer. Standards were prepared with matched matrices, and lithium was added to enhance sensitivity.

RESULTS

Location and geological setting of the new occurrences

Witherite occurs in septarian fracture-fillings in a horizon of large septarian concretions in the Middle Devonian Hamilton Group. This sequence was deposited as part of the clastic wedge of the Devo-

nian Catskill deltaic complex (Brett & Baird 1985). The concretions constitute a band in the black shales of the Chittenango Member of the Marcellus Formation, located about 30 m above the boundary between the Marcellus Formation and the Onondaga limestone. Three exposures of this band of concretions that contain witherite are shown in Figure 1. Occurrence 1 is a small shale pit intermittently operated by the Town of Pompey just south of Route 173 and east of Gates Road, east of the village of Jamesville (Jamesville Quadrangle, New York – Onondaga County, USGS 7.5-minute topographic series). Occurrence 2 is along the west side of Cedarvale Road 1.75 km south of Cards Corners, where the West Branch of Onondaga Creek cuts through Onondaga Hill (Marcellus Quadrangle, New York – Onondaga County, USGS 7.5-minute topographic series). Occurrence 3 is southeast of the village of Marcellus, in a small roadcut on the north side of Pleasant Valley Road, 1.3 km east of its intersection with Route 175 (Marcellus Quadrangle, New York – Onondaga County, USGS 7.5-minute topographic series). At occurrences 1 and 3, only one layer of large concretions is exposed. At occurrence 2, several layers of concretions are exposed, but only one layer is septarian. Hand specimens of septarian fracture-fillings from these three occurrences are virtually indistinguishable. Although the qualitative description applies to all three occurrences, the quantitative data presented here pertain to specimens from occurrence 1.

Description of septarian concretions

The mineralized septarian concretions form a sin-

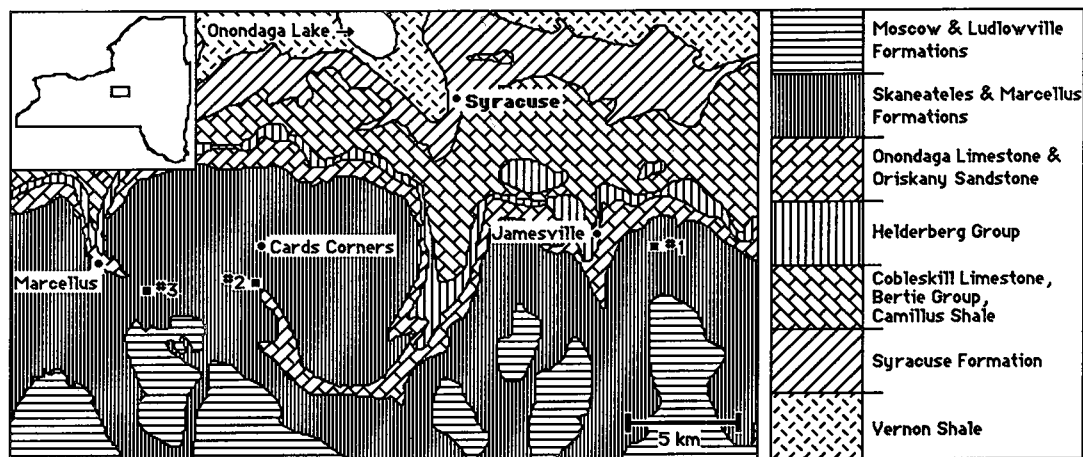


FIG. 1. Three new occurrences of witherite in the Marcellus Formation near Syracuse, New York. The relationship of the occurrences to the local stratigraphy is shown. Detailed descriptions of the locations are in the text. (Adapted from the Finger Lakes Sheet of the Geologic Map of New York, published by The University of the State of New York, 1961).

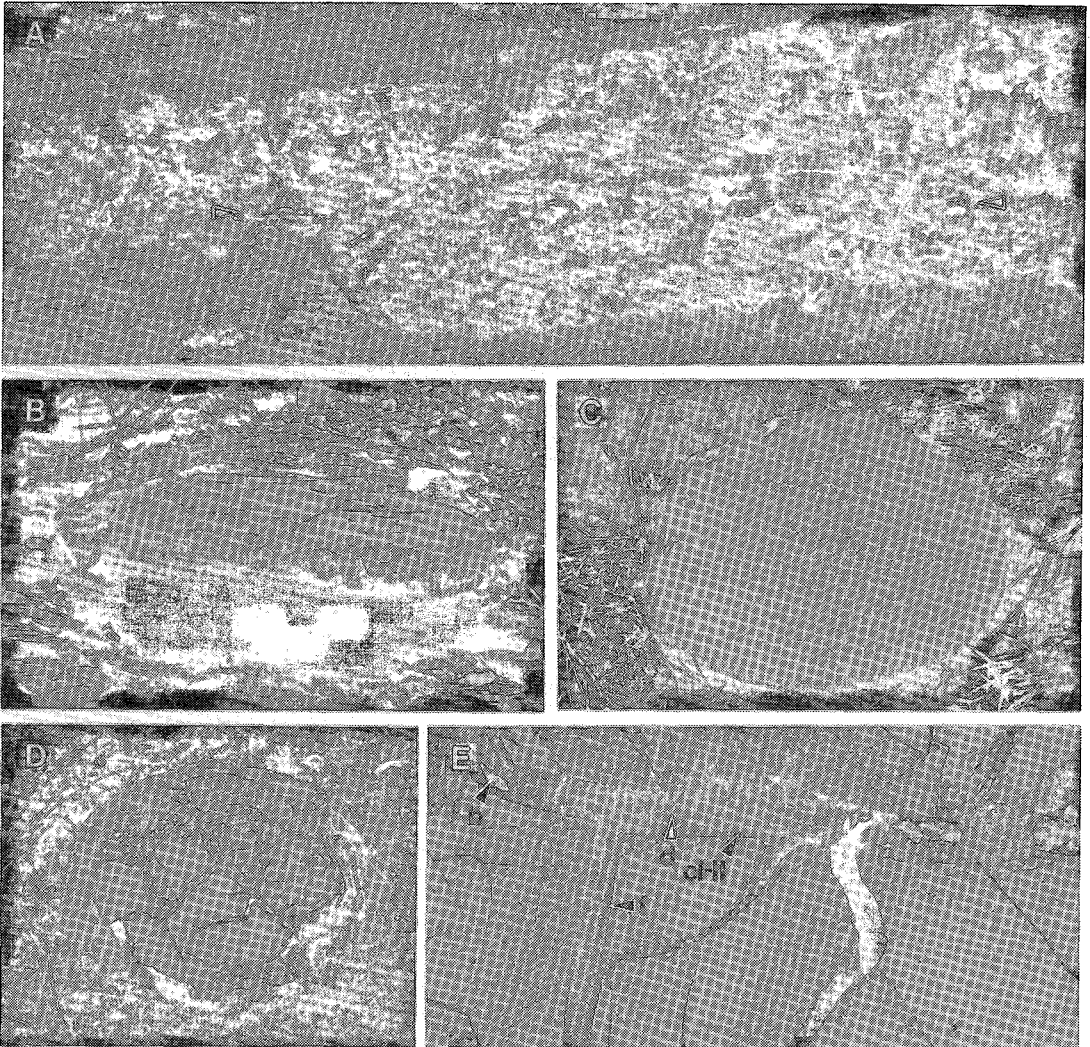


FIG. 2. Septarian concretions containing witherite in the Chittenango Member of the Marcellus Formation. A. Exposure of the Chittenango Member in the shale pit at occurrence 1. A single intermittent layer of concretions is shown between the arrows. B. Concretion *in situ* at occurrence 2. Note the bending of the shale lamination around the concretion. C. One of many concretions exposed and discarded during quarrying operations at occurrence 1. Note the visible external fractures that give groundwater access to the interior. D. Concretion partly broken away to reveal internal septarian fractures. E. Mineralization of septarian fractures. b barite, d ferroan dolomite, cI-II calcite I and calcite II, f late fractures running along edges of mineralized septarian fractures.

gle intermittent layer in the bedding of the enclosing shales (Fig. 2A). The lamination of the shale bends around the body of the concretion (Fig. 2B) consistent with formation of the concretions early in the burial sequence, before compaction of the enclosing sediments (Dix & Mullins 1985). The concretions have a circular profile in the bedding plane and an elliptical profile normal to the bedding plane (Figs. 2B, C), and range in size from 50 cm in diameter and 30 cm thick to 1 m in diameter and 50

cm thick. The boundary between the concretion and the enclosing shale is smooth and distinct. All of the concretions in this horizon have well-developed septarian fractures (Figs. 2D, E) that do not extend to the surface of the concretion (Figs. 2B, C). The interior of the concretions is presently accessible to ground waters, but through late fractures (Fig. 2C). Normally the interior is dry when opened, but after a brief shower, it is wet. Also, breaking intact concretions reveals internal fractures that cut across the

septarian structure, along which oxidation and weathering (e.g., surficial alteration of ferroan dolomite to goethite) have occurred.

Description of mineral species

The septarian fractures are mineralized from the edges in a sequence that is remarkably uniform from concretion to concretion. The major features of this mineralization are shown in Figure 3.

Matrix. The walls of the septarian fractures are composed of the same material as the body of the concretion. The matrix is a fine-grained calcite containing disseminated particles and larger globular masses of hydrocarbon. The composition of the car-

bonate (calcite) in the matrix is $(Ca_{0.97}Mg_{0.02}Fe_{0.01})CO_3$.

Calcite I. The walls of most septarian fractures are lined with fine black rhombohedral crystals of calcite. The composition of this calcite is $(Ca_{0.96}Mg_{0.02}Fe_{0.02})CO_3$. The crystals are too small and rough to measure with certainty, but the primary form appears to be the steep rhombohedron $\{40\bar{4}1\}$.

Pyrite I. Microscopic crystals of pyrite are observed to be variously on, within, or underneath calcite I, depending upon which fractures are examined. The crystals are dominated by the cube $\{001\}$ modified by the octahedron $\{111\}$.

Calcite II. A second phase of more coarsely crystallized calcite covers the first. This calcite is dark brown next to calcite I, and grades through tan to white toward the centre of the fracture. The overall composition of this calcite is $(Ca_{0.96}Mg_{0.02}Fe_{0.02})CO_3$, and the primary crystal-form is the trigonal scalenohedron $\{21\bar{3}1\}$.

Barite. Coarse laths of white to colorless barite form latticeworks that span the fractures. Many crystals show microscopic phantoms of particles of hydrocarbon, indicating successive phases of barite formation.

Pyrite II. The surfaces of barite crystals are sparsely coated with a second generation of pyrite that began to crystallize just before the barite finished. The morphology of these crystals is unusual. They were measured by R. Peter Richards to determine the forms present. Two distinct habits are found. One is equant (Fig. 4A) and shows relatively equal development of the octahedron $\{111\}$, the trisoctahedra $\{144\}$ and $\{188\}$, the trapezohedron $\{113\}$ and the diploid $\{1107\}$, with lesser development of somewhat curved faces of the dodecahedron $\{011\}$. Note that the indices of the diploid are approximate. The other habit is flattened normal to the three-fold axis $[111]$ (Fig. 4B) and is dominated by the trisoctahedron $\{144\}$ with lesser development of the trisoctahedron $\{188\}$ and the trapezohedron $\{113\}$.

Dolomite and Calcite III. Most of the remaining space in the septarian fractures is filled with reddish brown carbonate. Chemical analysis, thin sections, and X-ray diffraction indicate that this is a mixture of calcite and a member of the dolomite group. The bulk composition of the mixture is $(Ca_{0.58}Mg_{0.24}Fe_{0.18})CO_3$. Assuming that the calcite is pure $CaCO_3$ gives a composition for the dolomite-group species of $Ca(Mg_{0.57}Fe_{0.43})(CO_3)_2$, which is a ferroan dolomite. Occasionally, cavities in the massive dolomite are lined with characteristic curved crystals of dolomite of basic rhombohedral form $\{10\bar{1}1\}$. Calcite III occurs as small grains that can only be observed in thin section.

Quartz. Transparent, colorless crystals of quartz occur on dolomite crystals or on barite crystals in

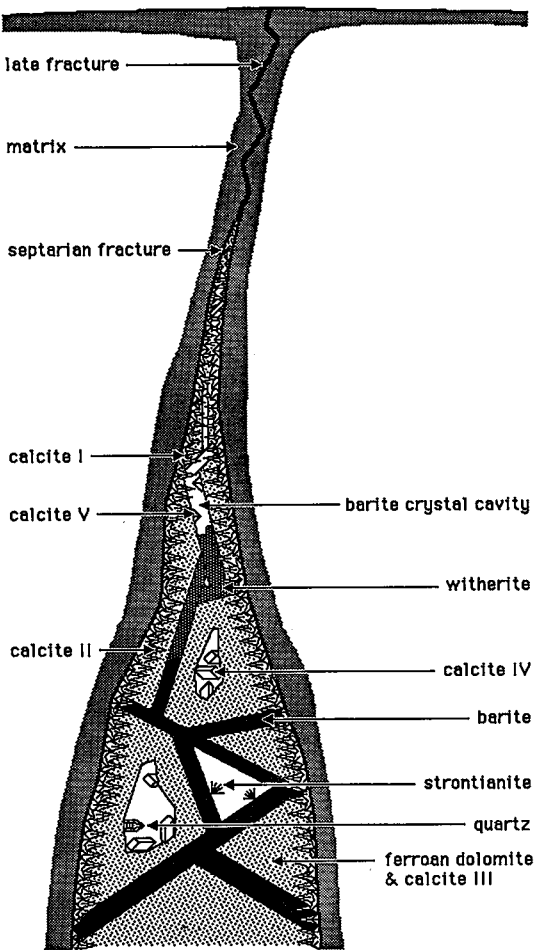


FIG. 3. Diagram illustrating the mineralization of septarian fractures. Late fractures connect the mineralized septarian fractures in the centre (bottom) with the outside of the concretion (top). See text for details.

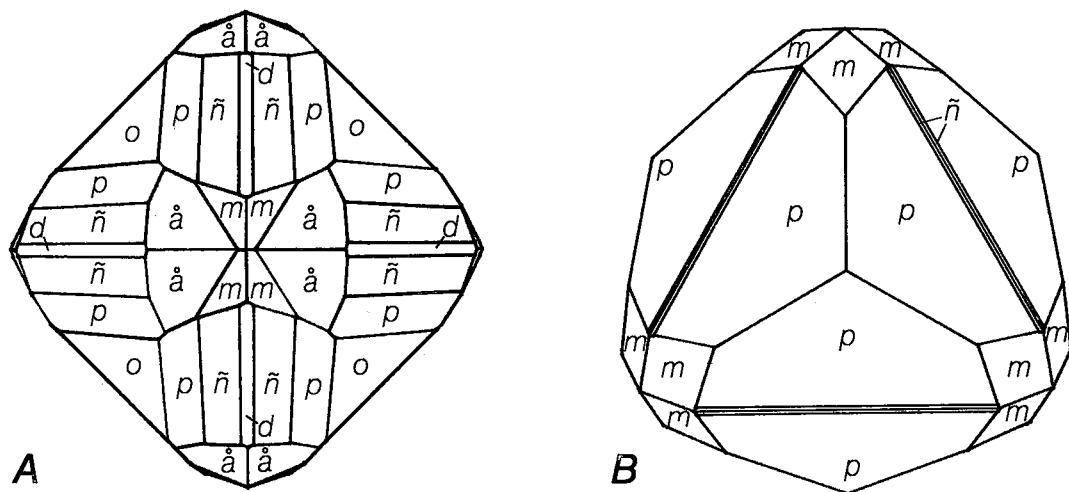


FIG. 4. Drawings of the two major habits of pyrite II. A. Equant habit viewed along a two-fold axis. The octahedron $o\{111\}$, two trisoctahedra $p\{144\}$ and $\tilde{n}\{188\}$, diploid $\tilde{a}\{1\ 10\ 7\}$ (approximately) and trapezohedron $m\{113\}$ show relatively equal development. The dodecahedron $d\{011\}$ shows less development. B. Flattened habit viewed along a three-fold axis. The trisoctahedron $p\{144\}$ dominates. The trisoctahedron $\tilde{n}\{188\}$ and the trapezohedron $m\{113\}$ are smaller. Note that the designations \tilde{n} and \tilde{a} are temporary and are not intended as permanent designations for the forms $\{188\}$ and $\{1\ 10\ 7\}$, respectively.

cavities that were not filled with dolomite. Some crystals show hydrocarbon inclusions. Crystals are prismatic with $\{10\bar{1}0\}$ and are terminated by rhombohedra $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$. Some terminations show nearly equal development of the rhombohedra; others are dominated by one or the other.

Calcite IV. Transparent, colorless crystals of calcite occur on dolomite or quartz crystals. The composition of this calcite is $(\text{Ca}_{0.98}\text{Mg}_{0.01}\text{Fe}_{0.01})\text{CO}_3$. The primary crystal form is the rhombohedron $\{10\bar{1}1\}$, which is modified by other forms in complex ways.

Strontianite. Strontianite occurs as sprays of minute white to colorless acicular crystals on calcite IV or directly on barite in cavities not filled with dolomite. The crystals are curved and striated and appear to have the same morphology as those described by Speer (1976).

Barite-dissolution cavities. In all concretions examined, a peripheral zone of the septarian fractures exhibits selective dissolution of the barite crystals (Fig. 5). The walls of these cavities are unaltered and are composed principally of matrix, calcite I and II, dolomite, and pyrite I and II. In different concretions and in different fractures within a concretion, the relationships between the wall minerals and the barite may be different.

Witherite. Witherite occurs as an alteration product of barite. Broken concretions usually exhibit a peripheral zone of barite-dissolution cavities, an intermediate zone where the barite has been replaced

by opaque white witherite, and a central zone of unaltered, white to translucent barite (Fig. 5). The witherite occurs as pseudomorphs after barite, as botryoidal coatings on dolomite, quartz and calcite IV in open cavities or on the walls of barite-dissolution cavities, and as individual twinned crystals or groups of twinned crystals of hexagonal outline (Fig. 6).

Calcite V. Rarely, minute isolated brown crystals of calcite are found on the walls of barite-dissolution cavities or on witherite. The primary form appears to be the steep rhombohedron $\{40\bar{4}1\}$.

Goethite. Goethite has formed as a superficial alteration product of pyrite II in voids between barite crystals not filled by ferroan dolomite, of both pyrite I and II on the walls of barite-dissolution cavities, and of ferroan dolomite along surfaces of recent fractures.

Paragenesis

We have divided the paragenetic sequence into six stages based largely on the sequence of carbonate minerals formed. This sequence is derived from exhaustive independent examination by two of us of 41 specimens from 18 different concretions. Our results are summarized in Figure 7.

Stage I. Formation and Fracturing of the Concretion. The initial step in the formation of the mineral assemblage was the precipitation and subsequent fracturing of the body of the concretion.

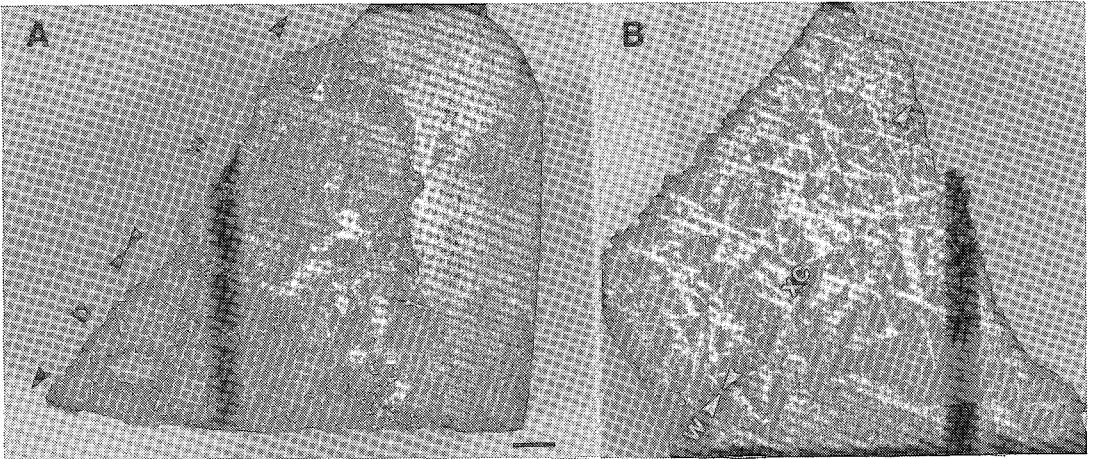


FIG. 5. Arrangement of unaltered barite, witherite, and barite-dissolution cavities in septarian concretions. The arrows lie along a line from the centre (lower left) toward the outside (upper right) of each concretion. A. Toward the centre is a zone of unaltered barite crystals (b) adjacent to a zone where the barite has been replaced by witherite (w). B. A small zone of witherite (w) toward the centre of the concretion is adjacent to a well-developed external zone of barite-dissolution cavities (xc). The length of the bar in A represents 9 mm in A and 16 mm in B.

Stage II. Formation of Calcite and Barite. All but a few septarian fractures are lined with a thin layer of calcite I. Those that are not may represent a second stage of fracturing. Pyrite I formed during this stage, apparently concurrently with calcite I, since it sometimes is under, sometimes within and often on top of calcite I. Calcite I contains significant hydrocarbon as inclusions. Calcite II can always be distinguished from calcite I by its different color and crystal form. In all cases, calcite II formed on top of calcite I except in those fractures where calcite I is missing and the walls are lined with calcite II directly. In the majority of cases, barite formed next after calcite II; however, a significant percentage of the concretions examined show barite forming before calcite II, and several show barite forming before calcite I. These relationships are most clear where barite-dissolution cavities are observed. Whenever barite formed in the sequence, pyrite II began to form just before barite deposition stopped and continued briefly thereafter. The rear surfaces of crystals of pyrite II embedded in the walls of barite-dissolution cavities consistently show a central spine that represents outward growth of the pyrite from an original site of nucleation in competition with the formation of the final layers of barite. The diversity in the time of formation of barite relative to calcite I and calcite II suggests that all three formed in rapid sequence and that variations in local conditions may have varied the sequence of deposition from concretion to concretion.

Stage III. Formation of Ferroan Dolomite and Quartz. After the deposition of barite, most of the remaining space was filled with tan to red ferroan

dolomite. The dolomite contains minor amounts of calcite III, which precipitated concurrently. Quartz generally formed after the dolomite, but in several instances quartz preceded the completion of dolomite deposition. This suggests that quartz and dolomite formed in rapid succession or, in some cases, at the same time. Quartz crystals commonly contain significant amounts of hydrocarbon inclusions, and dolomite crystals that formed in remaining open spaces were generally coated with films of hydrocarbon before the start of Stage IV. Rarely, fractures contain an open latticework of barite laths that was never filled with ferroan dolomite. Transparent crystals of calcite IV formed on top of dolomite crystals in voids in the massive dolomite and on barite crystals where no dolomite filled the spaces between them.

Stage IV. Formation of Strontianite. Strontianite crystals occur with, and occasionally coat, calcite IV in voids between barite crystals that were not filled with dolomite. Strontianite crystals are, however, not found with calcite IV in cavities within the massive ferroan dolomite. The differential occurrence of strontianite suggests that it formed from groundwaters long after the completion of Stage III, when the concretions had developed cracks penetrating from the outside especially along mineralized septarian fractures. This occurred before any dissolution of the barite because no strontianite has been found formed on the walls of barite-dissolution cavities.

Stage V. Dissolution of Barite and Formation of Witherite. At some time after the crystallization of strontianite, large amounts of barite were dissolved

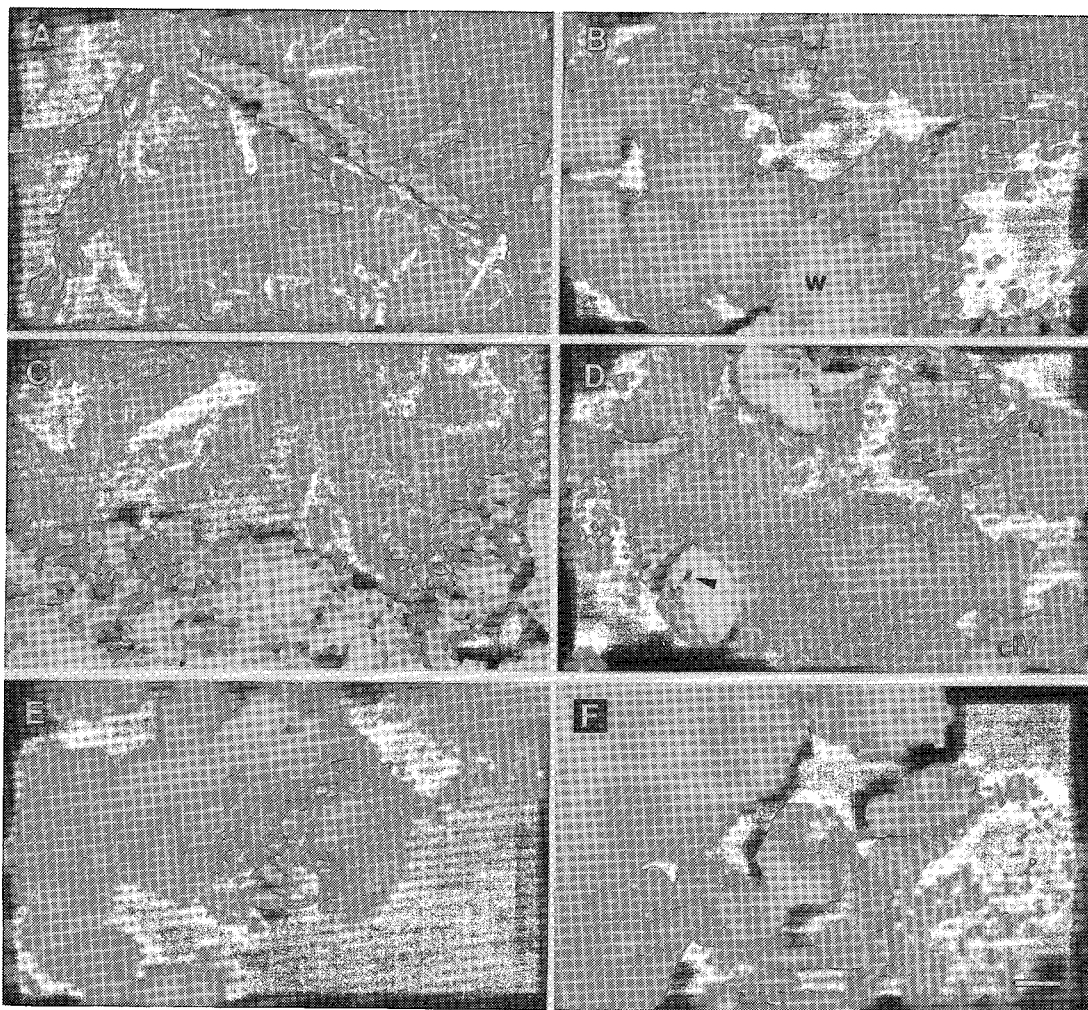


FIG. 6. Photomicrographs of witherite from Jamesville, NY. A. Part of fracture-filling mineralization that has broken along the outer wall of the septarian fracture. Numerous barite-dissolution cavities are visible. Several are partly filled with aggregates of tabular witherite crystals. B. Interface between barite (b) and witherite (w). The barite at upper right is unaltered. Witherite formed at the expense of barite is at lower left. The barite along the interface began to dissolve along cleavage planes. C. Interface between witherite and barite-dissolution cavities. The lower portion of the frame shows witherite filling barite-dissolution cavities. The upper portion shows empty barite-dissolution cavities. Flat-sided remnants of calcite II (cII) are separated by the concretion matrix covered by scattered tiny crystals of pyrite I. D. Botryoidal witherite with quartz (q) and calcite IV (cIV). Note the flakes of hydrocarbon (arrow) embedded in the witherite; these were originally crystallographically oriented in barite crystals. E. Rosette of twinned witherite crystals. F. Single twinned witherite crystal. The length of the bar in F represents 0.9 mm in A, 0.8 mm in B, 1 mm in C, 1 mm in D, 0.2 mm in E, and 0.1 mm in F.

away. As noted above (Fig. 5), the dissolution proceeded along the septarian fractures from the periphery of the concretion toward the centre. In most cases, an obvious peripheral zone of empty cavities and a central region of pristine barite are separated by a band of witherite pseudomorphs after barite occupying the dissolution cavities. The circumstances of the dissolution of the barite seem rather

specific, since no obvious alterations in even the surface luster of any of the adjacent minerals can be seen in the walls of the dissolution cavities. Witherite formed as pseudomorphs after barite, as isolated masses in barite-dissolution cavities, and as coatings and crystals on top of calcite IV, dolomite, and quartz in vugs in the massive dolomite. In places where strontianite crystals formed directly on barite,

Stage Species	Stage I	Stage II	Stage III	Stage IV	Stage V	Stage VI
barite		————			————	
calcite		I — II	III — IV			V
dolomite			————			
goethite						————
matrix	————					
pyrite		I — II				
quartz			————			
strontianite				————		
witherite					————	

FIG. 7. Sequence of formation of minerals filling septarian fractures at Jamesville, NY. Stage I: concretion formation and fracturing; stage II: calcite and barite formation; stage III: ferroan dolomite and quartz formation; stage IV: strontianite formation; stage V: barite dissolution and witherite formation; stage VI: late mineralization and weathering.

these strontianite sprays and fragments of hydrocarbon (Fig. 6D) originally embedded in the barite are occasionally found completely or partly embedded in masses of witherite, where they have fallen when their barite matrix disappeared.

Stage VI. Late Mineralization and Weathering. Subsequent to the dissolution of barite and formation of witherite, minor amounts of calcite V formed on top of witherite and on the walls of barite-dissolution cavities. Oxidative weathering of ferrous minerals (pyrite I, II, ferroan dolomite) has proceeded along recent fractures through the concretions, depositing thin layers of goethite.

Stable-isotope composition of witherite

We have determined the ratios of the stable isotopes of carbon and oxygen in witherite from five septarian concretions from occurrence 1 near Jamesville, New York, and from 26 other occurrences of witherite. The results are presented in Table 1 and shown graphically in Figure 8.

Witherite specimens from all other localities have values of $\delta^{13}\text{C}$ (PDB) in the range $-29.41\text{‰} \leq \delta^{13}\text{C} \leq +1.16\text{‰}$. The witherite specimens from septarian concretions near Jamesville have values of $\delta^{13}\text{C}$ in the range $+2.11\text{‰} \leq \delta^{13}\text{C} \leq +14.77\text{‰}$, which are completely outside the range of values of witherite from all other occurrences. The range of values of $\delta^{18}\text{O}$ (PDB) for septarian witherite specimens, $-15.42\text{‰} \leq \delta^{18}\text{O} \leq -13.78\text{‰}$, is completely within the range, $-17.87\text{‰} \leq \delta^{18}\text{O} \leq -9.15\text{‰}$, for specimens from other occurrences.

DISCUSSION

Like witherite from numerous other localities,

witherite in septarian concretions in the Marcellus shale of central New York formed as a direct alteration product of barite (Baldasari & Speer 1979). The geological setting of these occurrences, however, precludes the alteration of barite by low-temperature hydrothermal solutions rich in carbonate since there is no hydrothermal mineralization of fractures in the enclosing shale and no local or regional source for such solutions. Furthermore, the marked differences in stable-carbon-isotope composition between the septarian witherite and that from a wide range of other occurrences suggests that a different mechanism must be involved.

We propose that this witherite was formed as the result of bacterial activity, which produced both sulfate reduction and methane fermentation (e.g., Fenchel & Blackburn 1979, Stumm & Morgan 1981, Berner 1981, Stetter & Gaag 1983) in anoxic solutions that penetrated the concretions in the geologically recent past. The following observations are consistent with this proposal. The relatively great enrichment in heavy carbon in the Jamesville witherite requires a fractionation mechanism such as methane fermentation (Oana & Deevey 1960, Irwin *et al.* 1977, Kelts & McKenzie 1980, Pisciotto & Mahoney 1981). Abundant hydrocarbon is available for this purpose, both in the matrix of the concretions and in the mineralization of the fractures, including hydrocarbon embedded in the barite itself. The bacterial conversion of barite to witherite has been observed in the laboratory (Römer & Schwartz 1965). The fact that the barite dissolution proceeded from the outside of the concretions toward the centre suggests the action of external solutions entering through late fractures. We have observed that the concretions are presently open to external solutions

TABLE 1. STABLE ISOTOPE COMPOSITION OF WITHERITE

Locality	Source	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
Jamesville, NY	Septarian #4	+14.77	-14.80
Jamesville, NY	Septarian #3	+12.10	-14.41
Jamesville, NY	Septarian #2	+10.14	-13.78
Jamesville, NY	Septarian #5	+9.26	-14.56
Jamesville, NY	Septarian #1	+5.62	-13.91
Jamesville, NY	Septarian #15	+4.76	-15.42
Jamesville, NY	Septarian #14	+2.11	-14.86
Spania Dolina (Herregrund), Slovakia, Czechoslovakia	H #119630	+1.16	-10.70
Hassai Mine, Hinshu, Akita Prefecture, Japan	H #119622	+0.10	-11.03
Fallowfield Mine, Hexham, Northumberland, Great Britain	P	-0.61	-13.12
Sec. 34, T29N, R17E, Montana, USA	H #97713	-2.01	-12.84
Alston Moor, Cumbria, Great Britain	P	-2.94	-13.00
Neuberg, Styria, Austria	H #76151	-4.08	-12.99
Jorex Prop., Mile 497, Alaska Hwy., Cassiar Dist., British Columbia, Canada	N #34999	-8.13	-15.43
Anglesarke Moor, Chorley, Lancashire, Great Britain	H #119614	-8.19	-17.87
Durham, Great Britain	P	-8.22	-16.50
Snailbeach Mine, Minsterley, Shropshire, Great Britain	P	-8.45	-16.67
Northumberland, Great Britain	C #6650	-8.67	-12.94
Settlingstones Mine, Hexham, Northumberland, Great Britain	C #5955	-9.61	-14.30
Archysm, Karatschajewo, Caucasus, RSFSR, USSR	H #119627	-10.27	-16.28
Ushaw Moor Colliery, Durham, Great Britain	H #88193	-10.37	-14.30
12 km E NE of Arrowhead Lake, Hess Mtns., Yukon Terr., Canada	G #64435	-11.12	-9.15
Mahoning Mine, Cave in Rock, Hardin County, Illinois, USA	C #6260	-12.06	-10.13
Pibram, Bohemia, Czechoslovakia	H #93990	-14.26	-16.55
Gargantua North Showing, Selwyn Mtns., Yukon Terr., Canada	G #64469	-14.65	-13.22
Deutsch-Feistritz, Styria, Austria	S #B10144	-15.00	-14.75
Peggau, Styria, Austria	P	-15.02	-15.65
El Portal, Mariposa County, California, USA	S #157135	-15.52	-13.15
Porcupine Mine, Gillies Twp., Thunder Bay Dist., Ontario, Canada	G #1681	-16.18	-13.44
Tom Deposit, Selwyn Mtns., Yukon Terr., Canada	G #64439	-16.67	-11.40
Pigeon Roost Mine, Montgomery County, Arkansas, USA	C #6265	-19.05	-10.32
Wanlockhead Mine, Dumfriesshire, Great Britain	H #88195	-23.24	-10.89
Beaver Mine, O'Connor Twp., Thunder Bay Dist., Ontario, Canada	N #38587	-29.41	-13.62

Carbon and oxygen stable isotope compositions for witherites from Jamesville, NY and other occurrences worldwide. The values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are relative to the PDB standard. Source codes: C - Chamberlain Collection; G - Collection of the Geological Survey of Canada, Ottawa, Ontario, Canada; H - Collection of Harvard University Mineralogical Museum, Cambridge, MA; N - Collection of the National Museum of Natural History, Ottawa, Ontario, Canada; P - Collection of the Paris School of Mines, Paris, France; S - Collection of the Smithsonian Institution, Washington, D. C.

such as rain water. Furthermore, we suggest that the sulfide produced by sulfate reduction and the methane produced by fermentation were both free to escape as dissolved gases in solution through these late fractures, since no sulfides were precipitated on the walls of the barite-dissolution cavities.

We have attempted to reconstruct the geological processes involved in the sequence of mineralization of these concretions. The detailed results of measurements of the stable-isotope ratios of the various species of minerals and their interpretation are beyond the scope of this paper and are reported elsewhere (Siegel *et al.* 1986). Only a summary can be given here. The concretions formed at shallow depths during burial and diagenesis of the surrounding shale (Dix & Mullins 1985). The calcite body of the concretions has a carbon-isotope ratio near zero, which is typical of marine limestones (*e.g.*, Hudson 1977) rather than a "light" carbon ratio typical of concretions formed during sulfate reduction (*e.g.*, Hudson 1978) or a "heavy" carbon ratio typical of concretions formed during methane fermentation (*e.g.*, Fritz *et al.* 1971, Curtis *et al.* 1972). The pattern of carbon-isotope ratios in the sequence of carbonates from calcite I to calcite IV suggests that calcite I

formed during sulfate reduction ($\delta^{13}\text{C} = -14.8\text{‰}$) and that subsequent carbonate minerals formed during progressive fermentation of methane. Dolomite ($\delta^{13}\text{C} = -6.9\text{‰}$) probably marks the end of sulfate reduction (Baker & Kastner 1981). Mineralogical and isotopic data both suggest that calcite IV was the last species to form during burial and diagenesis. It has a heavy carbon-isotope ratio ($\delta^{13}\text{C} = +12.6\text{‰}$) typical of carbonates formed during methane fermentation. The strontianite and witherite also have a heavy carbon-isotope ratio, but both the mineralogical evidence and the oxygen-isotope ratios suggest that they formed well after diagenesis and separately from each other. The values of the oxygen-isotope ratio $\delta^{18}\text{O}$ for calcite IV, strontianite, and witherite are -5.4 , -11.2 and -14.5‰ , respectively. These results suggest that three separate periods of methane fermentation are recorded by the sequence of mineralization. We have hypothesized (Siegel *et al.* 1986) that the strontianite was deposited by the upward displacement of strontium-rich brines from the underlying Salina Formation by the advancing edge of Pleistocene glaciation and that the barite was dissolved and the witherite deposited as anoxic meltwaters were deeply driven under heavy glacial loading.

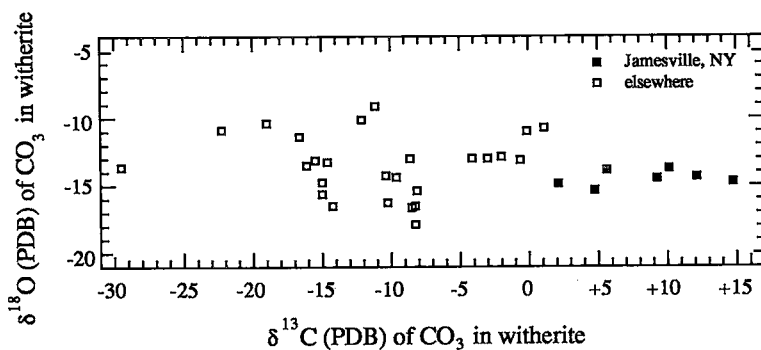


FIG. 8. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for witherite from Jamesville, NY, and other localities worldwide. The carbon isotopes are significantly heavier for the Jamesville witherite than for other localities.

The alteration of barite to witherite by bacterial action could be a relatively widespread mechanism. Gilkeson *et al.* (1981) speculated that in the anaerobic zones of the Cambrian-Ordovician aquifer system in northeastern Illinois, where concentrations of barium in groundwater are elevated and sulfate concentrations are severely reduced by bacterial sulfate reduction, secondary witherite could be precipitated, but their study did not demonstrate the occurrence of such witherite. Our isotope determinations on witherite from a wide range of localities failed to uncover any other examples with carbon δ -values as heavy as those for witherite from septarian concretions.

The other localities are, however, of several types. The Porcupine mine (Traill 1970) and Jorex property (Woodcock & Smitheringale 1957) in Canada, Peggau and Deutsch-Freistritz in Austria, Příbram and Spania Dolina in Czechoslovakia (Hintze 1930), Mahonning mine (Grawe & Nackowski 1949, Jolly & Heyl 1964) in Illinois, the Pigeon Roost mine (Scull 1958) in Arkansas, and the various occurrences in Great Britain (Carruthers *et al.* 1916, Loch 1946) are all low-temperature, hydrothermal veins. The occurrence near El Portal, California is a replacement of a bed of limestone by barium-rich solutions from an underlying body of granite. Fitch (1931) believed that the witherite is a primary replacement of calcite and that barite in the deposit is derived from the witherite. The occurrence in Montana consists of pods of massive witherite emplaced in solution cavities in a dolostone (Fuller 1924). The occurrences from the Yukon Territories are stratiform deposits of barite, sphalerite and galena believed to be the results of direct precipitation from hydrothermal discharge (Lydon *et al.* 1979). Unfortunately, none of these localities have unique isotopic ratios that separate them from the overall grouping. Witherite from Spania Dolina, Czechoslovakia, has the heaviest value for $\delta^{13}\text{C}$ (+1.16‰) of all the other occur-

rences. The associated minerals include other carbonates and sulfates such as azurite, malachite, barite, celestite, langite, devilline, brochantite, liroconite and chalcantite, some of which have formed by the alteration of tetrahedrite and chalcopyrite (Hintze 1930). This locality may merit further study to determine the paragenesis of its witherite.

A number of specimens in our data base are samples from exactly the same specimens used by Baldasari & Speer (1979) for chemical analyses of witherite by microprobe. We have not observed any striking correlations; however, others may wish to scrutinize the two sets of data. Our results support the suggestion that witherite can form from barite under conditions of sulfate reduction and methanogenesis in anoxic groundwaters. Witherite formed in this way might occur in geological settings where it is not normally expected and, thereby, could easily be overlooked. In fact, we have already found an unrecognized specimen of witherite in the Oren Root Collection at Hamilton College, from a fourth locality in central New York.

Our results may suggest a new look at the formation of strontianite from celestite or cerussite from anglesite. Mechanisms similar to what we have proposed for witherite may operate in some environments and lead to similar fractionation of the carbon isotopes in these carbonates.

ACKNOWLEDGEMENTS

The co-operation of many people was essential to the completion of this study. We thank George Robinson, National Museums of Canada; Gary Ansell and Richard Herd, Geological Survey of Canada; William Metropolis and Carl Francis, Harvard University; Pete Dunn and John White, Smithsonian Institution; Joseph Peters and George Harlow, American Museum of Natural History;

Pierre Guillemin, École des Mines de Paris; Robert King, National Museum of Wales; and David Bierbrauer, Wausau, WI, for making specimens available. We thank R. Peter Richards for measuring and drawing the crystals of pyrite II. We thank Paul Mankiewicz for making the stable-isotope measurements. We thank George Dix for helpful discussions. We thank J. Alex Speer and an anonymous referee for their helpful suggestions. This study was funded in part by a grant from the Syracuse University Senate Research Fund.

REFERENCES

- BAKER, P.A. & KASTNER, M. (1981): Constraints on the formation of sedimentary dolomite. *Science* **213**, 214-216.
- BALDASARI, A. & SPEER, J.A. (1979): Witherite composition, physical properties, and genesis. *Amer. Mineral.* **64**, 742-747.
- BERNER, R.A. (1981): A new geochemical classification of sedimentary environments. *J. Sed. Petrology* **51**, 359-365.
- BRETT, C.E. & BAIRD, G.C. (1985): Carbonate-shales cycles in the Middle Devonian of New York: an evaluation of models for the origin of limestones in terrigenous shelf sequences. *Geology* **13**, 324-327.
- CARRUTHERS, R.G., EASTWOOD, T., WILSON, G.V., POCOCK, R.W. & WRAY, D.A. (1916): Special reports on the mineral resources of Great Britain. II. Barytes and witherite. *Mem. Geol. Surv. Great Britain*.
- CURTIS, C.D., PETROWSKI, C. & OERTEL, G. (1972): Stable carbon isotope ratios within carbonate concretions: a clue to place and time of formation. *Nature* **235**, 98-100.
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1962): *Rock-Forming Minerals. 5. Non-silicates*. J. Wiley & Sons, New York.
- DIX, G.R. & MULLINS, H.T. (1985): Early diagenesis and sequential stratigraphic development of calcite concretions from the Middle Devonian Hamilton Group, central New York State. *Geol. Soc. Amer. Abstr. Programs* **17**, 564.
- DOSSERT, W.P., CHAMBERLAIN, S.C. & SIEGEL, D.I. (1984): A new occurrence of witherite near Syracuse, New York. *Rocks and Minerals* **59**, 224.
- FENCHEL, T. & BLACKBURN, T.H. (1979): *Bacteria and Mineral Cycling*. Academic Press, New York.
- FITCH, A.A. (1931): Barite and witherite from near El Portal, Mariposa County, California. *Amer. Mineral.* **16**, 461-468.
- FRITZ, P., BINDA, P.L., FOLINSBEE, F.E. & KRAUSE, H.R. (1971): Isotopic composition of diagenetic siderites from Cretaceous sediments in western Canada. *J. Sed. Petrology* **41**, 282-288.
- FULLER, M.B. (1924): An occurrence of witherite in the Altyn limestone at Many Glacier, Montana. *Amer. Mineral.* **9**, 154.
- GILKESON, R.H., PERRY, E.C., JR. & CARTWRIGHT, K. (1981): Isotopic and geologic studies to identify the sources of sulfate in groundwater containing high barium concentrations. *Illinois Dep. Energy Nat. Resources, Final Rep. Proj. A-100-III*.
- GRAWE, O.R. & NACKOWSKI, M.P. (1949): Strontianite and witherite associated with southern Illinois fluorite. *Science* **110**, 331.
- HANCOX, E.G. (1934): Witherite and barytes. *Mining Mag.* **51**, 76-79.
- HINTZE, C. (1930): *Handbuch der Mineralogie (Vol. 1, Part 3)*. Walter De Gruyter & Co., Berlin.
- HOLLAND, H.D. (1967): Gangue minerals in hydrothermal deposits. In *Geochemistry of Hydrothermal Ore Deposits* (H.L. Barnes, ed.). Holt, Rinehart & Winston, New York.
- HUDSON, J.D. (1977): Stable isotopes and limestone lithification. *Quart. J. Geol. Soc. London* **133**, 637-660.
- _____ (1978): Concretions, isotopes, and the diagenetic history of the Oxford Clay (Jurassic) of central England. *Sedimentology* **25**, 339-370.
- IRWIN, H., CURTIS, C. & COLEMAN, M. (1977): Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. *Nature* **269**, 209-213.
- JOLLY, J.L. & HEYL, A.V. (1964): Mineral paragenesis and zoning in the central Kentucky mineral district. *Econ. Geol.* **59**, 596-624.
- KELTS, K.R. & MCKENZIE, J.A. (1980): Formation of deep sea dolomite in anoxic diatomaceous earth. *Int. Geol. Congress 26th (Paris)* **1**, 24 (abstr.).
- LOCH, C.W. (1946): Forgotten mines in Lancashire. *Mining Mag.* **74**, 290-297.
- LYDON, J.W., LANCASTER, R.D. & KARKKAINEN, P. (1979): Genetic controls of Selwyn Basin stratiform barite/sphalerite/galena deposits: an investigation of the dominant barium mineralogy of the Tea deposit, Yukon. *Geol. Surv. Can. Paper* **79-1B**, 223-229.
- OANA, S. & DEEVEY, E.S. (1960): Carbon-13 in lake waters, and its possible bearing on paleolimnology. *Amer. J. Sci.* **258A**, 253-272.

- PALACHE, C., BERMAN, H. & FRONDEL, C. (1951): *Dana's System of Mineralogy 2 (7th edition)*. J. Wiley & Sons, New York.
- PISCIOTTO, K.A. & MAHONEY, J.J. (1981): Isotopic survey of diagenetic carbonates, deep sea drilling project leg 63. *Initial Rep. Deep Sea Drilling Project* **63**, 595-609.
- RÖMER, R. & SCHWARTZ, W. (1965): Geomikrobiologische Untersuchungen. V. Verwertung von Sulfatmineralien und Schwermetall-Toleranz beim Desulfurizierern. *Z. Allg. Mikrobiologie* **5**, 122-135.
- SCULL, B.J. (1958): Origin and occurrence of barite in Arkansas. *Arkansas Geol. and Cons. Comm. Inf. Circ.* **18**.
- SIDORENKO, A.V. (1947): The genesis of witherites of the western Kopet-Dag. *Dokl. Acad. Sci. URSS, Earth Sci. Sect.* **55**, 149-151.
- SIEGEL, D.I., CHAMBERLAIN, S.C. & DOSSERT, W.P. (1986): The isotopic and chemical evolution of mineralization in septarian concretions, Marcellus Shale, New York: Multiple episodes of methane fermentation? *Geol. Soc. Amer. Bull.* (in press).
- SPEER, J.A. (1976): Pennsylvania minerals: II. Strontianite. *Mineral. Rec.* **7**, 69-71.
- STETTER, K.O. & GAAG, G. (1983): Reduction of molecular sulphur by methanogenic bacteria. *Nature* **305**, 309-311.
- STUMM, W. & MORGAN, J.J. (1981): *Aquatic Chemistry (2nd edition)*. Wiley-Interscience, New York.
- TRAILL, R.J. (1970): A catalog of Canadian minerals. *Geol. Surv. Can. Pap.* **69-45**.
- WELLER, J.M., GROGAN, R.M. & TIPPIC, F.R. (1952): Geology of the fluorite deposits of Illinois. *Illinois State Geol. Surv. Bull.* **76**.
- WOODCOCK, J.R. & SMITHERINGALE, W.V. (1957): Fluorite-witherite deposit at Lower Liard Crossing, British Columbia. In *The Geology of Canadian Industrial Mineral Deposits. Commonwealth Mining and Metallurgical Congress, 6th (Vancouver)*, 244-247.

Received July, 20 1985, revised manuscript accepted September 18, 1985.