

WHEWELLITE FROM A SEPTARIAN LIMESTONE CON-  
CRETION IN MARINE SHALE NEAR HAVRE,  
MONTANA\*

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ABSTRACT

Whewellite, calcium oxalate monohydrate, has been found as a crystal perched on terminated, unetched, drusy calcite crystals in a septarian limestone concretion in the marine Bearpaw shale of Late Cretaceous age near Havre, Montana. Its occurrence resembles that in marl concretions in the Caucasus but differs from occurrences in other regions. The inorganic precipitation of whewellite probably occurred in an alkaline environment, and the oxalate was probably derived from nearby organic material through the action of ground water. Other geological occurrences of whewellite are reviewed and the conclusion expressed that hypotheses suggesting hydrothermal derivation of the oxalates or their natural precipitation in deep sea sediments need confirmation.

INTRODUCTION

In June 1952 Robert B. McGraw, Jr., collected from a septarian limestone concretion near Havre, Montana, a vuggy specimen of yellow calcite containing a mineral since identified as whewellite, calcium oxalate monohydrate. This is the first North American locality reported for the mineral. In casual field examination, whewellite might easily be mistaken for calcite or barite; so a detailed account of its occurrence and identity is recorded here as an aid to future discoveries of the mineral in the same or similar environment. Dr. George Switzer of the U. S. National Museum provided for comparative study a specimen from Pchery, Schlan, Bohemia (Czechoslovakia), the occurrence of which is described by Slavik (1908). The specimen from the new locality described in this paper has been deposited in the U. S. National Museum as specimen No. 106555.

OCCURRENCE

A single crystal of whewellite was found in a fossiliferous, septarian limestone concretion in the marine Bearpaw shale of Late Cretaceous age near the center of sec. 33, T. 32 N., R. 17 E., about 7 miles southeast of Havre, Montana, via the Havre-Clear Creek road, and about 300 feet southeast of a bridge that crosses Statten Coulee. Here several limestone concretions 1 to 4 feet in diameter are exposed in the shale. The enclosing shale is dark gray, for the most part fissile, and locally bentonitic and gypsiferous. Some of the concretions are fossiliferous and many

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are septarian. The whewellite-bearing concretion contained invertebrate fossil shells.

Yellow to brownish-yellow calcite in irregular and interconnecting veins characterizes the marine septarian concretions of this region. Although minerals other than calcite are extremely rare in the concretions, barite, gypsum, and quartz have been collected from several. The general mineralogy and chemical composition of these concretions will be reported at some future time to augment the information already published by Rubey and Bass (1925), Cobban (1951), and others.

The concretion containing the whewellite had the form of an oblate spheroid with a diameter of about 2 feet and a thickness of 1 foot. The exterior surface is dark grayish brown and freshly broken surfaces are olive gray. The septarian vein development ranges in width from about 3 inches down to barely perceptible fractures lined with calcite. In contact with the rock of the concretion and separating it from the coarse calcite of the septarian veins is a thin layer of fibrous calcite ( $\omega = 1.659$ ), rarely more than 2 mm. thick, that fluoresces bright yellow in a short-

TABLE 1. PHYSICAL PROPERTIES OF WHEWELLITE

	Havre, Mont.	Burgk, Saxony	Maikop, Caucasus
$\alpha$	1.491	1.4909	1.49
$\beta$	1.555	1.5554	1.55
$\gamma$	1.654	1.6502	1.65
$2V (+)$	82°	83°55'	82.5°
Orientation	—	X=b Z $\wedge$ c = +30°	—
Gr.	2.21 ± 0.01	2.226	2.22
Hardness	3	—	3.5

wave ultraviolet light. The coarse, nonfluorescent calcite ( $\omega = 1.662$ ) crystals are yellow to pale yellow, attain a maximum diameter of 8 mm., and have rhombohedral terminations that project into the vuggy parts of the veins. Locally the veins of the coarse calcite transect cracks filled with the fibrous fluorescent calcite. Gypsum sparsely encrusts the coarse calcite crystals in some vugs and also has formed along cracks that transect both calcite layers. The whewellite crystal is perched on coarse calcite crystals that have rhombohedral terminations, are pale yellow, and show no evidence of etching. The surface of the whewellite is coated by a thin pink-colored incrustation of very fine grained aragonite and pink calcite that conceals the transparent interior of the mineral.

TABLE 2. MEASURED  $d$ -SPACINGS OF  $x$ -RAY POWDER PATTERNS OF WHEWELLITE FROM MONTANA AND SCHLAN, BOHEMIA (CZECHOSLOVAKIA)

Montana (USGS film No. 3960)		Schlan, Bohemia <sup>2</sup> (USGS film No. 3963)	
Intensity <sup>1</sup>	$d(\text{\AA})$	Intensity <sup>1</sup>	$d(\text{\AA})$
100	5.95	100	5.94
5	5.81	10	5.80
5	4.53	5	4.52
5	3.773	5	3.779
90	3.652	90	3.650
1	3.414	1	3.402
1	3.321	—	—
5	3.105	1	3.106
1	3.002	—	(F)
50	2.971	60	2.966
10	2.906	10	2.909
10	2.842	10	2.842
1	2.639	—	(F)
20	2.497	40	2.494
1	2.455	—	—
1	2.422	—	—
1	2.388	—	—
80	2.357	80	2.354
20	2.262	30	2.263
5	2.213	10	2.212
1	2.135	1	2.129
10	2.076	30	2.079
5	1.978	10	1.978
5	1.955	10	1.954
5	1.930	10	1.930
5	1.891	10	1.890
1	1.859	—	—
1	1.848	5	1.850
1	1.826	—	—
1	1.818	10	1.818
1	1.794	10	1.792
1	1.737	10	1.737
1	1.693	1	1.696
1	1.644	1	1.638
1	1.588	1	1.589
1	1.552	1	1.556
—	—	1	1.548
1	1.528	1	1.528
1	1.505	1	1.504
1	1.480	1	1.482
1	1.458	—	—

F, faint lines; not measured.

<sup>1</sup> Estimated.<sup>2</sup> U. S. National Museum specimen No. 86913.

## DESCRIPTIVE MINERALOGY

The whewellite crystal, as originally found in the concretion, had a prismatic habit and dimensions of 25 by 8 by 3 mm. Identification as whewellite was made from its optical data and  $x$ -ray powder-diffraction pattern. Its physical properties are compared in Table 1 with those reported by Jezek (1911, p. 18) for whewellite from Burgk, Saxony, and by Vassoyevicz and Razumovsky (1928) for whewellite from the Maikop region, northern Caucasus. A summary of properties for whewellite is given by Wherry (1922).

The hardness of whewellite from Montana is about 3 and its specific gravity, determined with a Berman balance, is 2.21. Morphology of the mineral is well described by numerous authors who had many crystals to work with.

$X$ -ray power-diffraction photographs of whewellite from Montana and from Pchery, Schlan, Bohemia, are almost identical; and since some of the previously published powder data for the monohydrate are incomplete or inaccurate, the  $d$ -spacings and intensities for both specimens are given in Table 2.

Honnegger (1952), for example, has tabulated powder data for whewellite from four different sources. Supposedly, only the stronger  $\alpha$ -reflections are included; however, the medium strong line with a  $d$ -spacing of 4.03–4.05 Å is almost certainly a  $\beta$ -reflection of the strong line with a  $d$ -spacing of 3.64 Å. This line was not observed on the photographs taken for this paper nor in several patterns which are included in the *A.S.T.M.* files. The  $d$ -spacings published in this paper were corrected for film shrinkage by the back reflection method and are given for many weaker lines which have not been previously listed for whewellite.

## CHEMICAL DATA

Whewellite, fluorescent and nonfluorescent calcite, and the pink coating on whewellite were submitted for spectrographic examination and the results are shown in Table 3. The whewellite is exceptionally pure. The calcite is ferroan, and the fluorescent variety has the more strontium, barium, and magnesium. No explanation for the pink color of the coating on the whewellite can be offered other than organic dye.

## GEOLOGICAL ENVIRONMENT

Whewellite and other hydrated oxalates have been reported from a wide variety of organic and inorganic environments. Oxalates are widely distributed in living plant tissues and have been identified in sedimentary beds containing lignite or other organic substances. Both the monohydrate and the dihydrate (weddellite) are associated with a great variety

TABLE 3. QUALITATIVE SPECTROGRAPHIC ANALYSES OF WHEWELLITE AND OTHER MINERALS FROM A LIMESTONE CONCRETION NEAR HAVRE, MONT.  
(R. S. Harner, *analyst*)

	Mn	Fe	Mg	Sr	Ba
1. Whewellite (clear, colorless)	—	0.00X	0.00X	0.00X	0.00X
2. Calcite (fluorescent variety)	0.0X	X	0.X	0.X	0.0X
3. Calcite (nonfluorescent variety)	0.X	X	0.0X	0.00X	0.00X
4. Pink coating on whewellite	0.00X	0.0X	0.X	0.0X	0.00X

Not found in samples: Cu, Ag, Au, Hg, Ru, Rh, Pd, Os, Ir, Pt, Mo, W, Re, Ge, Sn, Pb, As, Sb, Bi, Se, Te, Za, Cd, Tl, In, Co, Ni, Al, Ga, Cr, V, Sc, Y, La, Ce, Ti, Zr, Hf, Th, Nb, Ta, U, Be.

of urinary calculi in mammals (see Prien and Frondel, 1947; Milton and Axelrod, 1951).

The hydrated calcium oxalates can be prepared by simple reaction between calcium salts and oxalates in water solution. Bramlette (Bradley and Bramlette, 1942, p. 29), for example, calls attention to the formation of hydrated calcium oxalate during mechanical analysis experiments where sodium oxalate was added to washed muds obtained from the North Atlantic floor. He verified their presence in the pipette samples but their absence in the untreated sediments. Crystals of calcium oxalate dihydrate (weddelite) were identified by Bannister (Earland, et al., 1936) in bottom sediments collected during the cruise of the *Scotia* in 1902 to 1904 in the Weddell Sea, Antarctica, at seven stations where depths ranged from 4,434 to 5,008 meters. Gypsum crystals were also identified in sediments collected on the same cruise at five stations; and earlandite, a hydrated calcium citrate, was found as warty nodules in sediments collected at one station. The natural occurrence of weddelite in bottom sediments of the deep Weddell Sea is accepted by Earland and Bannister, but perhaps some reasonable doubt may be raised in view of the description of the sample storage. Earland (Earland, et al., 1936, p. 6) states: "Most of the deposits received by me were in their original containers. . . . The containers were principally bottles and jars in which provisions had been preserved, many still bearing the original labels. Their condition varied, some being in perfect preservation after thirty years in store, while others, owing to defective corks, had dried up." The nature of the food originally stored in the containers is not mentioned.

Many excellent crystals of whewellite have been reported as attached to walls of vugs in a great number of carbonate-sulfide veins of mesothermal association in central Europe (Ungemach, 1909; Jezek, 1911; and others). In these deposits the mineral association includes carbon-

ates (calcite, siderite, ankerite, and dolomite), barite, and sulfides (sphalerite, pyrite, pyrrhotite, marcasite, chalcopyrite, tetrahedrite, millerite, and linnaeite). Ungemach (1909) accepts this association as evidence in support of the hydrothermal rather than supergene derivation of the oxalate, although the occurrences are not deep-seated and the veins traverse rocks that are locally lignitic or graphitic.

The occurrence of whewellite in calcite veins up to 2 cm. thick at a single locality in Devonian argillite in southern Timan is reported by Kalyuzhnyi (1948) who ascribes the origin of the oxalate to incomplete oxidation of organic material contained in the argillite itself.

A geological occurrence closely resembling that near Havre, Montana, is described by Vassoyevicz and Razumovsky (1928) in the Maikop district (northern Caucasus). Tabular, well-developed, wine-yellow crystals of whewellite occur in compact marl concretions that are abundant in the upper part of an Eocene foraminiferal claystone that is somewhat calcareous and bituminous. The origin of the oxalate is ascribed to oxidation of organic matter in the rock.

#### CONCLUSIONS

Precipitation of whewellite in a limestone concretion near Havre, Montana, took place well after the development of the septarian calcite veins. The unetched faces of the contiguous calcite crystals support the existence of an alkaline environment for the formation of the whewellite here.

Although hydrous oxalates are widely distributed in nature and have formed by organic as well as inorganic processes, hypotheses suggesting hydrothermal derivation of the oxalates or their natural precipitation in a deep sea environment to explain some inorganic occurrences may need further confirmation. Occurrences in consolidated sedimentary rocks are best explained by deposition from circulating ground water that has acquired oxalate from nearby organic material in the sediments.

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