

NEW DATA ON WHEWELLITE

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ABSTRACT

Whewellite, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, occurs in septarian nodules near Milan, Erie Co., Ohio, associated with calcite, dolomite, barite, and pyrite. Complete chemical and spectrochemical analyses of the whewellite show that it is quite pure and of ideal composition. Refined unit-cell dimensions and a new indexing of the X-ray powder pattern are included, together with a summary of the dispersed data on the cell dimensions and structure of the mineral. Available free energy data indicates that whewellite is metastable in almost all natural environments. It may form from the metastable precipitation of oxalates released during the decomposition of organic matter.

INTRODUCTION

In 1963 Mr. Clarence E. Raver of Wakeman, Ohio discovered masses of a white cleavable mineral, which proved to be whewellite, in septarian nodules exposed in the bed of the Huron River between Milan and Monroeville, Erie County, Ohio. The U. S. National Museum obtained a large suite of specimens from him, and these form the basis of this paper. Hyde and Landy (1966) reported the locality and circumstances of the find in a brief note.

This is the third reported locality for whewellite in the United States. The first was near Havre, Montana, where a single crystal was found in a septarian limestone concretion in marine shale (Pecora and Kerr, 1954); the occurrence is very similar to the one described in this paper. The second find was of two isolated crystals from a fault in San Juan County, Utah (Gude *et al.*, 1960).

OCCURRENCE AND MINERALOGY

The bedrock in the region of the present find is the Huron Shale member of the Ohio Shale, of Upper Devonian age. (Hoover, 1960). The rock is largely a grayish black, fissile shale, locally fossiliferous. It was apparently deposited under stagnant ocean bottom conditions, as it contains considerable carbonaceous material. Carbonate concretions, containing both dolomite and calcite, are quite abundant throughout the Huron member and may reach several yards in diameter, although most are less than six feet (Clifton, 1957). The concretions show a marked parting in the plane of the bedding of the shale, and those over about a foot in diameter are ellipsoidal, flattened in the plane of the bedding. The whewellite specimens were collected from such concretions.

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The specimens show two kinds of matrix. One is a dark gray crystalline calcite, with individual cleavages as much as 1 cm across. The whewellite forms coarsely crystalline masses embedded in this matrix. Closely associated with one of the masses are fragments of an arthrodiran (armoured) fish plate. The other type of matrix is a light gray mixture of dolomite and calcite, ranging from fine to coarse grained, with cleavages 1 cm. In both the matrices the whewellite is in white, translucent masses with well defined cleavages up to 8 cm across. No terminated crystals were seen in any of the specimens. Under the binocular microscope the whewellite shows numerous inclusions, perhaps fluid filled, although H_2O^- in the chemical analysis is not high (Table 1). Optically, the whewellite is

TABLE 1. CHEMICAL ANALYSES OF WHEWELLITE FROM ERIE CO., OHIO

	1	2	3
Ca	27.43	27.35	27.33
C_2O_4	60.24	59.50	59.40
H_2O^+	12.33	13.01	n.d.
H_2O^-	—	0.13	—
P_2O_5	—	0.006	—
Total	100.00	99.99 ₆	—

1. $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.
2. Whewellite, near Milan, Erie Co., Ohio. Lois M. Jones, U.S.G.S. analyst.
3. Whewellite, near Milan, Erie Co., Ohio, from Hyde and Landy, 1966.

biaxial (+), $\alpha = 1.489$, $\beta = 1.553$, $\gamma = 1649$, all ± 0.003 , $2V$ about 80° , $x = b$, in good agreement with published values (Palache, Berman, and Frondel, 1951). The hardness is about 3. The specific gravity is 2.21, from measurement of five grains on the Berman balance with temperature compensation, or 2.22 calculated from the unit-cell data of this paper. The cleavages in the conventional morphological orientation are ($\bar{1}01$) very good, (001) and (010) distinct, inclined to be curved, (110) indistinct.

A thin selvage of friable calcite, locally showing minute, simple rhombohedral crystals, surrounds the whewellite masses. Much of the whewellite is deeply etched and permeated along cleavage cracks with thin films of calcite, which is apparently an alteration product of the whewellite. The calcite fluoresces a cream yellow color, more strongly under long wave than short wave ultraviolet light. A few of the whewellite specimens are permeated with calcite which shows a rose pink fluorescence, sometimes very bright, in long wave radiation.

Several other minerals, including barite, dolomite and ferroan dolomite, and pyrite, are associated with the whewellite; all are found be-

tween the whewellite masses and the concretion matrix. The barite is in cleavages as much as 5 cm across and in rough crystals, 1 to 2 cm long, projecting into the whewellite. The dolomite ranges in color from pale buff to dark brown. It occurs as crusts and masses, showing bands of different colors between the whewellite and the matrix, and as dark brown, isolated crystals embedded in the whewellite. The ω index of these dark crystals is approximately 1.695, indicating an Mg:Fe ratio of about 4:1 (Palache, Berman, and Frondel, 1951). All the ferroan (brown) dolomite fluoresces a warm yellow color in long wave ultraviolet light; the darkest dolomite is weakly fluorescent showing the same color under short wave ultraviolet light. The pale buff dolomite is not fluorescent. Pyrite occurs as minute, stalactitic masses in the pockets in the dolomite and as tiny crystalline grains in the whewellite and barite.

CHEMISTRY

A complete chemical analysis of the Erie County whewellite was made for this paper by Lois M. Jones of the USGS. A partial analysis of similar material was presented by Hyde and Landy (1966). The two analyses are given in Table 1 in terms of Ca and C_2O_4 and are compared with the theoretical composition of whewellite. Agreement among the three is excellent.

A semiquantitative, spectrographic analysis of the whewellite showed the following elements, in percent: Si 0.3, Al 0.001, Mg 0.003, Ba 0.0003, Be 0.0007, Cr 0.0003, Cu 0.0001, Sr 0.001, Y 0.003, Yb 0.0002; P was not detected.¹

X-RAY DATA

X-ray powder diffraction data of the Erie Co. whewellite, taken on a 114.6 mm camera with filtered Cu radiation, was analysed by a least-squares treatment, using a program written for the Burroughs 220 digital computer by Evans *et al.* (1963), to yield refined unit-cell dimensions. For the analysis of the whewellite, the space group ($P2_1/n$) and unit cell dimensions of Hoffman (1961) were used as preliminary data; the results are listed in Table 2, along with other values from the literature.

The true b -axis of whewellite is twice that chosen on morphological grounds; the value given by ASTM card 14-789 is also half the true value. In the conventional orientation the space group of whewellite is ($P2_1/n$), but for structural reasons Cocco (1961) chose a new orientation for whewellite, such that the space group is ($P2_1/c$). He took the conventional ($\bar{1}01$), which is the twin plane and plane of most prominent cleav-

¹ Joseph L. Harris, U.S.G.S. analyst. Results are reported to the nearest number in the series 1. 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, *etc.*, which represent approximate midpoints of interval data on a geometric scale. The assigned interval for semiquantitative results will include the quantitative value about 30% of the time.

age, as (100), retaining the other two axial pinacoids unchanged. The transformation matrix from Hoffman to Cocco is $\bar{1}00/010/101$. In this orientation a and b remain unchanged; c and β , calculated from the data of the present paper, become 10.14 Å and 109°9', respectively. Cocco's values differ from these somewhat; he may have given the cell dimensions for the conventional orientation.

TABLE 2. CRYSTAL STRUCTURE DATA ON WHEWELLITE (UNIT-CELL DIMENSIONS IN Å)

Reference	Space group	a	b	c	β	$a:b:c$
Present Study	$P2_1/n$	6.27 ₆	14.56 ₁	10.01 ₂	107°5'	0.431:1:0.688
Hoffman (1961)	$P2_1/n$	6.29 ₃	14.59	9.97 ₅	107°1.5'	0.431:1:0.684
Cocco (1961)	$P2_1/c$	6.24	14.58	9.89	107°	0.428:1:0.678
Arnott <i>et al.</i> (1965)	$P2_1/c$	6.61	14.46	10.07	116.5°	0.475:1:0.696
Arnott <i>et al.</i> (1965) (alternate)	$P2/c$	6.28	14.46	11.10	109.4°	0.434:1:0.768
ASTM 14-789	—	6.30	7.287	9.96	106°59'	0.865:1:1.367
Becke (1907)	—	—	—	—	107°00'	0.8628:1:1.3677

Arnott *et al.*, (1965) chose the conventional planes (101) and ($\bar{1}01$) as (100) and (001), respectively, in their determination of the space group of whewellite. In this orientation β equals 116.5°. The transformation matrix from Hoffman (the conventional orientation) to Arnott *et al.*, is $10\bar{1}/010/202$. Figure 1 shows the relative orientations of the unit cells of Hoffman, Cocco, and Arnott *et al.* An alternative orientation for whewellite suggested by Arnott *et al.* (1965) is the same as that used by Cocco (1961) if the 11.10 Å c is a misprint for 10.10 Å, as would seem most likely from geometrical considerations.

The crystal structure of whewellite has been determined by Cocco (1961), and refined by Cocco and Sabelli (1962). From a structural point of view, their orientation is the most advantageous one; the crystal morphology, however, follows a subcell of the structure, and shows a halved b and a prominent development of prism faces in Cocco's zone [101].

PARAGENESIS

Thermodynamic data on whewellite at 25°C and one atmosphere total pressure are available in Latimer (1952). Using these data, one may calculate the stability of whewellite with respect to calcite. For the reaction



$$\begin{aligned} \Delta F_r^0 = \sum \Delta F_f^0 \text{ products} - \sum \Delta F_f^0 \text{ reactants} = & -269.78 + (-94.6) + (0) \\ & - (-360.6) = -3.78 \text{ Kcal} \end{aligned}$$

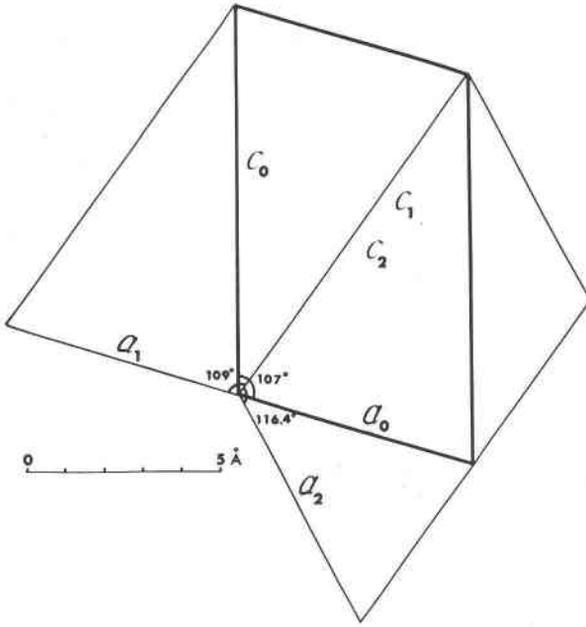


FIG. 1. Axes a and c of different unit cells used in space group investigations of whewellite: $a_0, c_0 = a$ and c axes, respectively, of this study, of Hoffman (1961), and of the conventional morphological orientation $\beta = 107^\circ 5'$. a_1, c_1 : a and c axes, respectively of Cocco (1961), and of the alternative orientation of Arnott *et al.* (1965). $\beta = 109^\circ 9'$. a_2, c_2 : a and c axes, respectively, of Arnott *et al.* (1965). $\beta = 116.4^\circ$. The axis c_1 (c_2) is the direction of the glide component of the mirror plane.

At equilibrium between calcite and whewellite.

$$\Delta F_r^0 = -RT \ln K = -1.364 \log K \quad \text{at } 25^\circ\text{C}$$

where K is the equilibrium constant of the reaction. Hence,

$$-3.78 = -1.364 \log [\text{CaCO}_3][\text{CO}_2][\text{H}_2]/[\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}]$$

since the activities of the pure solids are unity at standard conditions,

$$\log [\text{CO}_2][\text{H}_2] = 3.78/1.364 = 2.77$$

$$[\text{CO}_2][\text{H}_2] = p_{\text{CO}_2} p_{\text{H}_2} = 10^{2.77} = 330$$

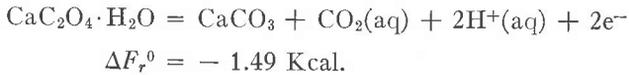
The lowest confining pressure would be found at

$$p_{\text{CO}_2} = p_{\text{H}_2} = (330)^{\frac{1}{2}} = (18 \text{ atm.}) = 270 \text{ psi}$$

It seems doubtful that any low-temperature natural environments include 18 atmospheres of H_2 and CO_2 pressures.

An alternative way to treat the reaction is in terms of oxidation poten-

tial (Eh), pH, and activity of dissolved CO₂ (Garrels and Christ, 1965). In this case, the reaction is written



At unit activities,

$$E^0 = \Delta F_r^0 / nf = -1.49 / 2 \times 23.06 = -.03 \text{ volts}$$

where n is the number of electrons in the reaction, and f is the faraday, 23.06 kcal per volt-gram equivalent.

In general,

$$\text{Eh} = E^0 + \left(\frac{RT}{nf} \right) \ln Q$$

or, at 25°C, and 1 atm. total pressure.

$$\text{Eh} = E^0 + (0.059n) \log Q$$

where Q has the same form as the equilibrium constant K , but does not necessarily represent equilibrium conditions. For the reaction under consideration,

$$\begin{aligned} \text{Eh} &= (-.03) + 0.059/2 \log [\text{H}^+]^2 [\text{CO}_2] \\ &= (-.03) - 0.059 \text{ pH} + 0.029 \log [\text{CO}_2] \end{aligned}$$

Water and hydrogen gas at one atmosphere pressure are in equilibrium at an E^0 of 0 volts and along the line $\text{Eh} = -0.059$ (pH) volts. This equilibrium is known as the lower stability limit of water; at lower voltages water should decompose, releasing hydrogen gas.

A detailed discussion of equilibrium fields is out of place here, for the calculations above have not considered such problems as the complications of equilibrium between oxalate and carbonate species under different conditions of Eh and pH. Carbonate equilibria (but not oxalate equilibria) are discussed in detail in Garrels and Christ (1965); and are diagrammed by Ross in Schmitt (1962). It is enough to observe that at 25°C and one atmosphere total pressure, the equilibrium field of whewellite lies below the lower stability limit of water.

Such environments are rare in natural systems (Garrels and Christ, 1965), but organic matter decomposing in the absence of air can bring water below its lower stability limit. In the laboratory undervoltages of about 0.5 volt are necessary to decompose water at an appreciable rate. Native iron is stable with respect to magnetite 0.084 volt below the lower stability limit of water, and reports of naturally occurring

native iron in carbonaceous sediments (Allen, 1897) indicate that under special conditions such environments may persist for some time in nature. Under these conditions whewellite probably would be stable with respect to calcite.

More often, whewellite may form as a metastable mineral in waters above the lower stability limit. Latimer (1952) notes that although the E^0 for the oxidation of oxalic acid to carbonate is -0.49 volts, the oxidation does not proceed rapidly at room temperature, even with as strong an oxidizer as permanganate. Oxalic acid is thus metastable in water solution, but it is extremely persistent.

Because the solubility product of whewellite is extremely small (1.3×10^{-9}) and because the precipitation reaction is very rapid, calcium in solution is precipitated with oxalate as whewellite in chemical analysis, even though the reaction is metastable with respect to the breakdown of oxalate into carbonate and the precipitation of the calcium as carbonate.

Many plants contain oxalic acid, whewellite, or other oxalates (Esau, 1965, p. 29; Fogg, 1962, p. 478), and in natural environments persistent metastable oxalate released into solution by organic decomposition may cause whewellite to precipitate outside of its normal field of stability. In such situations the appearance of whewellite is a reflection not of equilibrium, but of reaction rates. Thus, the association of whewellite with coal beds, or, as in the present occurrence, with black shales, may reflect not reducing conditions below the lower stability limit of water, but the availability of metastable oxalate in solution.

Clifton (1957) felt that the concretions of the Ohio Shale formed "after deposition of the enclosing sediments, but before complete compaction of the muds." This was probably a period of strongly reducing conditions and active decomposition of organic material, and the occurrence of whewellite in the concretions is entirely compatible with the theory of their development at this time. If this is so, the whewellite has persisted since its formation in what were probably relatively unfavorable environments for a long period of geologic time. The friable calcite coatings found on many of the whewellite masses probably come from the alteration of whewellite under the attack of near-surface ground water in relatively recent geologic time.

Lippman (1955) described a very similar occurrence of calcite, barite, and whewellite in septaria from near Hoheneggelsen, Germany. He suggested that during crystallization of these minerals, cracks in the septaria were open and under hydrostatic pressure, whereas the surrounding sediments were under greater lithostatic pressure. Since the solubility of solids increases with pressure, pore water could be undersaturated with respect to a mineral in the sediments but oversaturated with the mineral in the lower pressure cracks.

His calculations showed that this pressure difference was of the right order to explain the occurrence of the minerals in the septaria only; the fact that whewellite may be metastable rather than truly stable during its formation does not affect this analysis.

STABILITY OF WHEWELLITE AT OTHER TEMPERATURES AND PRESSURES

The free energy of the reaction



will vary with temperature and with total pressure. Because of the high entropy of the gases, the free energy of the assemblage on the right-hand side of the equation increases more swiftly with rising temperature than does the free energy of whewellite. That is, an increase in temperature increases the stability of gases plus calcite relative to whewellite. In addition, high temperatures would be expected to discourage the metastable persistence of oxalate in solution and to speed up its decomposition to carbonate.

A decrease in temperature will favor whewellite relative to calcite plus gases; however, a primitive but useful calculation of the sort

$$\Delta F_r^0(T) = \Delta H_r^0(298) - T\Delta S_r^0(298)$$

indicates that even at 0°C calcite is stable with respect to whewellite even at several atmospheres $\text{CO}_2 + \text{H}_2$ pressure.

The molar volume of calcite is smaller than that of whewellite; consequently, an increase in total pressure—not pressure of carbon dioxide or of hydrogen—would require higher fugacities of the gases at equilibrium. That is, calcite would be stable with respect to whewellite over a broader range of conditions than it is at low pressure, although confinement which permitted the buildup of H_2 and CO_2 pressures might stabilize whewellite.

Pecora and Kerr (1954) suggested that the occurrence of whewellite in some low temperature hydrothermal ore veins were not primary, but that the whewellite was deposited from ground waters carrying oxalate from near-by organic material. It was pointed out above, that increased temperature or total pressure broadens the field of stability of calcite with respect to whewellite, and that the appearance of whewellite in low temperature environments may in many cases be dependent on the availability of organically derived metastable oxalate in solution. These facts encourage the belief that whewellite is not a primary vein mineral.

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