

WARDSMITHITE, $5\text{CaO}\cdot\text{MgO}\cdot 12\text{B}_2\text{O}_3\cdot 30\text{H}_2\text{O}$, A NEW BORATE
MINERAL FROM THE DEATH VALLEY REGION,
CALIFORNIA¹

RICHARD C. ERD, JAMES F. McALLISTER, AND ANGELINA C. VLISIDIS,
*U. S. Geological Survey, Menlo Park, Calif. 94025, and
Washington, D. C. 20242*

ABSTRACT

Wardsmithite, $5\text{CaO}\cdot\text{MgO}\cdot 12\text{B}_2\text{O}_3\cdot 30\text{H}_2\text{O}$, is a new borate found at two localities in the Death Valley region, Inyo County, California, on weathered veins of colemanite or priceite in the Furnace Creek Formation (Pliocene). It occurs as nodules and coatings in gowerite, ulexite, and colemanite.

The mineral is hexagonal (or pseudohexagonal) with a platy habit and cleavage $\{0001\}$. Typically, it occurs as aggregates of subparallel plates to $75\ \mu\text{m}$ in diameter, uncommonly as single crystals to $15\ \mu\text{m}$ in diameter. The strongest lines in the X-ray powder diffraction pattern (*unindexed*) are, in Å: 13.5 (100), 12.3 (62), 6.12 (55), 3.358 (51), 4.721 (42), 2.744 (26).

Infrared absorption peaks (in cm^{-1}) are 790, 810, 890, 1000, 1070, 1335, and 1615.

Crystals of wardsmithite are colorless. Optically it is uniaxial (-), with $\omega = 1.490 \pm 0.002$, $\epsilon = 1.476 \pm 0.002$. Hardness is $2\frac{1}{2}$; specific gravity, 1.88 ± 0.02 .

Chemical analysis gave, in weight percent, B_2O_3 48.58, CaO 16.50, MgO 2.26, H_2O 32.44, sum 99.78. Spectroscopic analysis showed Si, Al, Na, Mn, Ba, Cu, and Pb in small amount.

Wardsmithite is named after Ward C. Smith, geologist of the U.S. Geological Survey

INTRODUCTION

Further study of the borate minerals produced by weathering of priceite and colemanite in the Furnace Creek Formation shows that the mineral referred to as an "undescribed calcium borate" mineral associated with nobleite (Erd *et al.*, 1961, p. 561) is the first known natural occurrence of $5\text{CaO}\cdot\text{MgO}\cdot 12\text{B}_2\text{O}_3\cdot 30\text{H}_2\text{O}$, wardsmithite. The new mineral is named after Ward C. Smith, geologist of the U.S. Geological Survey, in recognition of his advancement of borate studies in southwestern United States.²

Samples containing a small quantity of the mineral were collected in 1956 by McAllister while mapping the geology of the Furnace Creek borate area in the Death Valley region, California, for the U.S. Geological Survey in cooperation with the California Division of Mines and Geology. Preliminary determination of some optical and chemical properties of the mineral by him in 1959 seemed to indicate an undescribed calcium borate; and X-ray diffraction data obtained by Erd were con-

¹ Publication authorized by the Director, U.S. Geological Survey.

² The mineral and the name have been approved by the Commission on New Minerals Names, IMA.

clusive for such a borate. Another occurrence in the area was found by Erd in 1961. Enough wardsmithite for chemical analysis was separated from samples collected in 1965 from the first locality. Type material will be deposited in the U.S. National Museum, Washington, D. C.

OCCURRENCE

Rare and inconspicuous among the efflorescent borate minerals, wardsmithite has been found at two localities about 2 miles apart. The first locality, on the Hard Scramble patented mining claim of the United States Borax & Chemical Corporation, is on the western slope of low foothills of the Black Mountains, 1.9 miles N. 72° W. from Ryan. The second occurrence, which is on the north bank of the wash running northwest from U. S. mineral monument 47 to the junction of California Highway 190 and the road to Dantes View, lies 2.1 miles N. 17° W. from Ryan. It is on the old Neglect claim, which was merged with the Oliver claim when patented as the Oliver Consolidated claim by the United States Borax & Chemical Corporation.

At both places the wardsmithite is on weathered veins of colemanite or priceite in deformed Furnace Creek Formation of Pliocene age. The colemanite veins on the Neglect claim are in lacustrine gypsiferous mudstone and sandstone derived from siliceous volcanic rocks and closely associated with some algal limestone. The priceite veins on the Hard Scramble claim are in altered fragmental basalt, which is stratigraphically below the gypsiferous zone and considerably above the zone of commercial borate deposits in the formation.

Wardsmithite at the main occurrence on the Hard Scramble claim is considerably rarer than gowerite, nobleite, microgranular colemanite, and particularly ulexite. These minerals and some ginorite, hungchaoite, rivadavite, macallisterite, kurnakovite, inderite, thenardite, gypsum, and calcite, in various proportions, form aggregates near the surface, in continuation with priceite and colemanite veins below them. A coarse boxwork of calcite or fine-grained colemanite remains on some outcrops. Some of the aggregates enclose remnants of the priceite veins and the transition downward from efflorescent minerals to priceite alone is complete within several tens of centimeters below the surface. The wardsmithite, in exceedingly fine-grained, soft clots, lies on and fills in between gowerite blades radiating from compact cores, and it lies on tufts of ulexite in a characteristic specimen. Some of this ulexite is on the gowerite, and both are attached to solid aggregates of nobleite.

The scanty amount of wardsmithite collected at the Oliver Consolidated locality occurs as very fine-grained nodules, commonly as much as 2 mm in diameter, and irregular coatings on a specimen of coarse cole-

manite and gypsum. The colemanite is anhedral or subhedral; the largest subhedral crystal noted is about 15 mm by 5 mm. Abundant fine-grained gypsum that fills fractures and incrusts surfaces is associated with some fine-grained celestite, meyerhofferite, and inoyoite and microcrystals of colemanite. The wardsmithite formed on surfaces of corroded colemanite and between small spherules of fine-grained ulexite, the most abundant efflorescent borate, on crusts of gypsum.

CRYSTALLOGRAPHY

X-ray data. The X-ray data for wardsmithite are reported in Table 1. No variation in patterns was found for various samples of the mineral from the two localities. Crystals are too small to permit investigation of the crystallography of the unit cell by single-crystal techniques. Considering the optical evidence for hexagonal symmetry, knowing the approximate volume of the unit cell for one formula molecular weight (or multiples of this), and equating either of two sets of spacings with enhanced intensities with the "basal" spacing, we were still unable to index the X-ray powder data on the basis of a hexagonal cell. Attempts to obtain an electron diffraction pattern were also unsuccessful, as grains small enough to be useful in selected-area electron diffraction decomposed in the beam before a pattern could be obtained. We conclude that ward-

TABLE 1. X-RAY DIFFRACTION DATA FOR WARDSMITHITE

d_{hkl} (Å)	<i>I</i>	d_{hkl} (Å)	<i>I</i>	d_{hkl} (Å)	<i>I</i>	d_{hkl} (Å)	<i>I</i>
13.5	100	4.482	4	3.060	14	2.320	8
12.3	62	4.285	4	3.014	14	2.150	15
10.8	7	4.162	20	2.985	12	2.104	7
9.17	5	4.079	5	2.937	14	2.059	9
7.93	11	3.967	11	2.918	20	2.037	9
7.43	19	3.836	6	2.859	6	1.983	14
6.82	12	3.711	10	2.806	11	1.949	16
6.73	22	3.613	19	2.744	26	1.916	14
6.51	12	3.577	18	2.686	10	1.906	14
6.12	55	3.414	12	2.673	11	1.872	8
5.423	6	3.358	51	2.627	7	1.855	12
5.263	13	3.246	11	2.586	11	1.832	7
4.987	6	3.202	15	2.480	9	1.789	4
4.721	42	3.095	14	2.424	11	1.752	9

Plus additional lines all with $I < 5$

Split of analyzed sample. X-ray diffractometer data, Chart X3205: Cu/Ni radiation, $\lambda_{CuK\alpha_1} = 1.54051$ Å; silicon used as internal standard; scanned at $\frac{1}{4}^\circ$ per minute from $2-65^\circ 2\theta$.

smithite is pseudohexagonal and that the true symmetry is monoclinic or lower. Until the true symmetry is established, it is convenient to describe the properties of wardsmithite with reference to a hexagonal cell.

Morphology. Wardsmithite crystals are anhedral to subhedral with a hexagonal outline (an individual grain with interfacial angles very near to 60° is shown in the electronmicrograph, Fig. 1) and a platy habit $\{0001\}$.

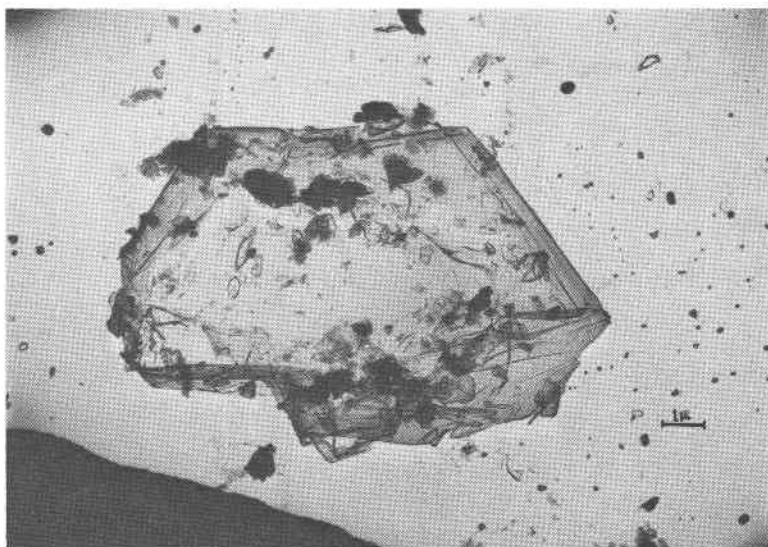


FIG. 1. Electron micrograph of wardsmithite crystal showing hexagonal outline. Aggregates of smaller crystals of wardsmithite appear as nearly opaque grains on the surface of the large crystal.

Under the microscope, wardsmithite typically appears as aggregates to $75\mu\text{m}$ in diameter composed of subparallel plates and, less commonly, as single crystals up to $15\mu\text{m}$ in diameter and $2\mu\text{m}$ in thickness.

PHYSICAL AND OPTICAL PROPERTIES

There appears to be a good cleavage parallel to the "base" $\{0001\}$. The hardness ($2\frac{1}{2}$) was determined by rubbing wardsmithite on clear surfaces of gypsum and calcite and examining the surfaces under the microscope. The specific gravity, determined by the sink-float method in bromoform-acetone mixtures checked with a Westphal balance, is 1.88 ± 0.02 . By a pycnometric method (following Fahey, 1961), the specific gravity of a 400 mg sample was found to be 1.85 at 25°C . There

is excellent agreement between the measured specific gravity (with the value 1.88 giving a better fit), indices of refraction, and chemical composition using the Gladstone-Dale relationship (see Jaffe, 1956). Aggregates of the mineral are white (Munsell color N9) and have a vitreous luster. The mineral is not fluorescent.

Wardsmithite is colorless in transmitted light. It is uniaxial negative (or biaxial negative with a very small $2V$) with $\omega = 1.490 \pm 0.002$ and $\epsilon = 1.476 \pm 0.002$. Hexagonal plates show no birefringence on basal surfaces and have straight extinction when viewed edge-on. Dispersion could not be determined.

CHEMICAL PROPERTIES

Analysis. A 450 mg sample of the mineral from the Hard Scramble locality was obtained by separation in bromoform-acetone mixtures. About 3 percent gowerite, which could not be mechanically or chemically separated, was present in the sample analyzed. This was the only impurity noted optically; no lines attributable to gowerite are present in the X-ray powder pattern of the analyzed sample. The X-ray powder patterns of samples from the two localities are identical; this, together with the optical evidence, strongly suggests that only one phase is present.

A split of the sample that weighed 200 mg was dissolved in 30 ml of 1 N HCl. This solution was adjusted to a pH of 2.5 and then passed through an ion exchange column in order to separate B_2O_3 from the cations (following Martin and Hayes, 1952). Borate was determined by titration in the usual way with standard sodium hydroxide after addition of mannite to the neutralized borate solution. The cations were recovered from the column and determined by the standard methods of quantitative analysis outlined by Hillebrand *et al.* (1953). Water was determined by heating a 150 mg sample to $500^\circ C$ in a thermostatically-controlled electric furnace and then measuring the loss of weight of the sample. It was found that at higher temperatures (about $700^\circ C$) loss of B_2O_3 resulted. The results of the analysis are shown in Table 2. The empirical formula $5CaO \cdot MgO \cdot 12B_2O_3 \cdot 30H_2O$ is suggested as the simplest formula containing one atom of Mg, as substitution of Mg for Ca in borates seems to be very limited. The correct structural formula must remain unknown until larger crystals are found that will permit determination of the crystal structure.

Synthesis. We did not attempt the synthesis of wardsmithite. A compound close to this composition, $4CaO \cdot 2MgO \cdot 12B_2O_3 \cdot 30H_2O$ (her formula doubled for comparison), was prepared by Kurnakova (1953, p. 57-60) by a reaction between inderborite and an aqueous solution of boric acid at $25^\circ C$ that required 297 days for completion. This compound, plus impurities, was also obtained in 215 days at $25^\circ C$ by a reaction between aqueous solutions of boric acid, $Ca(OH)_2$, and $Mg(OH)_2$. The only properties given for this compound are the indices of refraction, $\gamma = 1.538$ and $\alpha = 1.486$, determined by E. E. Burovaya (Kurnakova, 1953). An approximate value for the density, $1.98 \pm 4 \text{ g/cm}^3$, can be calculated from the optical data and the chemical composition using the Gladstone-Dale relationship.

There are no compounds of the type $MO:2B_2O_3:5H_2O$ (wardsmithite

TABLE 2. CHEMICAL ANALYSIS OF WARDSMITHITE

	Weight percent ^a	Recalc. ^b	Molecular proportions	Ratios	Calculated composition ^c (weight percent)
MgO	2.26	2.34	0.0578	0.98	2.38
CaO	16.50	16.56	0.2953	5.02	16.52
B ₂ O ₃	48.58	48.37	0.6946	11.81	49.25
H ₂ O	32.44	32.73	1.8167	30.88	31.85
R ₂ O ₃	0.30	—			
Insol. residue	0.20	—			
Total	100.28	100.00			100.00

^a A. C. Vlisidis, analyst. Sample W-16693 (USGS) from the Hard Scramble claim. Spectroscopic analysis by J. L. Harris also showed the following elements, in weight percent: Si, 0.05; Al, <0.001; Na, 0.15; Mn, 0.007; Ba, 0.0005; Cu, 0.02; and Pb, 0.001. For limits of sensitivity see Bastron *et al.* (1960).

^b Recalculated to 100 percent after subtracting 3 percent gowerrite.

^c For 5CaO·MgO·12B₂O₃·30H₂O.

composition in simplest ratio) known in the separate systems CaO-B₂O₃-H₂O or MgO-B₂O₃-H₂O. The synthetic compound CaO·2B₂O₃·4H₂O was reported by Ditte (1883, p. 1668) and the names bechilite and borocalcite have been used for minerals said to have this composition. These "minerals" have been found to be mixtures, and there is no modern confirmation of Ditte's synthesis (*see* summaries in Palache *et al.*, 1951, p. 345, 347, 365; Nies and Campbell, 1964, p. 127).

Solubility. Wardsmithite is insoluble in methyl alcohol, is very slightly soluble in cold water, slightly soluble in hot water, and readily soluble in cold dilute acids.

Pyrognostics. Heated in a closed tube, wardsmithite gives off water, sinters, and then fuses to a gray mass which, with continued heating, becomes a clear glass. There was insufficient sample available for thermal analyses.

INFRARED ABSORPTION ANALYSIS

Absorption spectra of wardsmithite and of an unidentified dehydration(?) product were prepared by Dr. C. E. Weir and are shown in Figure 2. Two different specimens of wardsmithite were run under three different conditions and all the results agreed within experimental error.

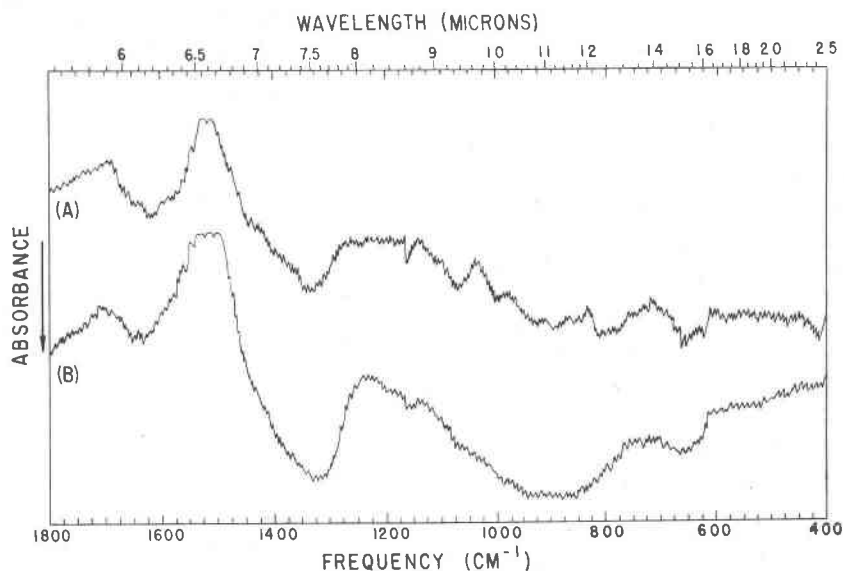


FIG. 2. Infrared spectra of wardsmithite (A) and of an unidentified dehydration(?) product (B) in the region 1800–400 cm^{-1} . C. E. Weir, analyst.

This further demonstrates the homogeneity of the wardsmithite samples used in this study. Infrared absorption peaks (in cm^{-1}) are 790, 810, 890, 1000, 1070, 1335, and 1615. Weir (personal commun., 1966) notes the presence of both boron tetrahedra and triangles in wardsmithite. Tetrahedra are indicated by strong absorption with broad bands below 1000 cm^{-1} , which is characteristic of 4-fold boron, triangles by the broad band at 1335 cm^{-1} . The weak band near 1615 cm^{-1} is assigned to H-O-H bending. Further interpretation is not possible; the difficulties involved in the interpretation of the infrared spectra of the hydrated borates have been pointed out by Weir (1966, p. 163–164).

The spectra of wardsmithite and the unidentified dehydration(?) product are very similar except that the bands may be shifted slightly and show less band structure for the unidentified material. Also the band near 1615 cm^{-1} is more shallow for the unidentified material, strengthening the suggestion that this is a dehydration product of wardsmithite. Further description of this material is given below.

UNIDENTIFIED DEHYDRATION(?) PRODUCT

An unidentified borate mineral was found in one sample of material from the Hard Scramble locality. It appeared to be a small clump of wardsmithite, about 5 mm in diameter, but having a duller luster. Under

the microscope, however, it was colorless and isotropic with $n = 1.502 \pm 0.002$. There were many anhedral grains less than $1\mu\text{m}$ in diameter, some bearing a resemblance to rounded hexagonal plates of wardsmithite, but most of the material consisted of aggregates of about the same size range as wardsmithite. The only impurity present was gowerite, less than one percent.

The isotropic borate is amorphous to X-rays. The infrared spectra (Fig. 2), however, are similar to those of wardsmithite and are discussed above. Insoluble or only slightly soluble in cold water, the material is slightly to moderate soluble in hot water and recrystallizes in part to minute rhomb-shaped euhedra having high birefringence and in part to amorphous material at the edge of the drop. The amount of material so dissolved and reprecipitated is too small to permit identification, however. The isotropic borate is easily soluble in cold dilute acids. Addition of a drop of H_2SO_4 to a solution of the mineral in dilute HCl gives, on evaporation, crystals of gypsum and sassolite. In a closed tube, the mineral gives off a slight amount of water, then sinters and fuses in the same manner as wardsmithite. The small amount of material precludes further tests, and data are insufficient to characterize this as a distinct mineral species. From the relationship with gowerite, appearance, infrared spectra, and chemical tests, this mineral appears to be a dehydration product of wardsmithite—the first essentially amorphous borate found in nature so far as we are aware. The amorphous material was sought for in other samples of wardsmithite (especially in the sample used for the chemical analysis), but none was found.

ACKNOWLEDGMENTS

The authors wish to thank their colleagues of the U.S. Geological Survey: Michael H. Carr for the electronmicrographs, G. Donald Eberlein for help in the optical study; Joseph L. Harris for the spectroscopic analysis; and T. E. C. Keith for the mineral separation. We also thank Dr. Charles E. Weir (U.S. National Bureau of Standards) for the infrared analyses and the U.S. Borax & Chemical Corporation for permission to visit and collect samples from their properties in the Death Valley region. Dr. Lorenzo F. Aristarain. Universidad Nacional Autónoma de Mexico, offered helpful suggestions on the manuscript.

REFERENCES

- BASTRON, HARRY, P. R. BARNETT, AND K. J. MURATA (1960) Method for the quantitative spectrochemical analysis of rocks, minerals, ores, and other materials by a powder d.c. arc technique. *U.S. Geol. Surv. Bull.* **1084-C**, 165–182.
- ERD, R. C., J. F. McALLISTER, AND A. C. VLISIDIS (1961) Nobleite, another new hydrous calcium borate from the Death Valley region, California. *Amer. Mineral.* **46**, 560–571.
- FAHEY, J. J. (1961) A method for determining the specific gravity of sand and ground rock or minerals. *U.S. Geol. Surv. Prof. Pap.*, **424-C**, C372–C373.
- HILLEBRAND, W. F., AND G. E. F. LUNDELL (1953) *Applied inorganic analysis*. 2nd ed.,

- rev. by G. E. F. LUNDELL, H. A. BRIGHT, AND J. I. HOFFMAN, John Wiley and Sons, Inc., New York, N. Y., 1034 p.
- JAFFE, H. W. (1956) Application of the rule of Gladstone and Dale to minerals. *Amer. Mineral.*, **41**, 757-777.
- KURNAKOVA, A. G. (1953) Troynye i chetvernye sistemy s bornoy kislotoy (Ternary and quaternary system containing boric acid). In A. F. Iyevin'sh, A. D. Keshan, and L. K. Lepin' (Eds.) *Khimiya Boratov [Chemistry of the Borates]*. Izdat. Akad. Nauk Latvyskoy SSR, Riga, 45-66.
- MARTIN, J. R., AND J. R. HAYES (1952) Application of ion exchange to the determination of boron. *Anal. Chem.* **24**, 182-185.
- NIES, N. P., AND G. W. CAMPBELL (1964) Inorganic boron-oxygen chemistry. In R. M. Adams, (ed.) *Boron, Metallo-boron Compounds and Borane*, Interscience Publishers, New York, N. Y., p. 53-231.
- PALACHE, C., H. BERMAN AND C. FRONDEL (1951) *The System of Mineralogy . . . of Dana*, 7th ed., vol. 2, John Wiley and Sons, New York, 1124 p.
- WEIR, C. E. (1966) Infrared spectra of the hydrated borates. *J. Res. Nat. Bur. Stand., A.* **70A** (2), 153-164.

Manuscript received, October 11, 1969; accepted for publication December 1, 1969.