Wheatleyite, $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$, a natural sodium copper salt of oxalic acid*

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Abstract

Wheatleyite, $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$, occurs as aggregates of blue acicular crystals associated with galena and sphalerite at the Wheatley mine, near Phoenixville, Pennsylvania. It is triclinic, $P\bar{1}$, with $a = 7.559(3)$, $b = 9.665(4)$, $c = 3.589(1)$ Å, $\alpha = 76.65(2)°$, $\beta = 103.67(2)°$, $\gamma = 109.10(2)°$, and $Z = 1$. The strongest powder X-ray diffraction lines are (d_{obs}, I_{obs}, hkl) 7.04(8)(100), 6.539(10)(110), 3.655(5)(210), 3.169(9)(121), 2.799(4)(221), 2.538(3)(021), 2.497(3)(231), and 2.344(3)(300). Measured and calculated densities are 2.27(4) and 2.250 g/cm³, respectively. The Mohs' hardness is 1 to 2, and there is a perfect {100} cleavage. Optically, wheatleyite is biaxial positive with indices $\alpha = 1.400(4)$, $\beta = 1.499(2)$, $\gamma = 1.667(2)$, and $2V = 83(5)°$. Dispersion is $r < v$; pleochroism is X = colorless, Y = pale blue, Z = dark blue; absorption is $Z > Y > X$. A crystal-structure determination shows wheatleyite to be identical to synthetic $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$.

Introduction

Although numerous salts of oxalic acid have been synthesized in the laboratory, these compounds are very rare in the geologic environment, both in terms of the number of species known and their frequency of occurrence. Strunz (1970) listed only seven oxalate minerals, of which only two, whewellite ($CaC_2O_4 \cdot H_2O$) and weddellite ($CaC_2O_4 \cdot 2H_2O$), occur in significant quantities. Crystalline oxalates, in particular the aforementioned calcium oxalates, are of much greater importance in the biosphere, being especially abundant in the tissues of many vascular plants and in human urinary calculi (Gibson, 1974; Levinson et al., 1985). The calcium oxalates are, in fact, the chief culprits in human urinary-stone disease.

The natural sodium copper oxalate to be described here was called to the attention of one of the authors (P.J.D.) by William Pinch of Rochester, New York, who had recognized its uncommon character and provided the type specimen for study. Subsequent investigation has shown the compound to be a new mineral species, which we have named wheatleyite after the type locality, the Wheatley mine, Chester County, Pennsylvania. The species and the name have been approved by the Commission on New Minerals and Mineral Names, IMA. Type material is preserved in the Smithsonian Institution, Washington, D.C., under catalogue number NMNH 162531.

Occurrence and paragenesis

The type (and only) specimen of wheatleyite was discovered on the dumps of the now-abandoned Wheatley mine located near Phoenixville, Chester County, Pennsylvania. The mines of that region have most recently been described by Smith (1977, 1978), who noted that the host rock for the ore vein is, for the most part, a Precambrian biotite gneiss. The northern part of the vein is in a red Triassic siltstone, the Stockton Formation. The Wheatley mine is in a vein-type lead-zinc deposit, which was also exploited at the Brookdale and Phoenix mines. Additional details concerning the geology and mining operations in the district are given by Rogers (1853), Smith (1855), and Miller (1923).

Wheatleyite is known from only one hand specimen, which consists mostly of massive galena and sphalerite in contact with quartz. Both sulfides are tarnished a pale metallic violet color. On an exposed surface, this primary assemblage is coated with secondary cerussite, wheatleyite, sphalerite, and an ill-defined, powdery lead oxalate. Wheatleyite forms single crystals and is clearly older than the secondary sphalerite that overlies it. These facts argue for its status as a naturally formed phase rather than an artifact. It must be emphasized, however, that the natural origin of wheatleyite should not be construed as proof of a similar origin, and hence mineral species status, for any other oxalates which may be found at the Wheatley mine. The mine dumps and shafts in this area have long been used for the disposal of refuse and animal waste. Crys-

talline oxalates and other unusual compounds may conceivably be formed as artifacts by reaction of these materials with mine or ground waters.

PHYSICAL AND OPTICAL PROPERTIES

Wheatleyite is bright blue in color and has a light blue streak. The mineral is very brittle, it has a Mohs' hardness of approximately 1 to 2, and the luster is vitreous on both fracture and cleavage surfaces. There is a perfect cleavage on {100} and two lesser cleavages of unknown orientation. The latter were observed only with the polarizing microscope under oil immersion. The density, measured with heavy-liquid techniques, is 2.27(4) g/cm^3, which agrees well with the calculated value of 2.250 g/cm^3. Wheatleyite is soluble in water.

Optically, wheatleyite is biaxial positive with $2V = 83(5)°$. The indices of refraction are $\alpha = 1.400(4)$, $\beta = 1.499(2)$, and $\gamma = 1.667(2)$ in sodium light. Dispersion is moderate $r < v$. One optic axis is approximately normal to the plane of the {100} cleavage. Wheatleyite is pleochroic with X = colorless, Y = very pale blue, and Z = intense dark blue. Absorption is $Z > Y > X$. The compatibility index, $1 - (K_p/K_c)$, is 0.051. There is no discernible fluorescence in ultraviolet radiation.

CHEMISTRY

Wheatleyite was chemically analyzed using an ARL-SEMQ electron microprobe operated at 15 kV and a sample current of 0.025 μA. The mineral had a marked tendency to decompose under the electron beam, but the very small amount of material available for analysis necessitated the use of the microprobe technique. A wavelength-dispersive scan indicated the absence of any elements of atomic number greater than 8, other than Na and Cu. A partial quantitative analysis, performed using cuprite (for Cu) and maricite (for Na) as standards, yielded the approximate concentrations 27% CuO and 20% Na$_2$O. For a qualitative determination of the light elements, the mineral was analyzed with the ion microprobe, which revealed the presence of C, O, and H in addition to Na and Cu. Using these data and the results of the crystal-structure analysis, it was possible to fix the formula of wheatleyite at Na$_2$Cu(C$_2$O$_4$)$_2 \cdot$2H$_2$O. This corresponds to the composition CuO 24.73, Na$_2$O 19.27, C$_2$O$_3$ 44.79, and H$_2$O 11.21%. Considering the unfavorable analytical conditions, the analytical values for CuO and Na$_2$O are in remarkably good agreement with the calculated ones. The presence of the oxalate ion in wheatleyite was verified by a qualitative chemical test, involving solution in HCl followed by addition of CaCl$_2$ and precipitation of weddellite with NH$_4$OH. The precipitate was identified by powder X-ray diffraction.

CRYSTALLOGRAPHY

Wheatleyite forms aggregates of thin acicular crystals, individual crystals being up to 2 mm in length. Study by the Weissenberg, precession, and oscillating crystal methods proved it to be triclinic, $P1$ or $P\bar{1}$, with $a = 7.559(3)$,

Table 1. Powder X-ray diffraction data

I	d_{obs}	d_{calc}	hkl	I	d_{obs}	d_{calc}	hkl
8	7.045	7.033	100	1	2.240	2.240	21̄1
10	6.539	6.531	1̄10	<1	2.193	2.193	1̄41
2	4.904	4.899	110	2	2.178	2.177	3̄30
1	4.414	4.414	12̄0	2	2.132	2.133	331
5	3.655	3.652	21̄0	1	2.107	2.107	131
1b	3.485	3.516	200	1	2.059	2.061	13̄1
		3.476	1̄11	1	2.013	2.014	230
≪1	3.406	3.407	011	1	1.967	1.967	221
9	3.169	3.165	1̄21	<1	1.955	1.957	1̄31
2	2.988	2.996	210	3	1.879	1.879	23̄1
		2.984	021	1	1.866	1.870	320
<1	2.901	2.895	101	<1	1.829	1.832	250
≪1	2.847	2.856	1̄11			1.828	1̄51
4	2.799	2.797	2̄21	≪1	1.810	1.810	4̄21
2	2.740	2.739	111			1.808	3̄11
≪1	2.700	2.700	2̄30	<1	1.796	1.796	141, 301
≪1	2.661	2.657	1̄31	≪1	1.774	1.774	1̄22
3	2.538	2.535	02̄1	<1	1.753	1.754	04̄1
3	2.497	2.496	2̄31			1.751	3̄2̄1
1	2.475	2.475	031	<1	1.740	1.742	1̄02
1	2.449	2.450	220			1.738	2̄22
		2.447	31̄0	<1	1.717	1.719	002
≪1	2.411	2.411	12̄1			1.718	051
1	2.371	2.371	2̄1̄1	<1	1.685	1.688	240
3	2.344	2.344	300	≪1	1.603	1.607	112
<1	2.262	2.268	201	≪1	1.581	1.582	2̄42
		2.257	3̄21	<1	1.558	1.557	11̄2
				<1	1.541	1.541	241

Note: 114.6-mm Gandolfi camera, Cu$K\alpha$ radiation, visually estimated intensities, b = broadened line. Indexed using the single-crystal intensity data.

$b = 9.665(4)$, $c = 3.589(1)$ Å, $\alpha = 76.65(2)°$, $\beta = 103.67(2)°$, and $\gamma = 109.10(2)°$. The axial ratio $a:b:c$ is 0.7821:1:0.3713 and the cell volume is 237.3(2) Å^3. There is also a body-centered pseudomonoclinic cell having parameters $a' = 13.5$, $b' = 3.59$, $c' = 10.1$ Å, $\alpha \sim \gamma \sim 90°$, and $\beta = 104.6°$. The parameters of the triclinic cell were refined by least-squares from the powder X-ray diffraction data (Table 1). The latter were obtained using a 114.6-mm diameter Gandolfi camera, Cu$K\alpha$ radiation, a polycrystalline sample, and NBS silicon ($a = 5.43088$ Å) as an internal standard. The crystal-structure determination fixed the space group at $P\bar{1}$ and the number of formula weights per cell at one. Twinning was sometimes observed on the single-crystal diffraction photographs, but the twin law was not determined.

The crystal structure of wheatleyite was solved by Patterson methods and refined to a conventional unweighted residual of 0.080 in space group $P\bar{1}$. Attempts to refine the model in $P1$ symmetry were unsuccessful. Shortly after the present study had commenced the structure of synthetic Na$_2$Cu(C$_2$O$_4$)$_2 \cdot$2H$_2$O was described independently by Gleizes et al. (1980) and Chananont et al. (1980). Comparison of their results with ours proves that the natural and synthetic phases are essentially identical, and the reader is therefore referred to the works of these authors for details of the wheatleyite structure.

DISCUSSION

Chemically, wheatleyite is a member of the series M$_2$Cu$\cdot$(C$_2$O$_4$)$_2 \cdot$2H$_2$O, where M = Cs$^+$, NH$_4^+$, K$^+$, and Na$^+$. The

ammonium and potassium salts are isostructural (Viswamitra, 1962; Weichert and Löhn, 1974) and are closely related to their Cs analogue (Pannhorst and Löhn, 1974). The wheatleyite structure is different from these but is isostructural with the thioxalates of the group $M_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$, where $M = Li^+$ and Na^+ (Maury and Gleizes, 1980). The anhydrous oxalate $Na_2Sn(C_2O_4)_2$ also chemically resembles wheatleyite, but its structure is quite different (Donaldson et al., 1976).

Inspection of the wheatleyite structure provides a ready explanation for the observed perfect cleavage on {100}. That is, the structure may be viewed as consisting of layers of slightly distorted CuO_6 tetragonal bipyramids and $NaO_5(H_2O)_2$ polyhedra linked by bridging oxalate groups. The layering is parallel to (100), with adjacent layers being linked only by H bonds through the water molecules and by Na–O bonds which are the second longest in the $NaO_5(H_2O)_2$ polyhedron. Cleavage will therefore occur preferentially through these weak interlayer linkages.

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