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Ogdensburgite from Mapimi and new data for the species

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Abstract

The second occurrence of ogdensburgite, at the Ojuela mine, Mapimi, Durango, Mexico, has yielded material superior to that found at the type locality, the Sterling Hill mine, Ogdensburg, New Jersey. At Mapimi, ogdensburgite occurs as dark brownish-red intergrown blades up to 1 mm in length, associated with arseniosiderite, adamite, chalcophanite, and villyaellenite. Cleavage: {001} perfect, {010} fair, and {100} poor. It is biaxial (−) with refractive indices $\alpha = 1.715(5)$, $\beta = 1.783(5)$, and $\gamma = 1.785(5)$; $X = \mathbf{c}$, $Y = \mathbf{b}$, $Z = \mathbf{a}$; absorption $X <<< Y < Z$ (X yellow, Y and Z red-brown). The measured specific gravity is 3.11 g/cm³. The optical properties and specific gravity differ significantly from those determined from type material, but the X-ray powder data and chemical analysis agree closely with those for the type locality. Single-crystal X-ray precession data indicate orthorhombic symmetry with permissible space groups *Bmmm, B*222, *B*2*mm, Bm*2*m,* or *Bmm*2. Cell parameters refined from the powder data are $a = 11.351(6)$, $b = 14.837(10)$, $c = 6.555(1)$ Å. Chemical analysis by electron microprobe provided Fe_2O_3 29.4, CaO 10.1, ZnO 3.0, MnO 2.4, As_2O_5 40.3; moisture-evolution analysis gave 14.8 H_2O, total 100.0 wt%. A new ideal formula is proposed, based upon the chemical analysis, cell constants, and specific gravity: $Ca_2Fe_4^{3+}(Zn,Mn)^{2+}(AsO_4)_4(OH)_6 \cdot 6H_2O$ (Z = 2); $D_{calc} = 3.39$. Site vacancies may account for the much lower observed specific gravity. It is hypothesized that the structure of ogdensburgite is based on a sheet of Fe octahedra.

Introduction

Ogdensburgite (Dunn, 1981) occurs at Sterling Hill, New Jersey, as thin (0.1 mm) incrustations of dark brownish-red platelets. As crystals suitable for single-crystal study were not found, the symmetry, space-group conditions, and unit-cell parameters of the new mineral could not be determined, and the chemical formula could only be hypothesized.

Recently, one of us (A.R.K.) identified ogdensburgite by X-ray powder diffraction on a specimen from the Ojuela mine, Mapimi, Durango, Mexico, in close association with villyaellenite. This is a new species recently described by Sarp (1984) from Sainte-Marie aux Mines, France. This study reports on the second occurrence of ogdensburgite and presents new mineralogical data on the species. The villyaellenite from Mapimi is currently under investigation.

Occurrence

Ogdensburgite has been identified at the Ojuela mine, Mapimi, Durango, Mexico, on a single specimen. This specimen was collected in 1981 from a section of the mine known as the San Judas Department during mining operations for exceptional purple adamite crystals (Wilson, 1982a, 1982b). Lotharmeyerite (Dunn, 1983; Kampf et al., 1984) was found in association with the purple adamite. The ogdensburgite specimen, provided for study by John Whitmire, is from the same ore pipe, but was not found in direct association with either lotharmeyerite or purple adamite. This specimen also contains villyaellenite as pink, prismatic crystals up to 4 cm in length, which form a divergent aggregate mostly filling a vug. The walls of the vug and some surfaces of this crystal aggregate are coated with alternating layers of cryptocrystalline arseniosiderite and bladed ogdensburgite. The ogdensburgite blades measure up to 1.0 mm in length and are generally oriented perpendicular to the layering. An aureole of massive chalcophanite surrounds the vug and extends from 1 to 3 cm into the host rock, a limonitic gossan. Subhedral to euhedral crystals and irregular stringers of colorless to pale green adamite are imbedded in the limonite, associated manganese oxides, and layered arseniosiderite-ogdensburgite assemblage.

Physical and optical properties

The ogdensburgite blades from Mapimi are roughly rectangular with an aspect ratio (*a*:*b*:*c*) averaging about 10:3:1. The Mapimi material possesses the same dark brownish-red color and one perfect cleavage noted for ogdensburgite from Sterling Hill. The perfect cleavage was

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TABLE 1. Unit-cell data for ogdensburgite

	Sterling Hill	Mapimi
a (Å)	11.381 (10)	11.351 (6)
b (Å)	14.829 (17)	14.837 (10)
c (Å)	6.569 (2)	6.555 (1)
V (Å^3)	1108.6	1104.0
Space group	*Bmmm, B222, B2mm, Bm2m, or Bmm2*	

determined in this study to correspond to {001}. Two other cleavages, {010} fair and {100} poor, were also detected.

The optical properties determined for ogdensburgite from Mapimi differ significantly from those determined by Dunn (1981) for material from Sterling Hill, most likely owing to the inferior quality of the available material from Sterling Hill. Mapimi ogdensburgite was determined to be biaxial (−) with a $2V$ between 5° and 10°. The refractive indices measured via grain mounts in Na light are $\alpha = 1.715$, $\beta = 1.783$, and $\gamma = 1.785$ (all ± 0.005). Strong pleochroism was observed with absorption $X <<< Y < Z$ (X yellow, Y and Z red-brown). The optical orientation is $X =$ **c**, $Y =$ **b**, $Z =$ **a** (β and $\gamma \parallel$ {001} cleavage).

The specific gravity of ogdensburgite from Mapimi, determined by suspension in Clerici solution, is 3.11 g/cm^3. This is considerably higher than the value of 2.92 reported by Dunn (1981) for the Sterling Hill material; again, the foliate and micaceous habit most likely contributed to the lower measured specific gravity. We have high confidence in the measured value for Mapimi material as the same result was arrived at independently in our respective laboratories.

TABLE 3. Microprobe analyses of ogdensburgite

	Sterling Hill (Dunn, 1981)*	Mapimi (this study)	$Ca_2Fe^{3+}_4(Zn_{0.5}Mn_{0.5})^{2+}(AsO_4)_4(OH)_6 \cdot 6H_2O$
SiO_2	0.5	0.0	—
Al_2O_3	1.0	0.0	—
Fe_2O_3	30.1	29.4	28.3
MgO	0.5	0.0	—
CaO	10.5	10.1	9.9
ZnO	3.1	3.0	3.6
MnO	2.1	2.4	3.1
As_2O_5	39.2	40.3	40.7
H_2O	13.0†	14.8‡	14.4
Total	100.0	100.0	100.0

Note: Accuracy of data: ±3% of the amount present.
* Analysis 1.
† Water by difference.
‡ Water determined by moisture-evolution analysis.

X-RAY CRYSTALLOGRAPHY

A single crystal of ogdensburgite from Mapimi, measuring 0.12 × 0.05 × 0.03 mm (**a**, **b**, **c**), was studied by precession X-ray single-crystal techniques. It yielded an orthorhombic unit cell with pronounced hexagonal pseudosymmetry ($a_{hex} = c_{ortho}$; $c_{hex} = b_{ortho}$). The systematic absences, (1) hkl with $h + l = 2n + 1$, (2) $0kl$ with $l = 2n + 1$, (3) $h0l$ with $h + l = 2n + 1$, (4) $hk0$ with $h = 2n + 1$, correspond to the space groups *Bmmm, B*222, *B*2*mm, Bm*2*m,* and *Bmm*2. The unit-cell constants, refined by least-squares analysis of selected diffraction data, are given in Table 1 for ogdensburgite from both localities. Because the precession film data was quite weak even

TABLE 2. X-ray powder-diffraction data for ogdensburgite from Mapimi

hkl	d_{calc}	d_{obs}	I/I_0	*hkl*	d_{calc}	d_{obs}	I/I_0
010	14.8	14.8	100	260	2.267	2.271	<5
020	7.42	7.39	20	161	2.267		
101*	5.68	5.67	10	052	2.200	2.210	<5
200*	5.68			351	2.200		
111*	5.30	5.30	25	103	2.146	2.147	<5
210*	5.30			402	2.145		
121*	4.51	4.51	35	501	2.145		
220*	4.51			113	2.124		
131	3.729	3.723	5	412	2.123	2.128	<5
230	3.729			511	2.123		
002*	3.278	3.278	30	252	2.051	2.054	5
301*	3.277			450	2.051		
311	3.200	3.202	5	171	1.986	1.992	<5
012	3.200			270	1.986		
240	3.105	3.109	5	610	1.877	1.871	<5
141	3.105			313	1.877		
321	2.998	2.982	5	333	1.767	1.768	5
022	2.998			630	1.767		
400	2.838	2.839	5	153	1.739	1.741	<5
202	2.838			452	1.739		
212*	2.788	2.787	20	551	1.738	1.640	10
410*	2.787			004	1.639		
331*	2.732	2.733	20	602	1.638	1.627	5 b
032*	2.732			014	1.629		
222*	2.651	2.650	40	612	1.629		
420*	2.650			034	1.556	1.559	5
060	2.473	2.473	20 b	632	1.555		

Note: 114.6-mm Gandolfi camera, Ni-filtered Cu$K\alpha$ radiation, visually estimated intensities.
* Data used for least-squares refinement of cell constants.

after 36-h exposures, there is a possibility that weaker diffraction nodes, corresponding to a doubling of the cell, were not detected.

The crystal used in the precession X-ray study was subsequently mounted on an automated four-circle diffractometer for structure-data collection, but proved inadequate in both size and quality for crystal-structure analysis. No other suitable crystal was found.

The X-ray powder-diffraction data for ogdensburgite from Mapimi closely match those reported by Dunn (1981). The powder patterns were indexed using the cell data and taking diffraction intensities from the precession films into consideration. The indexed powder data for d values greater than 1.5 Å are given for the Mapimi material in Table 2.

Chemistry

The ogdensburgite from Mapimi was chemically analyzed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a beam current of 0.15 μA. Standards used were olivenite (As), zincite (Zn), hornblende (Ca, Fe, Mg, Al), and manganite (Mn). The data were corrected using a modified version of the MAGIC-4 program. In Table 3, the analysis of Mapimi ogdensburgite is compared to analysis 1 reported by Dunn (1981) for Sterling Hill ogdensburgite; they are extremely similar in composition.

Water, directly determined on a 155-μg sample of Mapimi ogdensburgite using a 903-H DuPont moisture-evolution analyzer, yielded an analysis of 14.8%, in exact agreement with the difference from 100% provided for by the microprobe analysis. The water evolution peaked at 155 and 595°C with each peak corresponding to roughly half of the total H_2O evolved. This implies that approximately half of the water is more tightly bound, probably as (OH) groups.

Chemical formula

Dunn (1981) suggested $Ca_3ZnFe^{3+}_6(AsO_4)_5(OH)_{11}\cdot 5H_2O$ as the ideal formula for ogdensburgite, but acknowledged that "the formula must be considered tentative in the absence of the direct determination of water, or a crystal structure determination." The direct water determination confirms the original microprobe analysis 1, but Dunn's proposed formula is not consistent with the observed specific gravity in light of the unit-cell parameters determined in this study.

The chemical analysis, cell constants, and observed specific gravity for Mapimi ogdensburgite yield cell contents: Fe^{3+} 7.61, Ca 3.72, Zn 0.76, Mn^{2+} 0.70, As 7.25, H 33.97, and O 51.71. This suggests an empirical formula with significant site vacancies: $(Ca_{3.72}\square_{0.29})_{\Sigma 4}(Fe^{3+}_{7.61}\square_{0.39})_{\Sigma 8}(Zn_{0.76}Mn^{2+}_{0.70}\square_{0.54})_{\Sigma 2}[(AsO_4)_{7.25}\square_{0.75}]_{\Sigma 8}[(OH)_{11.44}\square_{0.56}]_{\Sigma 12}\cdot 11.27H_2O$. An empirical formula based on four arsenate groups $Ca_{2.05}(Fe^{3+}_{4.20}Zn_{0.42}Mn^{2+}_{0.39})_{\Sigma 5.01}(AsO_4)_4(OH)_{6.32}\cdot 6.21H_2O$ is consistent with full cation-site occupancies; however, the resulting calculated density is 3.43, significantly higher than the observed specific gravity of 3.11.

The new ideal formula that we propose, based on the data in hand, is $Ca_2Fe^{3+}_4(Zn,Mn)^{2+}(AsO_4)_4(OH)_6\cdot 6H_2O$ ($Z = 2$); however, this yields a calculated density of 3.39, also significantly higher than the observed specific gravity. Zn and Mn have been placed in a separate site for three reasons: (1) divalent and trivalent cations are often segregated into distinct structural sites, (2) substantial and similar amounts of Zn and Mn were found in ogdensburgite from both localities; this suggests that they may be essential to the structure, (3) there are no sites with equipoint rank of 5 or 10, whereas sites of rank 2, 4, and 8 are consistent with the permissible space groups for ogdensburgite. Because Zn often assumes tetrahedral coordination in secondary minerals, it is entirely possible that Zn and Mn actually occupy two distinct sites within the structure.

Discussion

Despite discrepancies in optical properties and specific gravity of material from Sterling Hill and Mapimi, the close correspondence of their powder data and chemical compositions leaves no doubt that they are one and the same mineral. As ogdensburgite from Mapimi occurs as crystals of superior quality, their measured optical and physical properties are considered more reliable than those previously determined by Dunn (1981). Indeed, the reliability of the chemical analysis, averaged refractive index, and observed specific gravity obtained for Mapimi ogdensburgite is supported by a Gladstone-Dale compatibility index of 0.024, within the range of excellent compatibility (Mandarino, 1981).

Significant site vacancies must be assumed in order to reconcile the calculated unit-cell contents to the ideal chemical formula proposed herein. Without a complete crystal-structure analysis, the presence of these site vacancies cannot be proven. Even in the absence of uncertainties in site occupancies, the only reliable determinant of a mineral's chemical formula is a crystal-structure analysis. We, therefore, stress that our proposed formula for ogdensburgite must be considered tentative at this time.

It is notable, however, that ogdensburgite occurs at both Sterling Hill and Mapimi in close association with other Zn- and Mn-bearing minerals and that the mineral, in both localities contains significant amounts of these two elements. We postulate that ogdensburgite may be dependent upon the presence of Zn and/or Mn for its formation; segregation of Zn and Mn into a separate site or two different sites within the ogdensburgite structure certainly seems reasonable.

Ogdensburgite is very similar in chemistry to arseniosiderite, $Ca_6(H_2O)_6[Fe^{3+}_9O_6(AsO_4)_9]\cdot 3H_2O$, a mineral with which it is intimately associated on the specimen from Mapimi. Moore and Araki (1977) determined that the structure of mitridatite, the phosphate analogue of arseniosiderite, is based on a compact sheet of composition $[Fe^{3+}_9O_6(PO_4)_9]^{12-}$. Although there is no obvious correspondence between the ogdensburgite and arseniosiderite cells, the a and b cell dimensions of ogdensburgite are

consistent with an Fe^{3+} octahedral sheet. Assuming that $E = 2.90$ Å for the average O–O edge distance for $Fe^{3+}O_6$, then $4E = 11.6$ Å ($a = 11.351$) and $3\sqrt{3E} = 15.07$ Å ($b = 14.837$). The perfect {001} cleavage and greater absorption of light for Y (= **b**) and Z (= **a**) in ogdensburgite crystals are additional indications that its structure is based on a sheet of Fe octahedra in the **a**–**b** plane.

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References

Dunn, P.J. (1981) Ogdensburgite, a new calcium–zinc–ferric iron arsenate mineral from Sterling Hill, New Jersey. Mineralogical Record, 12, 369–370.

——— (1983) Lotharmeyerite, a new mineral from Mapimi, Durango, Mexico. Mineralogical Record, 14, 35–36.

Kampf, A.R., Shigley, J.E., and Rossman, G.R. (1984) New data on lotharmeyerite. Mineralogical Record, 15, 223–226.

Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. Canadian Mineralogist, 19, 441–450.

Moore, P.B., and Araki, T. (1977) Mitridatite, $Ca_6(H_2O)_6[Fe^{III}_9O_6(PO_4)_9 \cdot 3H_2O$. A noteworthy octahedral sheet structure. Inorganic Chemistry, 16, 1069–1106.

Sarp, H. (1984) Villyaellenite, $H_2(Mn,Ca)_5(AsO_4)_4 \cdot 4H_2O$ un nouveau minéral de Sainte-Marie aux Mines (France). Schweizerische Mineralogische und Petrographische Mitteilungen, 64, 323–328.

Wilson, W.E. (1982a) What's new in minerals. Mineralogical Record, 13, 39–42.

——— (1982b) What's new in minerals. Mineralogical Record, 13, 181–184.

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