

## ELSMOREITE, CUBIC $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ , A NEW MINERAL SPECIES FROM ELSMORE, NEW SOUTH WALES, AUSTRALIA

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### ABSTRACT

Elsmoreite,  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$  (IMA 2003–059), is a new mineral species from the Elsmore tin deposit, Elsmore, in the New England region of northern New South Wales, Australia. The name is derived from the locality. It occurs as a white, microcrystalline powder (luster could not be observed) formed as a result of the oxidation of ferberite in the oxidized zone of weakly mineralized granitic pegmatite dykes containing Sn, W, Mo and Bi minerals, hosted in pegmatitic greisen veins in a granite stock. The mineral is cubic, space group  $Fd\bar{3}m$ , with  $a$  10.203(1) Å,  $V$  1062.1(2) Å<sup>3</sup>,  $Z = 16$ ,  $D_{\text{calc}}$  6.025 g cm<sup>-3</sup>, using refined unit-cell data from natural material and the ideal formula  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ . The density of the natural material could not be measured. The seven strongest lines in the X-ray powder diffraction pattern [ $d$  in Å( $I$ )( $hkl$ )] are: 5.884(100)(111), 2.944(78)(222), 3.075(62)(311), 1.804(23)(440), 1.964(17)(511), 1.725(14)(531) and 1.538(14)(622). Tungsten was the only cation detected by electron-microprobe analysis. An average of five spot-analyses (W) on individual grains and a single thermogravimetric analysis for  $\text{H}_2\text{O}$  gave 96.0%  $\text{WO}_3$  and 3.3%  $\text{H}_2\text{O}$ , yielding the formula  $\text{WO}_3 \cdot 0.44\text{H}_2\text{O}$ , based on one W atom, and ideally  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ . Elsmoreite is identical to the cubic synthetic phase of the same composition, and whose single-crystal structure is known. The structure is based on a defect pyrochlore lattice. Because of the minute grain-size of the natural material, its physical and optical properties were determined on synthetic  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ . Microcrystalline octahedral crystals of  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$  are colorless with a white streak, translucent, and possess an adamantine luster, with a very high index of refraction,  $2.24 \pm 0.005$  (white light). No luminescence was observed. The compatibility index (CI) is -0.164, which is classed as poor. Elsmoreite is brittle, has no apparent cleavage, a splintery fracture and a Mohs hardness of approximately 3. Crystals are octahedral, some of which seem to be twinned on the spinel law. The cubic tungstic acid is closely related to ferritungstite, alumotungstite and jixianite.

**Keywords:** elsmoreite, new mineral species, tungstic acid, pyrochlore, Elsmore, New South Wales, Australia, ferritungstite, alumotungstite.

### SOMMAIRE

Nous décrivons la elsmoreïte,  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$  (IMA 2003–059), nouvelle espèce minérale provenant du gisement d'étain de Elsmore, situé dans la région de Nouvelle-Angleterre du nord du Nouveau Pays de Galles, en Australie. Le nom est inspiré de la localité. La elsmoreïte se présente en amas microcristallins pulvérulents blancs (éclat non observable) formés par oxydation de la ferberite dans des filons de pegmatite granitique contenant des minéraux de Sn, W, Mo et Bi, dans un hôte de veines de greisen d'un massif de granite. Il s'agit d'un minéral cubique, groupe spatial  $Fd\bar{3}m$ , ayant  $a$  10.203(1) Å,  $V$  1062.1(2) Å<sup>3</sup>,  $Z = 16$ ; la densité, 6.025 g cm<sup>-3</sup>, est calculée à partir de la maille élémentaire du matériau naturel et de sa formule idéale,  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ . La densité n'a pu être mesurée directement. Les sept raies les plus intenses du spectre de diffraction X, méthode des poudres [ $d$  en Å( $I$ )( $hkl$ )] sont: 5.884(100)(111), 2.944(78)(222), 3.075(62)(311), 1.804(23)(440), 1.964(17)(511), 1.725(14)(531) et 1.538(14)(622). Le tungstène est le seul cation à être décelé par analyse à la microsonde électronique. Un résultat moyen de cinq analyses (W) de grains individuels et une détermination thermogravimétrique de la teneur en  $\text{H}_2\text{O}$  ont donné 96.0%  $\text{WO}_3$  et 3.3%  $\text{H}_2\text{O}$ , ce qui correspond à la formule  $\text{WO}_3 \cdot 0.44\text{H}_2\text{O}$ , fondée sur un atome de W, ou idéalement  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ . La elsmoreïte est identique à la phase synthétique cubique de la même composition, dont la structure cristalline est connue. La structure est fondée sur celle du pyrochlore avec lacunes. Vue la granulométrie infime, nous avons dû nous fier sur l'analogie synthétique pour obtenir les propriétés physiques et optiques. Les cristaux octaédriques microcristallins de  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$  sont incolores avec une rayure blanche, translucides, avec un éclat adamantin et un indice de refraction très élevé,  $2.24 \pm 0.005$  (lumière blanche). Aucune

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luminescence n'a été observée. L'indice de compatibilité,  $-0.164$ , indique une piètre concordance des données. La elsmoreïte est cassante, sans clivage apparent, une fracture en esquilles, et une dureté de Mohs d'environ 3. Les cristaux sont octaédriques, et maclés selon la loi du spinelle. L'acide tungstique est étroitement lié à la ferritungstite, l'alumotungstite et la jixianite.

(Traduit par la Rédaction)

*Mots-clés:* elsmoreïte, nouvelle espèce minérale, acide tungstique, pyrochlore, Elsmore, Nouveau Pays de Galles, Australie, ferritungstite, alumotungstite.

## INTRODUCTION

Elsmoreite,  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ , is a new mineral species discovered in the oxidized section of granitic pegmatite veins at the Elsmore tin deposit in the New England region of northern New South Wales, Australia. Tin mining first commenced in New South Wales at Elsmore in 1871 (Stacey 1998). The Elsmore Hill tin prospect comprises weakly mineralized quartz – white mica pegmatitic greisen veins in a granite stock. The lodes contain cassiterite, with accessory amounts of molybdenite, ferberite, arsenopyrite, minor chalcocopyrite and native bismuth (Cotton 1910, Carne 1911, 1912, Nicholson 1966). During a study of secondary bismuth, tungsten and molybdenum minerals in the upper sections of the veins (Rankin *et al.* 2001, 2002), we found a white encrustation on corroded ferberite to be identical to synthetic, cubic  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$  by powder X-ray diffraction. Other secondary minerals found nearby include betpakdalite, bismite, bismutite, bismutostibiconite, koechlinite, powellite, rooseveltite, russellite and scheelite.

The new mineral and the mineral name were approved by the Commission on New Minerals and Mineral Names, IMA (#2003–059). Type material has been deposited in the collection of the Australian Museum, Sydney, New South Wales, Australia (specimen no. D53020). The mineral is named after the locality where it was first found.

## OCCURRENCE

Elsmore Hill is located some 17 km east of Inverell and adjacent to the village of Elsmore, in the New England region of northern New South Wales, Australia. Weakly mineralized quartz – white mica greisen veins carrying Sn–Mo–W–As–Cu minerals have been strongly weathered, to the extent that ferberite is commonly replaced by secondary tungsten minerals, including scheelite and russellite (Rankin *et al.* 2002). In one sample, a vug in quartz was found to be filled with white, powdery elsmoreite, associated with minor secondary scheelite. Other secondary phases identified in close proximity to elsmoreite include betpakdalite, bismite, bismutite, bismutostibiconite, brochantite, koechlinite, metazeunerite, pharmacosiderite, barium pharmacosiderite, powellite, rooseveltite and scorodite (Rankin *et al.* 2001, 2002). The assemblage is formed

under comparatively acidic conditions, as indicated by the relative abundance of the heteropolymolybdate mineral betpakdalite and scorodite. Elsmoreite was subsequently identified (A.R. McKinnon, pers. commun.) as a product of oxidation of ferberite in the Wolfram Wonder prospect, a disseminated wolframite deposit containing minor molybdenite and pyrite (Weber *et al.* 1978), located 15 km north of the town of Cathcart in southern New South Wales, Australia. It also occurs (W.D. Birch, pers. commun.) as very small crystals on corroded wolframite at Pittong, Victoria, Australia (Baragwanath 1917, Herman 1920).

## CHEMICAL COMPOSITION AND CRYSTALLOGRAPHIC DATA

Tungsten was the only cation detected by electron microprobe analysis (wavelength-dispersion spectrometry mode, 30 kV, 2 nA, beam diameter 3  $\mu\text{m}$ ). An average of five spot-analyses on individual grains of natural elsmoreite using pure W as standard and a single thermogravimetric analysis for  $\text{H}_2\text{O}$  gave 96.0%  $\text{WO}_3$ , 3.3%  $\text{H}_2\text{O}$ , for a total of 99.3%, yielding the formula  $\text{WO}_3 \cdot 0.44\text{H}_2\text{O}$ , based on one W atom, and ideally  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ ; the calculated composition of  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$  is 96.26%  $\text{WO}_3$ , 3.74%  $\text{H}_2\text{O}$ . Nedjar *et al.* (1988) studied the role of structural  $\text{H}_2\text{O}$  in synthetic, cubic  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$  using thermogravimetric analysis and found that  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$  dehydrates completely between 100 and 300°C.

Table 1 lists powder X-ray-diffraction data for elsmoreite, together with reported data for cubic  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ . Elsmoreite is identical with the cubic synthetic phase of the same composition, and whose single-crystal structure is known (Günter *et al.* 1989, Nedjar *et al.* 1988). Günter *et al.* (1989) reported for single-crystal data (four-circle diffractometer) that  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$  is cubic,  $a$  10.305(3) Å,  $V$  1094.3 Å<sup>3</sup>, space group  $Fd\bar{3}m$ ,  $Z$  = 16. Data for natural elsmoreite were refined using least-squares methods (Langford 1973) to give  $a$  10.203(1) Å,  $V$  1062.1(2) Å<sup>3</sup>, with space group  $Fd\bar{3}m$  and  $Z$  = 16 by analogy with the synthetic material. Refinement of the structure of synthetic  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$  using electron-diffraction data in the same space group gave, *inter alia*,  $a$  10.206(3) Å (Nedjar *et al.* 1988), a result in excellent agreement with our data for the natural material.

## PHYSICAL AND OPTICAL PROPERTIES

Elsmoreite is colorless and, in natural material recovered so far, of very small grain-size. Because of the very small particle-size of natural elsmoreite, the following physical and optical properties refer to the synthetic material. Synthetic elsmoreite was prepared following the hydrothermal procedure of Günter *et al.* (1989). Digestion of varying proportions of 0.75 M aqueous sodium tungstate, 0.75 M aqueous magnesium chloride and 1.2 M hydrochloric acid in a Teflon-lined bomb for three days at 155°C gave a colorless crystalline product that was washed with water and alcohol and dried in air. In order to obtain cubic  $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ , the pH of the initial charge needs to be approximately 3.5. Magnesium chloride, used in the original synthesis by Günter *et al.* (1989) to obtain larger crystals, is not an essential reagent.

Synthetic elsmoreite is translucent and colorless with a white streak and possesses an adamantine luster. SEM imaging show it to consist of microcrystalline aggregates of octahedral grains up to 20  $\mu\text{m}$  in size. Some of the grains appear to be twinned on the spinel law. Grains crushed with a needle give splintery fragments, indicating an apparent absence of cleavage. The mineral is brittle, with a Mohs hardness of approximately 3. No luminescence was observed. The index of refraction of the mineral is very high and was determined to be  $2.24 \pm 0.005$  by the Becke line method using white light and

comparing it to sulfur–selenium melts, as outlined by Merwin & Larsen (1912). Gladstone–Dale constants derived using the data of Mandarino (1981) are  $K_C = 0.177$  and  $K_{P(\text{Dcalc})} = 0.206$ . The compatibility index (CI) of Mandarino (1979) for elsmoreite is  $-0.164$  (poor). It should be noted that for tungstite,  $\text{WO}_3 \cdot \text{H}_2\text{O}$ , the CI also is poor ( $-0.127$ ) using the data of Walker (1933) and Anthony *et al.* (1997).

## RELATIONSHIPS TO OTHER SPECIES

A number of crystalline hydrated tungsten trioxide compounds having the general formula  $\text{WO}_3 \cdot n\text{H}_2\text{O}$  with  $n = 0.33, 0.5, 0.75, 1$  and  $2$  have been reported. Of these, orthorhombic  $\text{WO}_3 \cdot \text{H}_2\text{O}$  corresponds to the mineral tungstite, and monoclinic  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ , to hydrotungstite (Anthony *et al.* 1997). Poorly crystalline, orthorhombic  $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$  (Gérand *et al.* 1981) has been identified as a product of alteration of scheelite in the Grantcharitz deposit, Bulgaria (Tarassov *et al.* 1998).

Elsmoreite, cubic  $\text{WO}_3 \cdot 0.5 \text{H}_2\text{O}$ , has a structure based on a defect pyrochlore lattice, of general formula  $A_2B_2O_6O'$ . Substitution can occur at all sites, and vacancies may occur at the *A* and *O'* sites. In elsmoreite, the *A* site is vacant, the *B* site contains  $\text{W}^{6+}$ , and the *O'* site is occupied by structural  $\text{H}_2\text{O}$ . Only the  $B_2O_6$  sublattice of the pyrochlore structure is retained (Günter *et al.* 1989). Other related species based on the same structural motif are known and include ferritungstite, alumotungstite and jixianite (Anthony *et al.* 1997). The secondary minerals of tungsten have been reviewed in terms of their nature and occurrence (Sahama 1981), as has the group based on the defect pyrochlore structure, and which includes elsmoreite, ferritungstite, alumotungstite and jixianite (Ercit & Robinson 1994). In ferritungstite,  $(\text{K,Ca,Na})(\text{W,Fe})_2(\text{O,OH})_6 \cdot \text{H}_2\text{O}$ , some of the  $\text{W}^{6+}$  is replaced by  $\text{Fe}^{3+}$ , and the charge is compensated by incorporation of  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Na}^+$  at the *A* site. An analogous situation obtains in alumotungstite,  $(\text{H}_2\text{O,Ca})_x(\text{W,Al})_2(\text{O,OH})_6 \cdot n\text{H}_2\text{O}$ , in which some  $\text{W}^{6+}$  is replaced by  $\text{Al}^{3+}$ . Jixianite,  $(\text{Pb},\square)_2(\text{W,Fe})_2(\text{O,OH})_7$ , where  $\square$  indicates a vacancy, is a Pb-bearing analogue of ferritungstite. Elsmoreite represents the end-member in which no  $\text{W}^{6+}$  is replaced by any other metal of lower charge, thus obviating the need for incorporation of cations at the *A* site.

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TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR ELSMOREITE

Elsmoreite*					synthetic, cubic $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}^\dagger$				
$t_{\text{obs}}$	$d_{\text{meas}}$	$d_{\text{calc}}$	<i>h k l</i>		$t_{\text{obs}}$	$d_{\text{meas}}$	<i>h k l</i>		
100	5.884	5.891	1 1 1		999	5.8924	1 1 1		
					1	3.6084	2 2 0		
62	3.075	3.076	3 1 1		379	3.0772	3 1 1		
78	2.944	2.945	2 2 2		557	2.9462	2 2 2		
12	2.551	2.551	4 0 0		111	2.5515	4 0 0		
8	2.341	2.341	3 3 1		290	2.3414	3 3 1		
3	2.082	2.083	4 2 2		2	2.0833	4 2 2		
17	1.964	1.964	5 1 1		122	1.9642	5 1 1		
23	1.804	1.804	4 4 0		183	1.8042	4 4 0		
14	1.725	1.725	5 3 1		93	1.7251	5 3 1		
					1	1.6137	6 2 0		
9	1.555	1.556	5 3 3		19	1.5564	5 3 3		
14	1.538	1.538	6 2 2		97	1.5386	6 2 2		
6	1.473	1.473	4 4 4		16	1.4731	4 4 4		
7	1.429	1.429	7 1 1		30	1.4291	7 1 1		
					1	1.3638	6 4 2		
6	1.328	1.328	5 5 3		21	1.3287	5 5 3		
2	1.276	1.275	8 0 0		11	1.2758	8 0 0		
					14	1.2469	7 3 3		
					1	1.2028	8 2 2		
					10	1.1785	7 5 1		
					17	1.1707	6 6 2		
					9	1.1411	8 4 0		
					12	1.1203	7 5 3		

\* Philips PW1820-25 powder diffractometer,  $\text{CuK}\alpha$  radiation, Ni filter ( $\lambda = 1.5418 \text{ \AA}$ ), pure Si as internal standard. The  $d$  values are reported in  $\text{\AA}$ .  $^\dagger$  ICDD card 84-1548.

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