The Canadian Mineralogist
Vol. 37, pp. 1261-1268 (1999)

WALFORDITE, A NEW TELLURITE SPECIES FROM THE WENDY OPEN PIT, EL INDIO – TAMBO MINING PROPERTY, CHILE

MALCOLM E. BACK[§]

Department of Earth Sciences, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario M5S 2C6, Canada

JOEL D. GRICE AND ROBERT A. GAULT

Research Division, Canadian Museum of Nature, P.O.Box 3443, Station "D", Ottawa, Ontario K1P 6P4, Canada

ALAN J. CRIDDLE

Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, U.K.

JOSEPH A. MANDARINO[*]

Department of Earth Sciences, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario M5S 2C6, Canada

ABSTRACT

Walfordite, a tellurite, is a new mineral species from the Wendy open pit, Tambo mine, El Indio – Tambo mining property, Coquimbo Province, Chile. It is orange, with an orange-yellow streak, and forms simple cubes 0.2 mm across, or cubes modified by octahedral faces. It has an adamantine luster and is opaque. Crystals are too small to provide measurements of the hardness, but they are brittle, with no observed cleavage or parting. Walfordite is isotropic, with $n >> 2.0$; the calculated value, 2.23, was obtained from the Gladstone–Dale relationship. An attempt to measure the index of refraction using the reflectance method resulted in an erroneously high value of n_{air}, 2.28. In a polished section in plane-polarized light, walfordite is pale gray, and is neither bireflectant nor pleochroic. An electron-microprobe analysis gave MgO 0.38, Fe_2O_3 8.30, TiO_2 1.11, TeO_2 81.74 and TeO_3 8.67, total 100.20 wt.%. Enough Te was calculated as $Te^{4+}O_2$ to give $Te^{4+} = 3$ *apfu* in the formula, the remainder was calculated as $Te^{6+}O_3$, and the Fe was calculated as Fe_2O_3 to maintain charge balance, on the basis of a crystal-structure analysis. This calculation yields the empirical formula $(Fe^{3+}_{0.61}Te^{6+}_{0.29}Ti_{0.08}Mg_{0.06})_{\Sigma 1.04}\,Te^{4+}_3\,O_8$ or, ideally, $(Fe^{3+},Te^{6+})Te^{4+}_3O_8$, $Z = 8$ and $D_{\mathrm{calc}} = 5.841$ g/cm^3. A crystal-structure analysis shows the mineral to be cubic, space group $I2_1/a\bar{3}$ (space group #206), with $a = 11.011(5)$ Å. The strongest lines in the X-ray powder pattern [d in Å(I)(hkl)] are: 4.486(29)(211), 3.175(100)(222), 2.943(23)(321), 2.749(37)(400), 2.592(22)(411), 1.944(44)(440) and 1.658(45)(622). The crystal structure of walfordite is similar to that of synthetic phases of the type $M^{4+}Te^{4+}_3O_8$, and to that of winstanleyite. It is the Fe^{3+} analogue of winstanleyite.

Keywords: walfordite, new mineral species, tellurite, crystal structure, El Indio – Tambo mining property, Chile.

SOMMAIRE

La walfordite, un tellurite, est une nouvelle espèce minérale provenant du puit à ciel ouvert Wendy, à la mine de Tambo, du camp minier El Indio – Tambo, province de Coquimbo, au Chili. Il s'agit d'un minéral orange, ayant une rayure orange jaunâtre, se présentant en cubes simples 0.2 mm de diamètre, ou des cubes modifiés par des faces octaédriques. Elle possède un éclat adamantin et est opaque. Les cristaux sont trop petits pour permettre une mesure de la dureté, mais ils sont cassants, sans clivage ou plan de séparation. La walfordite est isotrope, avec $n >> 2.0$; la valeur calculée, 2.23, découle de la relation de Gladstone–Dale. Nous avons essayé de mesurer l'indice de réfraction en utilisant la méthode de réflectance, mais la valeur obtenue dans l'air, 2.28, est trop élevée. Dans une section polie examinée en lumière polarisée, la walfordite est gris pâle, et ni biréflectante, ni pléochroïque. Une analyse à la microsonde électronique a donné MgO 0.38, Fe_2O_3 8.30, TiO_2 1.11, TeO_2 81.74 et TeO_3 8.67, pour un total de 100.20% (poids). Un quantité suffisante de Te a été calculée sous forme de $Te^{4+}O_2$ afin de donner trois atomes de Te^{4+} par unité formulaire. Le reste est calculé sous forme de $Te^{6+}O_3$, et le fer est calculé sous sa forme trivalente pour assurer l'électroneutralité. Sa présence concorde aussi avec les résultats de l'ébauche de la structure cristalline. Ce calcul mène à la formule empirique $(Fe^{3+}_{0.61}Te^{6+}_{0.29}Ti_{0.08}Mg_{0.06})_{\Sigma 1.04}\,Te^{4+}_3\,O_8$ ou, exprimée en termes simplifiés, $(Fe^{3+},Te^{6+})Te^{4+}_3O_8$, $Z = 8$ et $D_{\mathrm{calc}} = 5.841$ g/cm^3.

[§] *E-mail address*: malcolmb@rom.on.ca

[*] *Present address*: 94 Moore Avenue, Toronto, Ontario M4T 1V3, Canada.

D'après l'analyse structurale, ce minéral est cubique, groupe spatial $I2_1/a\bar{3}$ (groupe #206), avec *a* égal à 11.011(5) Å. Les raies les plus intenses de spectre de diffraction, méthode des poudres [*d* en Å(*I*)(*hkl*)] sont: 4.486(29)(211), 3.175(100)(222), 2.943(23)(321), 2.749(37)(400), 2.592(22)(411), 1.944(44)(440) et 1.658(45)(622). La structure de la walfordite ressemble à celles des phases synthétiques de type $M^{4+}Te^{4+}{}_3O_8$, et de la winstanleyite, dont c'est l'analogue Fe^{3+}.

(Traduit par la Rédaction)

Mots-clés: walfordite, nouvelle espèce minérale, tellurite, structure cristalline, camp minier El Indio – Tambo, Chili.

INTRODUCTION

Walfordite, a new tellurite mineral species, occurs in the Wendy Open Pit, Tambo mine, at the El Indio – Tambo mining property, located in Coquimbo Province, Chilean Andes, approximately 640 km north of Santiago, and 160 km east of La Serena. Mining claims in the area date from 1967, whereas full-scale mining did not begin until 1981. The current majority owner of the property is Barrick Gold Corporation, Toronto, which acquired it in late 1994. The cotype specimens were collected in 1992 by Mr. Phillip Walford, then Vice-president and Chief Geologist for LAC Minerals Ltd., when that company owned the mining rights at the mine. He collected most of the study material available from this locality, and brought this new mineral and four other new species to the attention of the senior author. Walfordite is named for Mr. Phillip Walford (b. 1945), of Toronto, Ontario, in recognition of this contribution. The new mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA. Cotype material is housed in the collection of the Royal Ontario Museum, Department of Earth Sciences, under catalogue numbers M47817 and M47818. In this paper, we provide the physical and chemical data that establish walfordite as a new species, and describe its structure and its relationship to the species winstanleyite.

OCCURRENCE

The El Indio – Tambo mining property covers 1295 square kilometers of the El Indio Belt, a prolific gold-, silver- and copper-enriched district located in Chile, close to the border with Argentina in the Andes (approximately 70°W longitude and 30°S latitude). The property consists of two working mines, the El Indio mine and the Tambo mine, located within five kilometers of each other in the south-central portion of the property, at an elevation of approximately 3,950 m. The Wendy open pit is one of three pits that have been worked at the Tambo mine.

The regional and local geology of the area has been described by Siddeley & Araneda (1986). These deposits are located in rhyolitic and dacitic pyroclastic volcanic rocks of Tertiary age (8–11 Ma) that are strongly hydrothermally altered. The Wendy pit is located on the south flank of Cerro Elefante, which is a north–south elongate accumulation of dacite tuffs. Hydrothermal breccias are a common feature of the Tambo mine, and consist of silicified clasts of dacitic tuffs cemented by silica, barite and alunite (Siddeley & Araneda 1986).

Walfordite must be considered as extremely rare. To date, only four specimens have been found, each containing only a few milligrams of material. Walfordite and many other tellurite minerals are found in the interstices of the silicified hydrothermal breccias. Associated minerals are alunite, rodalquilarite, gold, emmonsite, jarosite and pyrite. Other minerals identified in the same matrix include scorodite, paratellurite, tellurite, mackayite, poughite, barite, and four new iron tellurite species that are currently under investigation.

PHYSICAL AND OPTICAL PROPERTIES

Walfordite occurs as equant crystals 0.2 mm across. Most are simple cubes {100}, whereas some show octahedral modifications {111} (Fig.1). The crystals are opaque, orange, with a yellow-orange streak and an adamantine luster. Walfordite shows no fluorescence in short- or long-wavelength ultraviolet light. The crystals are too small to allow a measurement of the Mohs hardness, but they are brittle, with no observed cleavage or parting. For the same reason and because there were too few grains, the density could not be measured. The calculated density is 5.84 g/cm^3.

Walfordite is isotropic and, as tested with an immersion liquid of $n = 2.00$, its index of refraction exceeds 2.0. Using the calculated density and the Gladstone–Dale rule, with the constants of Mandarino (1981), the index of refraction is 2.23. A fragment of the mineral was mounted in epoxy resin, ground and polished. In reflected plane-polarized light, it is pale gray (in comparison with the reflectance of the epoxy resin). It is neither bireflectant nor pleochroic. Seen between crossed polars, the mineral is clearly transparent, as colorless to lemon-yellow internal reflections "flood" the crystal. The polished surface of the mounted fragment is a 120 × 80 × 60 μm triangular section of a very shallow buried pyramid. The shallowness of the pyramid explains the brilliance of the internal reflections. Reflectance measurements were undertaken with the knowledge that these internal reflections were bound to contribute a component of diffuse reflectance to the measured specular reflectance. The measurements were made with a Zeiss MPM800 microscope spectropho-

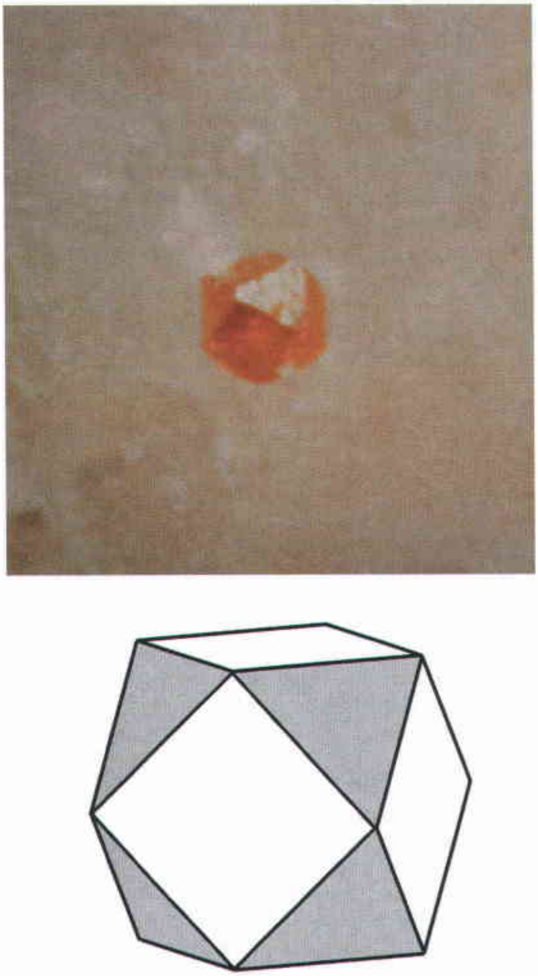

FIG. 1. Crystal of walfordite 0.2 mm across on a matrix of alunite. Below, drawing of a typical crystal, with {100} unshaded and {111} shaded.

tometer from 400 to 700 nm at a 10 nm interval (with the grating of the monochromator set to give a 5 nm bandwidth). The condenser aperture-diaphragm was closed to provide effective numerical apertures of 0.15 for the ×16 air and oil objectives. All measurements were related to a SiC standard (Zeiss. 472), and oil measurements were made in Zeiss oil, $N_D = 1.515$.

The dispersion of the measured reflectance spectra in Table 1 is ordinary and monotonous. Accepting the transparency of the mineral in the visible spectrum, the index of refraction corresponding to the reflectances should be calculated using the Fresnel equation (Criddle 1998). Taking 590 nm as an example, n corresponding to an R of 15.1% is 2.28, *i.e.*, 0.05 higher than the estimate obtained from the Gladstone–Dale calculations. It is reasonable to suppose that errors in the reflectance-derived value are almost entirely a consequence of diffuse reflectance. They are evidently incremental, but their size will vary depending, in part, on the index of refraction of the medium in which the specimen is measured and in part on the orientation of the specimen in the polished section, and the presence or absence within it of fractures and cleavage planes. Under favorable circumstances, these errors may be quantified, and the true specular reflectance determined (Dunn *et al.* 1988), but we were unlucky in walfordite. The Gladstone–Dale-calculated value for n should not be considered accurate, but a good guess would place the index between 2.23 and 2.25. At 2.23, the corresponding specular reflectance would be 14.5%, at 2.25, 14.8%. In a different sense, the reflectance values in oil in Table 1 are not to be taken as realistic for the species; they are included to show how much greater is the contribution of diffuse reflection to the total measured specular and diffuse reflectance. If it is accepted that the index of refraction in air lies between 2.23 and 2.25 and that the mineral is essentially transparent, then the reflectance in oil at 589 nm for these refringences should be 3.64% and 3.81%. For the refringence of 2.28 calculated from the measured value of reflectance in air, 15.1%, the corresponding reflectance in oil (for an oil of n = 1.515 at 590 nm) would be 4.06%. In fact, the measured value is 4.64%, 0.58% too high for this transparent mineral and grossly in error. This 0.58% may be attributed entirely to the contribution of diffuse reflectance. It is to be hoped that better material becomes available in future where internal reflections can be avoided in the measuring field.

CHEMISTRY

Chemical analyses were made with a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. The wavelength-dispersion mode was used. Data reduction was done with a conventional ZAF routine in the Tracor–Northern TASK series of programs. The operating voltage was 15 kV, the beam current was 0.20 μA, and the beam diameter was 20 μm. The sample was checked for homogeneity using the back-scattered

TABLE 1. MEASURED REFLECTANCE DATA FOR WALFORDITE

λ	R	^{im}R	λ	R	^{im}R
400 nm	17.4 %	5.34 %	560 nm	15.2 %	4.76 %
420	16.8	5.14	580	15.2	4.72
440	16.4	5.07	590	15.1	4.64
460	16.2	5.11	600	15.0	4.54
470	16.0	5.05	620	15.1	4.49
480	15.9	4.92	640	15.1	4.50
500	15.7	4.87	650	15.0	4.51
520	15.5	4.84	660	15.0	4.48
540	15.3	4.79	680	14.8	4.38
546	15.3	4.77	700	14.7	4.30

electron detector. An energy-dispersion scan indicated no elements with $Z > 8$ other than those reported here. A deterioration curve for Te, obtained by plotting a series of 5-s counts, indicated that decomposition of the sample of walfordite under the electron beam is negligible. The following standards were used: synthetic magnocolumbite (Mg*K*α), synthetic mackayite (Fe*K*α), rutile (Ti*K*α) and synthetic paratellurite (Te*L*α). Data for all elements in the sample were collected at 25 s or 0.50% precision, whichever was attained first. An infrared spectral analysis was done to check for the presence of OH or H_2O; neither was indicated. Enough Te was calculated as $Te^{4+}O_2$ to give $Te^{4+} = 3$ in the formula, the remainder was calculated as $Te^{6+}O_3$, and the Fe was calculated as Fe_2O_3 to maintain charge balance, on the basis of the results of the crystal-structure analysis. The average result of three analyses on one grain gave MgO 0.38 (0.35–0.41), Fe_2O_3 8.30 (8.12–8.46), TiO_2 1.11 (0.69–1.57), TeO_2 81.74 (80.64–82.63) and TeO_3 8.67 (8.50–8.75), total 100.20 wt.%. The empirical formula based on eight anions and three atoms of Te^{4+} per formula unit (taken from results of the crystal-structure analysis) is $(Fe^{3+}{}_{0.61}Te^{6+}{}_{0.29}Ti_{0.08}Mg_{0.06})_{\Sigma 1.04}Te^{4+}{}_3O_8$ or, ideally, $(Fe^{3+},Te^{6+})Te^{4+}{}_3O_8$. Thus, walfordite is the Fe^{3+}-dominant analogue of winstanleyite ($TiTe^{4+}{}_3O_8$), described by Williams (1979).

TABLE 2. WALFORDITE AND WINSTANLEYITE: X-RAY POWDER DIFFRACTION DATA

WINSTANLEYITE					WALFORDITE		
d_{meas} (Å)	$I_{est.}$	*h*	*k*	*l*	d_{meas} (Å)	d_{calc} (Å)	I_{meas}
5.482	20	2	0	0	5.552	5.501	5
4.474	60	2	1	1	4.486	4.492	29
3.877	20	2	2	0	-	-	-
3.165	100	2	2	2	3.175	3.176	100
2.930	40	3	2	1	2.943	2.940	23
2.741	70	4	0	0	2.749	2.751	37
2.583	40	4	1	1	2.592	2.593	22
2.452	30	4	2	0	2.460	2.460	10
2.151	30	4	3	1	2.157	2.158	14
2.001	20	5	2	1	2.007	2.009	7
1.938	80	4	4	0	1.944	1.945	44
1.881	30	4	3	3	1.888	1.887	11
1.825	5	6	0	0	-	-	-
1.778	30	6	1	1	1.785	1.785	11
1.734	20	6	2	0	1.743	1.740	9
1.692	30	5	4	1	1.697	1.698	12
1.653	80	6	2	2	1.658	1.659	45
1.617	30	6	3	1	1.622	1.622	13
1.582	20	4	4	4	1.588	1.588	11
1.551	20	5	4	3	1.556	1.556	9
1.493	20	7	2	1	1.498	1.497	9
1.466	10	6	4	2	1.470	1.470	7
1.392	40	6	5	1	1.397	1.397	15
1.371	10	8	0	0	-	-	-
1.350	40	7	4	1	1.354	1.354	13
1.330	20	8	2	0	1.334	1.334	4
1.311	20	6	5	3	1.316	1.315	7
1.293	5	8	2	2	-	-	-
1.275	40	8	3	1	1.279	1.279	7
1.258	30	6	6	2	1.261	1.262	4
1.226	30	8	4	0	1.230	1.230	10
1.211	10	8	3	3	-	-	-
1.197	30	8	4	2	1.201	1.200	5
1.183	30	7	6	1	1.186	1.186	8
1.157		9	3	2	1.135	1.135	6
		8	5	3	1.113	1.111	7
		10	2	0	1.080	1.079	8
		10	2	2	1.059	1.059	4
		10	4	0	1.021	1.022	4

114.6 mm Gandolfi camera Cu*K*α (Ni filtered) radiation. Film was scanned using an optical scanner calibrated for intensity and peak position using an external silicon standard. Indexing based on the refined cell of 11.002(1).

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

X-ray precession photographs show walfordite to be cubic, with space group $I2_1/a\bar{3}$ (space group #206), determined uniquely by extinction conditions. X-ray powder-diffraction data collected with a Gandolfi camera, 114.8 mm in diameter, with Cu*K*α (Ni-filtered) radiation are given in Table 2. The film was scanned using an optical scanner calibrated for intensity and peak position using an external silicon standard. The X-ray data were refined using the PC-based version of the least-squares refinement of powder-diffraction data program of Appleman & Evans (1973). The cell edge *a* was refined from the powder-diffraction data: 11.002(1) Å.

The single fragment of walfordite used for the collection of X-ray diffraction-intensity data measures 0.2 × 0.2 × 0.15 mm. Intensity data were collected on a fully automated Nicolet *P*3 four-circle diffractometer operated at 50 kV and 30 mA, with graphite-monochromatized Mo*K*α radiation.

A set of 25 reflections was used to orient the crystal and to subsequently refine the cell dimensions. Approximately four asymmetric units of intensity data were collected (for the acentric space-group) up to $2\theta = 60°$ using a θ:2θ scan mode, with scan speeds inversely proportional to intensity at rates of 4 to 29.3°/minute. The agreement among symmetry-related intensities was $R_{int} = 0.047$.

Reduction of the intensity data, structure determination, and structure refinement were done with the SHELXTL (Sheldrick 1990) package of computer programs. Data reduction included a correction for background, scaling, Lorentz, polarization, and absorption effects. For the ellipsoidal absorption correction, 11 intense diffraction-maxima in the range of 8 to 57°2θ were chosen for Ψ diffraction-vector scans after the method of North *et al.* (1968). The merging *R* for the Ψ-scan data set (396 reflections) decreased from 10.8% before the absorption correction to 3.4% after this correction. Information relevant to the data collection and structure determination are given in Table 3.

The structure was solved using direct methods. The mean value of $|E^2 - 1|$ was 0.649, an *E* statistic inconsistent with the centrosymmetric space-group. This inconsistency is due to the high percentage of large, evenly distributed intensities. In simple structures, like that of walfordite, where most atoms lie on special positions, the intensity-distribution statistics may be misleading

TABLE 3. WALFORDITE: STRUCTURE-DETERMINATION DATA

Ideal Formula:	$(Fe^{3+},Te^{6+})Te^{4+}{}_3O_8$	*a*	11.011(5) Å
Space Group:	$I2_1/a\bar{3}$ (#206)	*V*	1335.0(1) Å³
Crystal Size:	0.2 x 0.2 x 0.15 mm	*Z*	8
Rad/Mon:	Mo/graphite		
μ:	14.75 mm⁻¹	Total no. of *I*'s 1382	
ψ merge,before/after:	0.108/0.034	*F* unique 329	
Min. Transmission:	0.105	$F > 6\delta$ 325	
Max. Transmission:	0.206	Final $R = 3.49\%$	

because the heavy atoms on special positions shift the distribution toward acentricity (Hargreaves 1955, 1956). The *E*-map coordinates were assigned, with appropriate scattering curves, to one Fe, one Te and 2 O atomic sites. This initial model refined to $R = 4.7\%$. In the final least-squares refinement, the sites of all atoms were refined with anisotropic displacement-factors, to the final residual $R = 3.5\%$.

TABLE 4. WALFORDITE: ATOMIC COORDINATES, ISOTROPIC DISPLACEMENT COEFFICIENTS

ATOM	*x*	*y*	*z*	*U(eq)*
Fe	0	0	0	0.0114(3)
Te	0.21099(7)	0	1/4	0.0197(2)
O1	0.4361(6)	0.1335(6)	0.3962(6)	0.0248(17)
O2	0.1725(6)	0.1725(6)	0.1725(6)	0.0213(12)

TABLE 5. WALFORDITE: SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Fe polyhedron			Te polyhedron		
Fe – O1	O1–Fe–O1	180.0(0)	Te – O2,a	O2–Te–O1c	79.3(2)
1.991(7)	O1–Fe–O1	92.3(2)	2.125(2)	O2–Te–O1e	86.3(3)
× 6	O1–Fe–O1	87.7(2)	× 2	O2–Te–O1f	58.8(1)
			Te – O1c,e	O2–Te–O1i	138.8(3)
			1.880(7)	O2–Te–O2a	157.0(4)
			× 2	O1c–Te–O1e	102.2(4)
			Te – O1f,i	O1c–Te–O1f	134.8(3)
			2.904(6)	O1c–Te–O1i	92.1(2)
			× 2	O1c–Te–O2a	86.3(3)
				O1e–Te–O1f	92.1(2)
				O1e–Te–O1i	134.8(3)
				O1e–Te–O2a	79.3(2)
				O1f–Te–O1i	107.8(3)
				O1f–Te–O2a	138.8(3)
				O1i–Te–O2a	58.8(1)

TABLE 6. WALFORDITE: BOND-VALENCE CALCULATIONS

	Fe site	Te^{4+} site		Total
O1	0.639 × 1 × 6	1.3 × 1 × 2	0.082 × 1 × 2	2.02
O2	------	0.67 × 3 × 2		2.01
TOTAL	3.834	4.104		

	V_{ij}		R_{ij}
Fe^{3+}	0.534 × 0.61 =	0.326 *vu*	1.759 Å
Te^{6+}	0.819 × 0.29 =	0.238	1.917
Ti^{4+}	0.621 × 0.08 =	0.050	1.815
Mg^{2+}	0.416 × 0.06 =	0.025	1.693
Total		0.639	

The bond-valence calculations were done using the equation and constants of Brese & O'Keeffe (1991); $V_{ij} = \exp[(R_{ij} - d_{ij})/b]$, where $b = 0.37$ Å, and for the Fe site in this structure, $d_{ij} = 1.991$ Å. Bond valences are expressed in valence units (*vu*).

Table 4 contains the final positional and isotropic displacement-parameters for the walfordite structure, and Table 5 lists selected interatomic distances and angles. The observed and calculated structure-factors, as well as the anisotropic displacement-factors, have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

The scattering factor of the Fe site refined to 31.2(3) electrons. This value is higher than that of Fe (26 electrons). Using the cation ratios in the empirical formula, the site calculates to 33.4 e^-, in reasonably good agreement. That the electron-microprobe analysis was done on a different crystal may account for the difference. Bond-valence calculations using the same ratios also support the mixed-valence model. The bond-valence calculations (Table 6) were done using the equation and constants of Brese & O'Keeffe (1991); $V_{ij} = \exp[(R_{ij} - d_{ij})/b]$, where $b = 0.37$ Å, and for the Fe site in this structure, $d_{ij} = 1.991$ Å. The value for the Fe site is weighted for the substitutions.

DESCRIPTION OF THE STRUCTURE

Walfordite is isostructural with synthetic phases of the type $M^{4+}Te^{4+}{}_3O_8$. Meunier & Galy (1971) described this structure as of the fluorite type, with a face-centered cubic (FCC) array of cations in the subcell. They synthesized four phases of this type, with *M* representing Ti, Sn, Hf and Zr. The Ti analogue is the mineral winstanleyite. The important difference in the walfordite structure is the incorporation of Fe^{3+} and Te^{6+}, maintaining the charge balance, in the Ti site of winstanleyite.

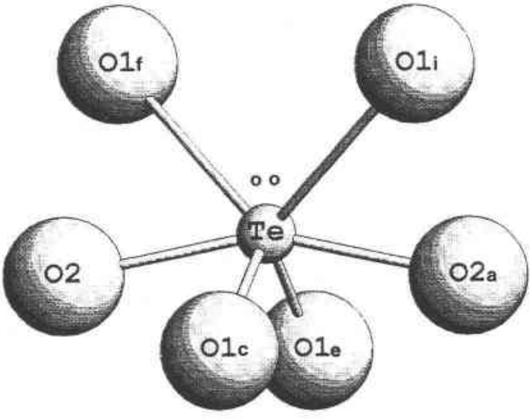

FIG. 2. Te polyhedron: distribution of oxygens atoms and position of non-bonding pair of electrons.

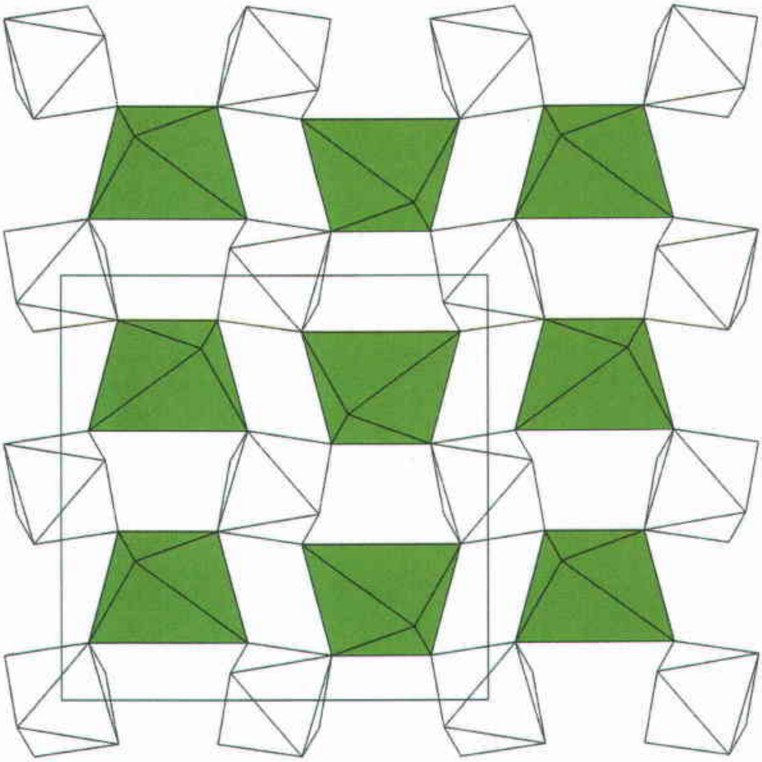

FIG. 3. The structure of walfordite projected onto (100). Te polyhedra shaded.

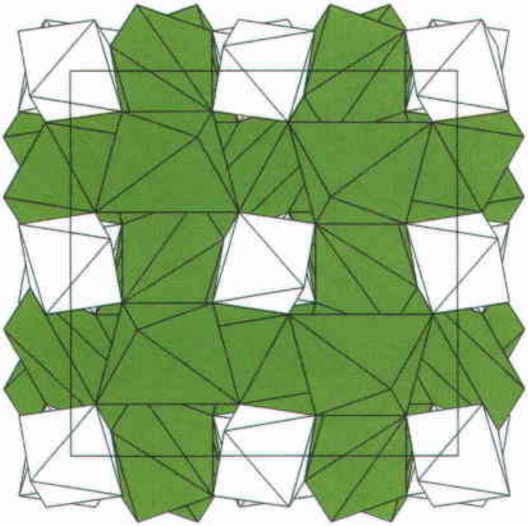

FIG. 4. The structure projected onto (100), showing the linking of the two types of polyhedra.

The walfordite structure is simple and densely packed. It consists of two types of six-fold coordination, a regular $[FeO_6]$ octahedron, within which Fe^{3+}, Te^{6+}, Ti^{4+} and Mg^{2+} are all compatible, and the highly distorted $[Te^{4+}O_6]$ polyhedron. The $[Te^{4+}O_6]$ polyhedron (Fig. 2), which has often been generally described as a distorted octahedron, consists of four shorter Te–O bonds of average length 2.00 Å, and two long bonds of 2.90 Å on the opposite side of what might be described as a sphenoid. The unique coordination is the result of the non-bonding lone pair of electrons associated with Te^{4+} atoms; it resembles that seen in the structures of denningite (Walitzi 1965), mackayite (Pertlik & Gieren 1977), α-$PbTeO_3$ (synthetic plumbotellurite) (Mariolacos 1969), sonoraite (Donnay *et al.* 1970), spiroffite (Cooper & Hawthorne 1996), and teineite (Effenberger 1977). The loci of the non-bonding pair of electrons would be between the long ligands (Fig. 2) and would manifest itself as an apparent hole in the structure above the long edge of the $[Te^{4+}O_6]$ polyhedron (Fig. 3). These pseudo-holes in the structure are a common feature of many of the tellurite structures, and can be seen in magnolite (Grice 1989), balyakinite (Lindqvist 1972) and denningite (Walitzi 1965), among others.

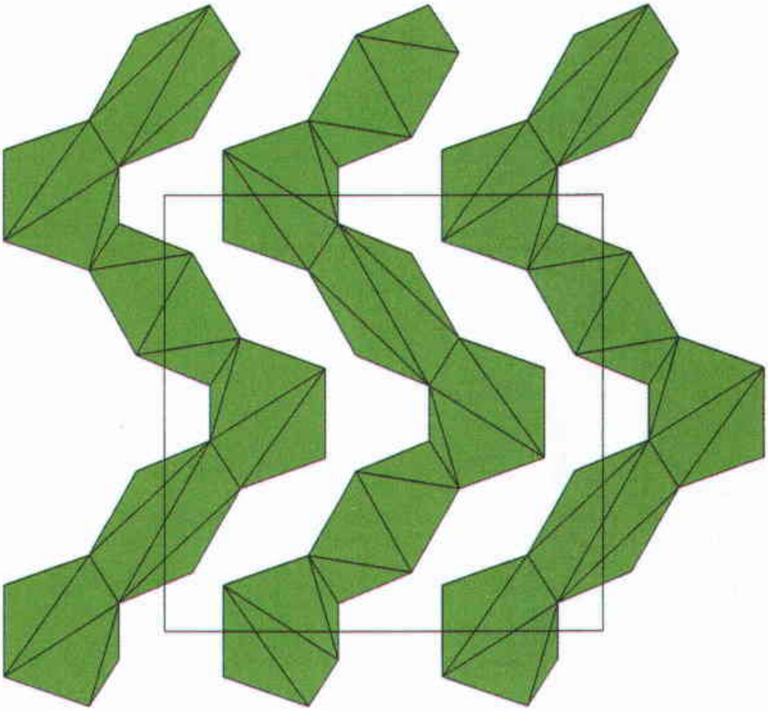

FIG. 5. The structure projected onto (100), showing the edge-sharing, zig-zag chains of TeO_6 polyhedra.

The structure of walfordite consists of two alternating types of slabs; each type appears twice within the unit-cell length of 11 Å (Fig. 4). The basal slab (Fig. 3) consists of isolated Fe and Te polyhedra, cross-linked through corner-sharing. One quarter of the unit cell outlined in Figure 3 would delineate the subcell of FCC cations described by Meunier & Galy (1971). The second slab (Fig. 5) is made up entirely of Te polyhedra that form zig-zag chains through edge-sharing. These chains run in all three directions, and the Te polyhedra also share a corner with the Fe polyhedra, making a very dense structure.

ACKNOWLEDGEMENTS

The authors thank Dr. F.C. Hawthorne, University of Manitoba, for the use of the four-circle diffractometer. Financial support for portions of this study came from the Royal Ontario Museum Foundation Fund by way of a research grant to Back and Mandarino. The authors acknowledge the cooperation of Barrick Gold Corporation. B.D. Sturman is thanked for advice on part of the optical study, and Dr. R.I Gait is thanked for advice and comments that improved the paper. Elizabeth Moffatt, Canadian Conservation Institute, Ottawa, conducted the IR study on walfordite. Helpful comments from Prof. Pier Francesco Zanazzi, an anonymous referee, and the editor, R.F. Martin, improved the quality of the manuscript.

REFERENCES

APPLEMAN, D.E. & EVANS, H.T., JR. (1973): Job 9214: indexing and least-squares refinement of powder diffraction data. *U.S. Geol. Surv., Comput. Contrib.* **20** (*NTIS Doc.* **PB2-16188**).

BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.

COOPER, M.A. & HAWTHORNE, F.C. (1996): The crystal structure of spiroffite. *Can. Mineral.* **34**, 821-826.

CRIDDLE, A.J. (1998): Ore microscopy and photometry (1890–1998). *In* Modern Approaches to Ore and Environmental Mineralogy (L.J. Cabri & D.J. Vaughan, eds.). *Mineral. Assoc. Can., Short Course Vol.* **27**, 1-74.

DONNAY, G., STEWART, J.M. & PRESTON H. (1970): The crystal structure of sonoraite, $Fe^{3+}Te^{4+}O_3(OH)\bullet H_2O$. *Tschermaks Mineral. Petrog. Mitt.* **14**, 27-44.

DUNN, P.J., PEACOR, D.R., CRIDDLE, A.J. & STANLEY, C.J. (1988): Ingersonite, a new calcium–manganese antimonate related to pyrochlore, from Långban, Sweden. *Am. Mineral.* **73**, 405- 412.

EFFENBERGER, H. (1977): Verfeinerung der Kristallstruktur von synthetischem Teineit $CuTeO_3{\bullet}2H_2O$. *Tschermaks Mineral. Petrog. Mitt.* **24**, 287-298.

GRICE, J.D. (1989): The crystal structure of magnolite, $Hg^{1+}{}_2Te^{4+}O_3$. *Can. Mineral.* **27,** 133-136.

HARGREAVES, A. (1955): Some observations on the probability distribution of X-ray intensities. *Acta Crystallogr.* **8**, 12-14.

________ (1956): The probability distribution of X-ray intensities: atoms in special positions. *Acta Crystallogr.* **9**, 191-192.

LINDQVIST, O. (1972): The crystal structure of $CuTeO_3$. *Acta Chim. Scand.* **26**, 1423-1430.

MANDARINO, J.A. (1981): The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* **19**, 441-450.

MARIOLACOS, K. (1969): Die Kristallstruktur von $PbTeO_3$. *Anz. Oesterr. Akad. Wiss., Math.–Naturwiss. Kl.* **106**, 128-130.

MEUNIER, G. & GALY, J. (1971): Sur une déformation inédite du réseau de type fluorine. Structure cristalline des phases MTe_3O_8 (M = Ti, Sn, Hf, Zr). *Acta Crystallogr.* **B27**, 602-607.

NORTH, A.C.T., PHILLIPS, D.C. & MATHEWS, F.S. (1968): A semi-empirical method of absorption correction. *Acta Crystallogr.* **A24**, 351-359.

PERTLIK, F. & GIEREN, A. (1977): Verfeinerung der Kristallstruktur von Mackayite, $Fe(OH)[Te_2O_5]$. *Neues Jahrb. Mineral., Monatsh.*, 145-154.

SHELDRICK, G.M. (1990): *SHELXTL, a Crystallographic Computing Package* (revision 4.1). Siemens Analytical Instruments, Inc., Madison, Wisconsin.

SIDDELEY, G. & ARANEDA, R. (1986): The El Indio – Tambo Gold Deposits, Chile. *In* Proc. Gold'86, an International Symposium on the Geology of Gold **1** (A.J. Macdonald, ed.). Konsult International, Toronto, Ontario (445-456).

WALITZI, E.M. (1965): Die Kristallstruktur von Denningit, $(Mn,Ca,Zn)Te_2O_5$. Ein Beispiel für Koordination um vierwertiges Tellur. *Tschermaks Mineral. Petrogr. Mitt.* **10**, 241-255.

WILLIAMS, S.A. (1979): Girdite, oboyerite, fairbankite, and winstanleyite, four new tellurium minerals from Tombstone, Arizona. *Mineral. Mag.* **43**, 453-457.

Received December 8, 1998, revised manuscript accepted August 20, 1999.