

THE CRYSTAL STRUCTURE OF LUDWIGITE

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ABSTRACT

We have refined the structure of ludwigite with a crystal taken from the Crestmore quarry, California; it is close to the end member in composition, ideally Mg_2FeBO_5 . The sample has a formula $\text{Mg}_{1.76}\text{Fe}_{1.22}\text{Al}_{0.02}\text{BO}_5$ and unit-cell dimensions a 9.2411(6), b 12.2948(9), c 3.0213(3) Å, V 343.27(5) Å³. The structure was refined in space group *Pbam*, to a final $R_w = 0.023$ for 948 observed unique reflections. The very low Al content allows the refinement of the distribution of magnesium and iron in the structure without assumptions as to the location of aluminum.

Keywords: ludwigite, vonsenite, pinakiolite group, crystal structure, Crestmore quarry, California.

SOMMAIRE

Nous avons affiné la structure de la ludwigite avec un cristal provenant de la carrière Crestmore, en Californie, et dont la composition est voisine de la composition idéale, Mg_2FeBO_5 . La formule est en fait $\text{Mg}_{1.76}\text{Fe}_{1.22}\text{Al}_{0.02}\text{BO}_5$, et les paramètres réticulaires sont: a 9.2411(6), b 12.2948(9), c 3.0213(3) Å, V 343.27(5) Å³. L'affinement, dans le groupe spatial *Pbam*, a mené à un résidu final R_w de 0.023 pour 948 réflexions uniques observées. La teneur très faible en Al permet un affinement de la distribution du magnésium et du fer dans la structure sans avoir à adresser la question de la distribution de l'aluminium.

(Traduit par la Rédaction)

Mots-clés: ludwigite, vonsenite, groupe de la pinakiolite, structure cristalline, carrière Crestmore, Californie.

INTRODUCTION

We present here the results of a refinement of the crystal structure of ludwigite; in the sample selected, from the Crestmore quarry, California, there is almost no aluminum substituting for Fe^{3+} . Ludwigite, with an ideal formula $\text{Mg}_2\text{Fe}^{3+}\text{BO}_5$, is an end-member of the ludwigite–vonsenite ($\text{Fe}^{2+}_2\text{Fe}^{3+}\text{BO}_5$) series. Manganese, aluminum and titanium commonly are found to substitute for magnesium and iron. This sample of ludwigite contains only magnesium and iron (with very minor aluminum), and the structure refinement provides information about the structure in the absence of the other substituents.

BACKGROUND INFORMATION

Takéuchi *et al.* (1950) solved the structure of ludwigite. It belongs to the pinakiolite group of minerals, in which metal ions are octahedrally coordinated by oxygen. The octahedra are linked together by edge-sharing to form what have been described as walls (*e.g.*, Bovin *et al.* 1981). Figure 1 shows the structure of

ludwigite viewed down the c axis. Swinnea & Steinfink (1983) refined the structure of synthetic vonsenite (Fe_3BO_5) and, on the basis of Mössbauer spectroscopy, concluded that ferrous and ferric iron occur in sites $M2$ and $M4$, whereas only ferrous iron occupies $M1$ and $M3$. They suggested that the distance between nearest-neighbor $M2$ and $M4$ sites of 2.79 Å is short enough for electron-hopping to occur. Norrestam *et al.* (1989) studied aluminian ludwigite and concluded, on the basis of site refinement of X-ray data and bond-valence calculations, that Mg occupies all four metal sites. They assumed that the aluminum is evenly distributed over all four sites. Bonazzi & Menchetti (1989) studied three structures in the ludwigite–vonsenite series and described the variation of cell dimensions and bond lengths with composition. Takéuchi & Kogure (1992) described the structure of a specimen of aluminian ludwigite and assigned aluminum to the $M4$ site.

EXPERIMENTAL

The crystal used is from the Crestmore quarry, Riverside, California, and was provided by the Canadian

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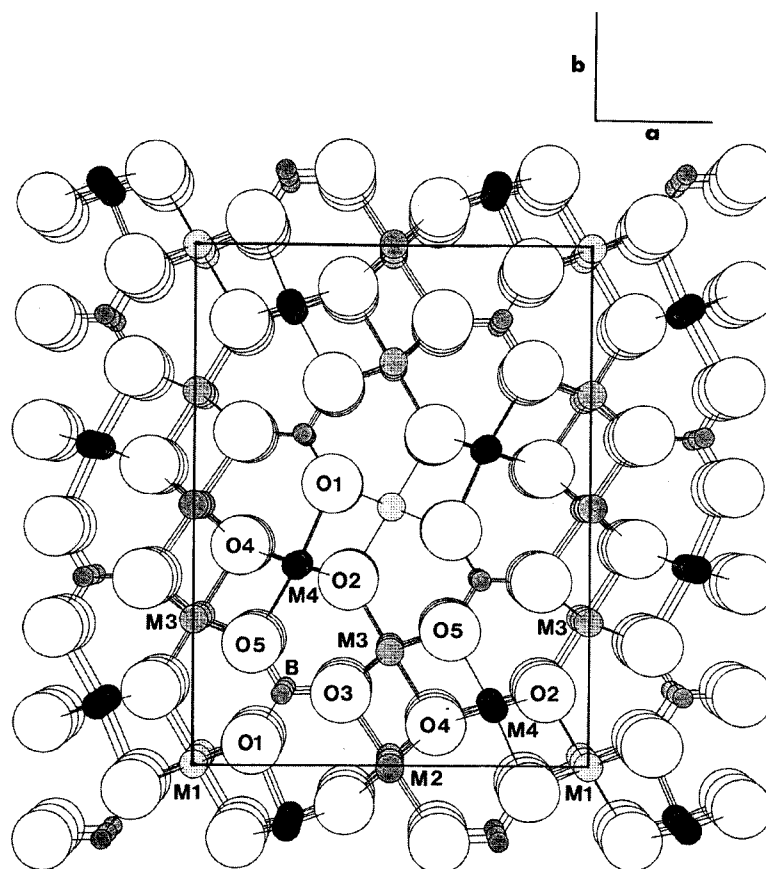


FIG. 1. The atomic structure of ludwigite viewed down the c axis. The symmetrically equivalent edge-sharing octahedra parallel to the c axis are linked to form interconnected sheets of octahedra, which also are parallel to the c axis.

Museum of Nature (catalogue #36092). The crystals, embedded in coarse-grained calcite in marble, were freed by dissolution of the matrix with dilute HCl. Polished grains were analyzed using an Applied Research Laboratories SEMQ electron microprobe in the Department of Geological Sciences at Queen's University. The sample of ludwigite was analyzed using energy-dispersion spectrometry at 15 kV and a beam current of approximately 20 nA. Standard NBS 470 K412 was used. Corrections were made using the procedure of Bence & Albee (1968) and the alpha corrections of Albee & Ray (1970). The formula determined for the ludwigite, $Mg_{1.76}Fe_{1.22}Al_{0.02}BO_5$, assumes stoichiometry, with three metal ions and one boron atom per formula unit. The crystal has dimensions $0.13 \times 0.22 \times 0.28$ mm. Intensity data were collected on an Enraf-Nonius CAD-4 single-crystal diffractometer with graphite-monochromatized $MoK\alpha$ radiation (λ 0.71069 Å), used in the $\omega - 2\theta$ scan mode. Twenty-five reflections with $10.2^\circ < \theta < 15.5^\circ$ were used to obtain the cell

parameters. A total of 1975 reflections were measured up to $2\theta = 80^\circ$ ($0 \leq h \leq 16$, $0 \leq k \leq 22$, $-5 \leq l \leq 5$). Equivalent reflections were averaged in space group $Pbam$ to give a total of 1015 unique reflections. Three intensity standards were monitored every 3600 seconds. Over the 55-hour collection time, the standard reflections changed in intensity by -2.7% . The intensities were corrected for Lorentz and polarization effects using the Structure Determination Package (Frenz 1985). An analytical absorption correction ($\mu = 56.2 \text{ cm}^{-1}$), with maximum and minimum transmission coefficients of 0.500 and 0.300, was done using the ABSCOR program of the Structure Determination Package. The agreement factor for averaging of reflections, R_{int} , was 0.014 on $|F_{obs}|$. The structure refinement was done using the XTAL 3.2 (Hall & Stewart 1990) package using 948 reflections with $F_{obs} > 3\sigma(F_{obs})$ and $1/\sigma_F$ weighting. The atomic coordinates reported by Bonazzi & Menchetti (1989) were used as starting values. The scattering factors used by the XTAL3.2 package are from

TABLE 1. ATOMIC FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS ($\text{\AA}^2 \times 100$), LUDWIGITE FROM CRESTMORE QUARRY

SITE	<i>x</i>	<i>y</i>	<i>z</i>	U_{Eq}	[Mg]	[Fe]	U_{11}	U_{22}	U_{33}	U_{12}
<i>M1</i>	0	0	0	0.57(4)	0.99(1)	0.01	0.53(9)	0.54(9)	0.65(4)	-0.08(6)
<i>M2</i>	1/2	0	1/2	0.70(2)	0.443(5)	0.557	0.95(1)	0.43(5)	0.65(5)	-0.04(3)
<i>M3</i>	0.0023(2)	0.2798(2)	0	0.52(3)	0.99(1)	0.01	0.57(6)	0.40(6)	0.58(6)	0.05(4)
<i>M4</i>	0.2399(1)	0.1145(1)	1/2	0.49(1)	0.08(1)*	0.92	0.48(3)	0.50(3)	0.49(3)	-0.10(2)
<i>B</i>	0.2743(5)	0.3600(3)	1/2	0.56(8)			0.62(16)	0.49(15)	0.57(14)	0.06(10)
<i>O1</i>	0.8502(3)	0.0434(2)	1/2	0.69(6)			0.63(11)	0.54(11)	0.90(11)	-0.07(9)
<i>O2</i>	0.3841(3)	0.0772(2)	0	0.72(6)			0.67(11)	0.57(11)	0.95(11)	0.06(8)
<i>O3</i>	0.6253(4)	0.1424(2)	1/2	0.72(6)			0.60(11)	0.64(11)	0.91(11)	0.03(8)
<i>O4</i>	0.1092(3)	0.1424(2)	0	0.64(6)			0.63(11)	0.53(11)	0.77(10)	0.01(8)
<i>O5</i>	0.8508(3)	0.2373(2)	1/2	0.75(6)			0.81(11)	0.48(11)	0.88(11)	0.04(9)

Anisotropic temperature factor = $\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}kbl^*c^*)]$, $U_{13} = U_{23} = 0$. * occupancy by Al.

the International Tables for X-ray Crystallography (1974). Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

An initial unconstrained refinement of populations indicated that the *M1* and *M3* sites are completely occu-

pled by magnesium, whereas the *M4* site is occupied by iron, and *M2* contains the remainder of the magnesium and iron. The site populations of the final refinement ($R = 0.028$) were constrained to the results of the chemical analysis, assuming full site-occupancy. Atomic parameters and site occupancies are given in Table 1, whereas bond lengths and polyhedron parameters are given in Table 2. Each octahedron in the structure shares six edges with other octahedra. All of these shared edges are shorter than unshared edges, as expected.

The volumes of the *M1*, *M2* and *M3* octahedra are very similar, which is consistent with the refined site-occupancies by either magnesium (*M1* and *M3*) or magnesium plus ferrous iron (*M2*). The volume of *M4* is considerably smaller as a result of occupancy by ferric iron. The refinement indicates that the *M4* site is not filled entirely with iron. If the site is assumed to be fully occupied, the reduction in scattering from this site can be attributed to the presence of aluminum or magnesium, or both. The chemical composition of the ludwigite must be consistent with the assigned site-occupancies. Unconstrained site-refinements show that the total amount of magnesium inferred to be at the *M1*, *M2* and *M3* sites equals the total amount of magnesium required by the chemical data. The refinement of the occupancy of site *M4* indicates that there is a small amount of aluminum present. The amount is consistent with the amount of aluminum indicated by the chemical formula. The preference of aluminum for *M4* is attributed to the small volume of this site. Figure 2 shows the volume of *M4* versus the proportion of aluminum in atoms per formula unit for published refinements of ludwigite. Vonsenite, with no aluminum in *M4*, is at one end of the series, and the volume of the aluminum-filled octahedra in corundum gives an estimate of the volume of *M4* if it were filled entirely with aluminum.

Figure 3 shows the volumes of *M1* and *M3* to decrease with increased magnesium substitution at these

TABLE 2. BOND DISTANCES (\AA), VOLUMES (\AA^3), AND DISTORTION PARAMETERS OF OCTAHEDRA, LUDWIGITE FROM CRESTMORE QUARRY

	This study	T & K (1992)		shared with		
<i>M1</i>	-O(4) ($\times 2$)	2.021(3)	2.021	O1-O4 ($\times 4$)	2.764(3)	<i>M4</i> volume 11.94
	-O(1) ($\times 4$)	2.118(2)	2.104	O1-O1 ($\times 2$)	2.967(3)	<i>M1</i> Q.E. 1.009
	mean	2.08	2.076	O1-O1 ($\times 2$)	3.021(3)	ang. var. 28.4
				O1-O4 ($\times 4$)	3.081(3)	
<i>M2</i>	-O(2) ($\times 4$)	2.081(2)	2.065	O3-O2 ($\times 4$)	2.809(3)	<i>M3</i> volume 11.98
	-O(3) ($\times 2$)	2.100(3)	2.069	O2-O2 ($\times 2$)	2.862(3)	<i>M2</i> Q.E. 1.008
	mean	2.087	2.066	O2-O2 ($\times 2$)	3.021(3)	ang. var. 25.81
				O3-O2 ($\times 4$)	3.095(3)	
<i>M3</i>	-O(4) ($\times 1$)	1.957(3)	1.96	O2-O5 ($\times 2$)	2.753(3)	<i>M4</i> volume 11.91
	-O(2) ($\times 1$)	2.070(3)	2.07	O3-O2 ($\times 2$)	2.809(3)	<i>M2</i> Q.E. 1.011
	-O(3) ($\times 2$)	2.119(2)	2.103	O3-O5 ($\times 2$)	2.936(3)	<i>M3</i> ang. var. 35.9
	-O(5) ($\times 2$)	2.125(2)	2.116	O3-O3 ($\times 2$)	3.021(3)	
	mean	2.086	2.078	O4-O3 ($\times 2$)	3.050(3)	
			O4-O5 ($\times 2$)	3.057(3)		
<i>M4</i>	-O4 ($\times 2$)	1.964(2)	1.93	O4-O2 ($\times 2$)	2.664(3)	<i>M4</i> volume 11.13
	-O2 ($\times 2$)	2.066(2)	2.059	O2-O5 ($\times 2$)	2.753(3)	<i>M3</i> Q.E. 1.016
	-O5 ($\times 1$)	2.093(3)	2.053	O1-O4 ($\times 2$)	2.764(3)	<i>M1</i> ang. var. 49.12
	-O1 ($\times 1$)	2.113(3)	2.094	O2-O2 ($\times 2$)	3.021(3)	
	mean	2.044	2.021	O1-O2 ($\times 2$)	3.027(3)	
				O4-O5 ($\times 2$)	3.075(3)	
<i>B</i>	-O1	1.379(3)	1.385	O1-B-O3	121.8°	
	-O3	1.377(3)	1.376	O1-B-O5	118.9°	
	-O5	1.390(2)	1.389	O3-B-O5	119.3°	
	mean	1.382	1.384			

Q.E.: quadratic elongation, ang. var.: angular variance. T & K: Takéuchi & Kogure.

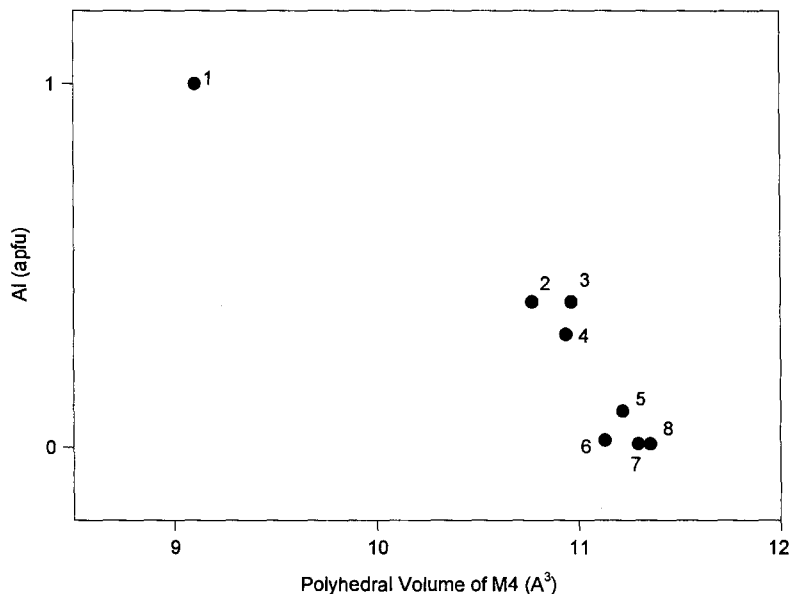


FIG. 2. The volume of the polyhedron *M4* versus the number of aluminum atoms per formula unit. Data points: (2): Takéuchi & Kogure (1992), (3): Mokeyeva (1968), (4): Norrestam *et al.* (1989), (5): CO of Bonazzi & Menchetti (1989), (6): this study, (7): RS of Bonazzi & Menchetti (1989). Corundum (1) and vonsenite (8) (CA of Bonazzi & Menchetti 1989), are examples of minerals in which octahedra contain 100% aluminum and ferric iron, respectively.

sites. Ferrous iron preferentially occupies *M2*. Therefore, *M2* does not show this steady decrease in volume with the decrease in total iron content. Only where *M1* and *M3* are completely filled with magnesium is there a decrease in the volume of *M2* with substitution for magnesium. Malisheva *et al.* (1971) found, using Mössbauer spectroscopy, that ferrous iron preferentially substitutes at the *M2* site, and only after this site is filled will iron substitute for magnesium at *M1* and *M3*.

Table 3 lists the bond-valence sums for each atomic site, as calculated with the program VALIST [A.S. Wills & I.D. Brown, *VaList*, CEA, France (1999). Program available from the first author at willsas@netscape.net]. The valence sum at *M2* is slightly larger than 2. The suggestion has been made by Swinnea & Steinfink (1983) that electron hopping takes place between *M2* and *M4*.

TABLE 3. BOND-VALENCE SUMMATION (ν) FOR LUDWIGITE FROM THE CRESTMORE QUARRY, CALIFORNIA

<i>M1</i>	2.07	<i>B</i>	2.92	O3	1.95
<i>M2</i>	2.06	O1	1.97	O4	1.96
<i>M3</i>	2.11	O2	1.98	O5	1.95
<i>M4</i>	2.81				

Coefficients from Brown & Altermatt (1985).

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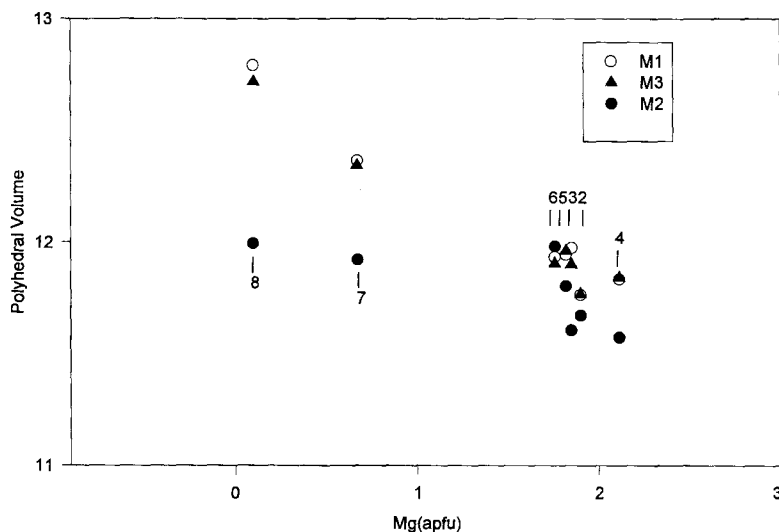


FIG. 3. The number of magnesium atoms per formula unit *versus* polyhedron volume. M1 is shown as open circles, M2 as filled circles, and M3 as filled triangles. Sample numbers correspond with those in Figure 2.

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