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WAGNERITE-*Ma*5*bc*, A NEW POLYTYPE OF $Mg_2(PO_4)(F,OH)$, FROM GRANULITE-FACIES PARAGNEISS, LARSEMANN HILLS, PRYDZ BAY, EAST ANTARCTICA

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ABSTRACT

Wagnerite-*Ma*5*bc*, a new polytype, occurs in paragneiss associated with banded cordierite–prismatine gneiss in the Larsemann Hills, East Antarctica. It forms anhedral to euhedral grains mostly 0.5–2 mm across, some with a tabular habit. Textures are consistent with a primary assemblage wagnerite-*Ma*5*bc* + plagioclase + apatite + magnetite + ilmenite–hematite that crystallized under granulite-facies conditions (750 – ~860°C, 6–7 kbar). Also present are biotite, quartz, K-feldspar, minerals of the monazite and xenotime groups, corundum, hercynite, and sulfide. Electron-microprobe analyses give P_2O_5 41.39, SiO_2 0.06, TiO_2 0.88, FeO 4.16, MnO 0.09, MgO 44.54, CaO 0.09, F 6.87, H_2O (calculated for OH + F = 1) 2.04, O=F –2.89, total 97.22 wt%, corresponding to $(Mg_{1.88}Fe_{0.10}Ti_{0.02})(P_{0.99}O_4)(F_{0.61}OH_{0.39})$. The space group is *Ia*. Lattice parameters: *a* 9.645(2), *b* 31.659(6), *c* 11.914(2) Å, β 108.26(3)°, *V* 3455(1) $Å^3$ for $Z = 40$. The crystal structure has been solved by direct methods and refined to $R_1 = 0.0413$ for the independent 4521 reflections [$I > 2\sigma(I)$] using Mo*K*α radiation. The primary difference between the wagnerite-*Ma*5*bc* and wagnerite-*Ma*2*bc* (*e.g.*, type locality) is ordering of the (F,OH) positions. F can occupy one of two positions, resulting in two distinct configurations along the *a* direction. In magniotriplite, the sequence of configurations in the *b* direction is disordered, whereas in wagnerite-*Ma*2*bc*, the sequence is ordered 121212… and in wagnerite-*Ma*5*bc*, 12112... Magniotriplite and the wagnerite polytypes do not overlap in composition: minerals richer in Fe and Mn (average ionic radius ≥ 0.76 Å) crystallize as the disordered minerals in the triplite group, whereas highly magnesian minerals (average ionic radius ≤ 0.73 Å or ≥ 86% of the Mg end member) crystallize as the ordered polytypes of wagnerite. Magniotriplite formed at moderate temperatures (*e.g.,* amphibolite-facies conditions), whereas wagnerite-*Ma*2*bc* is found in rocks formed under a wide range of *P–T* conditions. Compositional or kinetic factors (or both), rather than *P–T,* could play the leading role in determining the extent of F order; possibly many $M^{2+}{}_2PO_4F$ compounds originally crystallize in the disordered state, the *Mabc* polytype, and only magnesian varieties subsequently order on cooling, *i.e*., Mn^{2+} and Fe^{2+} inhibit ordering.

Keywords: wagnerite, magniotriplite, crystal structure, polytype, granulite facies, Larsemann Hills, Antarctica.

SOMMAIRE

On trouve la wagnerite-*Ma*5*bc*, polytype nouveau, dans des paragneiss associés à des gneiss rubanés à cordiérite–prismatine dans les collines Larsemann, dans le secteur oriental de l'Antarctique. Elle forme des grains xénomorphes à idiomorphes mesurant en général entre 0.5 et 2 mm de diamètre, dont certains sous forme de plaquettes. Les textures concordent avec le caractère primaire de l'assemblage wagnerite-*Ma*5*bc* + plagioclase + apatite + magnétite + ilménite–hématite, qui a cristallisé aux conditions du faciès granulite (entre 750 et ~860°C, 6–7 kbar). Sont aussi présents biotite, quartz, feldspath potassique, minéraux des groupes de la monazite et du xénotime, corindon, hercynite, et sulfures. Les analyses à la microsonde électronique ont donné P_2O_5 41.39, SiO_2 0.06, TiO_2 0.88, FeO 4.16, MnO 0.09, MgO 44.54, CaO 0.09, F 6.87, H_2O (calculé pour donner OH + F = 1) 2.04, O=F –2.89, pour un total de 97.22% (poids), correspondant à $(Mg_{1.88}Fe_{0.10}Ti_{0.02})(P_{0.99}O_4)(F_{0.61}OH_{0.39})$. Son groupe spatial est *Ia*. Les paramètres réticulaires sont: *a* 9.645(2), *b* 31.659(6), *c* 11.914(2) Å, β 108.26(3)°, *V* 3455(1) $Å^3$ pour $Z = 40$. Nous en avons établi la structure cristalline par méthodes directes et nous l'avons affiné jusqu'à un résidu R_1 de 0.0413 en utilisant 4521 réflexions

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indépendantes [I > 2σ(I)] et un rayonnement Mo*K*α. La différence principale entre ce polytype et la wagnerite-*Ma*2*bc* (l'échantillon holotype) porte sur le degré d'ordre des positions (F,OH). Le F peut se trouver dans une de deux positions, définissant ainsi deux agencements le long de l'axe *a*. Dans la magniotriplite, la séquence des agencements le long de *b* est désordonnée, tandis que dans la wagnerite-*Ma*2*bc*, la séquence serait ordonnée, 121212..., et dans la wagnerite-*Ma*5*bc*, 12112... La magniotriplite et les polytypes de la wagnerite ne se chevauchent pas en termes de composition; les minéraux plus riches en Fe et Mn (rayon ionique moyen ≥ 0.76 Å) cristallisent sous forme de minéraux désordonnés du groupe de la triplite, tandis que les minéraux fortement magnésiens (rayon ionique moyen ≤ 0.73 Å ou ≥86% du pôle Mg) cristallisent sous forme ordonnée comme polytypes de la wagnerite. La magniotriplite cristallise à des températures intermédiaires (c'est-à-dire aux conditions du faciès amphibolite), tandis que la wagnerite-*Ma*2*bc* se présente dans des roches formées sur un grand intervalle de conditions *P–T*. Des facteurs compositionnels ou cinétiques (ou les deux), plutôt que *P–T*, pourraient bien jouer un rôle déterminant dans la mise en ordre au site F. Il est possible que plusieurs composés de type $M^{2+}{}_2PO_4F$ aient cristallisé à l'origine sous une forme désordonnée, le polytype *Mabc*, et que seules les variétés magnésiennes ont par la suite atteint la forme ordonnée en refroidissant; en d'autres mots, le Mn^{2+} et le Fe^{2+} ne sembleraient pas favoriser la mise en ordre.

(Traduit par la Rédaction)

Mots-clés: wagnerite, magniotriplite, structure cristalline, polytype, faciès granulite, collines Larsemann, Antarctique.

INTRODUCTION

Minerals having the composition $(Mg,Fe,Mn)_2(PO_4)$ (F,OH) are relatively uncommon constituents of metamorphic and igneous rocks. Nonetheless, they have attracted increasing interest because of possible use as indicators of the physicochemical conditions of formation (*e.g.*, Brunet *et al.* 1998). In the F- and Mg-dominant members, only two minerals have been found, magniotriplite and wagnerite, and their crystal structures have been refined (Table 1). They are isostructural with zwieselite, $(Fe,Mn)_2(PO_4)(F)$, triplite, $(Mn,Fe)_2(PO_4)$ (F,OH), and triploidite, $(Mn, Fe)_2(PO_4)(OH)$, respectively (Coda *et al.* 1967, Tadini 1981, Irouschek &

TABLE 1. COMPARISON OF CRYSTALLOGRAPHIC, PHYSICAL AND OPTICAL PROPERTIES OF THE THREE Mg- AND F-DOMINANT MINERALS WITH THE FORMULA $(Mg,Fe,Mn)_2(PO_4)(F,OH)$

Group* Mg-, F-dominant member	Wagnerite-*Ma*5*bc*	Triploidite group Wagnerite-*Ma*2*bc* Werfen, Austria	Triplite group Magniotriplite Albères, France
Formula	$(Mg_{1.88}Fe_{0.10}Ti_{0.02})$ $(P_{0.99}O_4)[F_{0.61}(OH)_{0.39}]$	$(Mg_{1.96}Fe_{0.02}Mn_{0.02})$ $(P_{1.00}O_4)[F_{0.99}(OH)_{0.01}]$[1,3]	$(Mg_{0.89}Fe_{0.87}Mn_{0.23}Ti_{0.01})$ $(P_{1.00}O_4)[F_{0.68}(OH)_{0.31}]$[6]
Crystal system	monoclinic	monoclinic[2]	monoclinic
Space group ($c > a$)	*Ia*	$P2_1/c$ (source 2)	
Space group ($a > c$)		$P2_1/a$ (source 7)	$I2/a$ (source 7)
a (Å)	9.645(2)	9.644(7)[2]	*c* = 9.799(2)[7]
b (Å)	31.659(6)	12.679(8)[2]	6.432(4)[7]
c (Å)	11.914(2)	11.957(8)[2]	*a* = 12.035(5)[7]
β (°)	108.26(3)	108.30(15)[2]	108.12(2)[7]
V (Å³)	3455(1)	1388[2]	720.9[7]
Z	40	16	8
Powder pattern, most diagnostic line(s) *d* (Å)	6.232, 1.9129	5.66 but not 6.232[3]	no line with $d > 5.27$ Å[3,6]
Density, meas., g/cm³	not measured	3.153[4], 3.13[5]	3.59(2)[6]
Density, calc., g/cm³	3.18	3.11[2]	3.68[6]
α	1.571(2)	1.5678[1]	1.648[6]
β	1.577(3)	1.5719[1]	1.653[6]
γ	1.591(2)	1.5824[1]	1.664[6]
$2V_\gamma$ (°)	30(15)	28.4[1,3]	medium[6]
Dispersion	$r < v$, moderate	$r > v$[1] (*cf.* $r < v$[8]), weak	$r < v$[6] (*cf.* $r > v$, strong[9])
Color in hand specimen	reddish yellow	wine yellow, yellowish brown, reddish yellow[1,5]	amber yellow with orange tint to caramel chestnut[6]
Color in thin section	*X* pale yellow, *Y*, *Z* yellow	colorless or very pale	*X*, *Y* colorless, *Z* very pale yellow[6]

Sources: [1] Hegemann & Steinmetz (1927), [2] Coda *et al.* (1967), [3] Sheridan *et al.* (1976), [4] Richmond (1940), [5] Fuchs (1821), [6] Fontan (1981), [7] Tadini (1981), [8] Jaffe *et al.* (1992), [9] Ginzburg *et al.* (1951). * Strunz & Nickel (2001).

Armbruster 1984, Waldrop 1969, 1970, Rea & Kostiner 1972, Raade & Rømming 1986, Yakubovich *et al.* 1978, Strunz & Nickel 2001). The distinction between the two structures is subtle: differences in the coordination of the *M* sites are related to small shifts in the atomic positions and to the degree of order at the (F,OH) sites (Waldrop 1970, Tadini 1981). Although solid solution is complete between synthetic end-member wagnerite and its OH analogue (Raade & Rømming 1986), F-dominant end-members of the other four polymorphs of Mg_2PO_4OH (althausite, holtedahlite, and two synthetic modifications not yet discovered in nature) have not been found in nature or experiment (Raade 1990), nor has an OH-dominant analogue of magniotriplite been reported.

A metamorphic mineral having the composition and optical properties of wagnerite was found in a P-rich paragneiss in the Larsemann Hills, East Antarctica; the coordinates of the site are 69°25'S, 76°05'E (Fig. 1). However, single-crystal X-ray-diffraction studies show that the mineral is distinct in terms of cell dimensions and symmetry (Table 1). Similar wagnerite-like minerals have also been found by Chopin *et al.* (2003). Detailed crystallographic study shows that these minerals are not distinct species, but polytypes differing only in the pattern of order of (F,OH) positions. The model for this ordering was independently derived by Chopin *et al.* (2003) and by us (Ren *et al.* 2002, 2003), whereas Chopin *et al.* (2003, pers. commun.) were the first to recognize that the different structures are polytypes rather than polymorphs, as Tadini (1981) had proposed. The wagnerite polytypes have the same *a* and *c* dimensions; their *b* dimensions are integral multiples of 6.33–6.34 Å, which is approximately the *b* dimension of magniotriplite. Following the notation of Guinier *et al.* (1984), wagnerite from the type locality (Fuchs 1821, Hegemann & Steinmetz 1927, Coda *et al.* 1967) is the *Ma*2*bc* polytype, whereas the polytype to be described here is *Ma*5*bc*. Chopin *et al.* (2003) have discovered wagnerite-*Ma*7*bc* and wagnerite-*Ma*9*bc*. Strictly speaking, magniotriplite is magniotriplite-*Mabc*, but it is neither a polymorph (*cf.* Tadini 1981) nor a polytype of wagnerite because the proportion of Fe exceeds that of Mg at the *M*1 site (Table 2).

TABLE 2. POLYTYPES OF MINERALS HAVING THE COMPOSITION $(Mg,Fe)_2(PO_4)(F,OH)$

	Wagnerite	Magniotriplite	Zwieselite	Group
*M*1	Mg > Fe	Fe > Mg > Mn*	Fe	
*M*2	Mg > Fe	Mg > Fe > Mn*	Fe	
b ≈ 6.34 Å		Magniotriplite -*Mabc*	Zwieselite -*Mabc*	Triplite
b ≈ 12.68 Å	Wagnerite-*Ma*2*bc*			Triploidite
b ≈ 31.70 Å	Wagnerite-*Ma*5*bc*			
b ≈ 45 Å	Wagnerite-*Ma*7*bc*			
b ≈ 57 Å	Wagnerite-*Ma*9*bc*			

* Assuming that the Fe/Mn value is about the same at both sites. Sources: Coda *et al.* (1967), Yakubovich *et al.* (1978), Tadini (1981), Chopin *et al.* (2003), this paper.

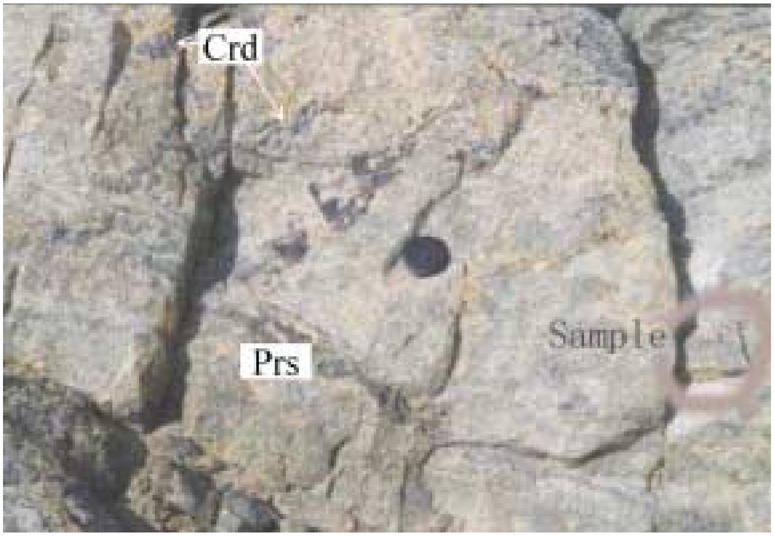

FIG. 1. Photograph of the outcrop near Zhongshan Station, Larsemann Hills, where the sample containing wagnerite-*Ma*5*bc* was collected. The diameter of the lens cap is 56 mm. Prs: coarse-grained aggregates of prismatine (dark); Crd: nodules of cordierite (blue).

OCCURRENCE

The gneiss containing wagnerite-*Ma5bc* occurs in the core of what appears to be a fold in banded cordierite–prismatine gneiss (Fig. 1). Prismatine and cordierite also form coarse-grained segregations and nodules associated with feldspathic segregations. Given the presence of the Al-rich minerals cordierite and prismatine, the gneisses illustrated in Figure 1 most likely have sedimentary precursors that were subsequently modified by migmatization.

The gneiss lacks an obvious foliation. Major constituents are plagioclase, wagnerite-*Ma*5*bc*, apatite and magnetite; subordinate are biotite, quartz, K-feldspar, cordierite (?), minerals of the monazite and xenotime groups, corundum, lamellar hematite–ilmenite intergrowths, hercynite and sulfide. Wagnerite-*Ma*5*bc* forms anhedral to euhedral grains mostly 0.5–2 mm across (maximum: nearly 2.5 mm) (Figs. 2–3). Some grains have a tabular habit, and their thickness can be less than 0.1 mm; a few show two terminal faces. Wagnerite-*Ma*5*bc* is commonly dusty with fine inclusions, or discolored by incipient alteration. Textures suggest two generations of apatite: (1) relatively coarse grains with aligned acicular inclusions (Fig. 2), and (2) rare margins fringing wagnerite-*Ma*5*bc* (Fig. 3) or overgrowths separating wagnerite-*Ma*5*bc* from oxide and sulfide inclusions (Fig. 4). Microscopic seams of apatite have also developed along cracks and grain boundaries of wagnerite-*Ma*5*bc* (Fig. 5), a texture very similar that observed in wagnerite from Star Lake, Manitoba (Leroux & Ercit 1992, Fig. 2). An isotropic material possibly derived by alteration of cordierite forms a narrow corona around oxide grains, and symplectitic intergrowths with K-feldspar. In summary, textures are consistent with a primary assemblage wagnerite-*Ma*5*bc* + plagioclase + apatite(1) + magnetite + ilmenite–hematite. Although apatite(2) is clearly secondary, the status of biotite and K-feldspar is less obvious.

Metamorphic temperatures are inferred to have peaked in the granulite facies at moderate pressures in the Larsemann Hills, *i.e.*, from 750 to ~860°C at 6–7 kbar, but evidence in a few samples suggests the possibility of an earlier event during which conditions could have reached ~10 kbar and 980°C (*e.g.*, Ren *et al.* 1992, Fitzsimons 1996, Carson *et al.* 1997, Tong & Liu 1997).

PHYSICAL AND OPTICAL PROPERTIES

Wagnerite-*Ma*5*bc* has two poor cleavages and is brittle. Its luster is vitreous, and its Mohs hardness is 5–6. Its color is reddish yellow, and the streak, pale yellow. The calculated density is 3.18(1) g/cm^3.

Wagnerite-*Ma*5*bc* is transparent and pale yellow in thin section; it is biaxial positive. The optical constants are α 1.571(2), β 1.577(3), γ 1.591(2), $2V_{meas}$ = 30(15)°, $2V_{calc}$ = 67°. Dispersion is moderate, $v > r$. The pleochroic scheme is *X* very pale yellow, *Y* and *Z* medium

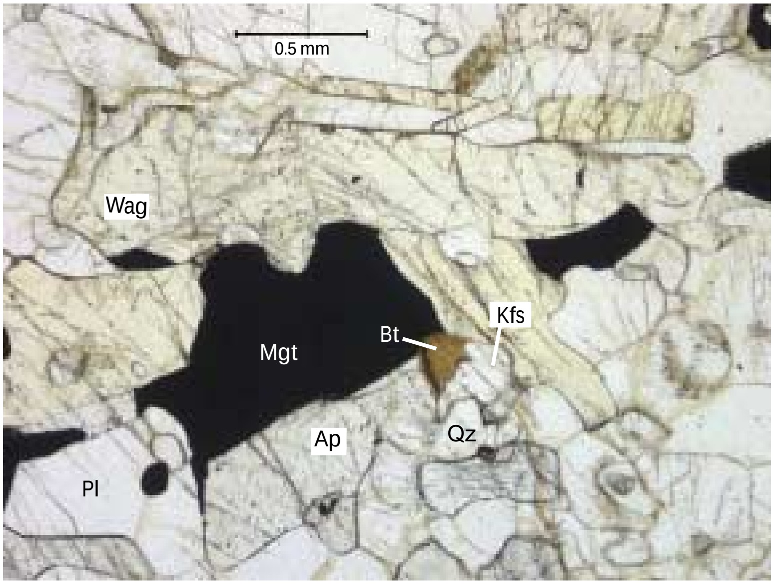

FIG. 2. Photomicrograph of wagnerite-*Ma*5*bc* (Wag, yellow and tabular in part) in plagioclase (Pl) with primary apatite (Ap, acicular inclusions); quartz (Qz) in rounded grains. Mgt: magnetite, Bt: biotite, Kfs: K-feldspar. Plane light.

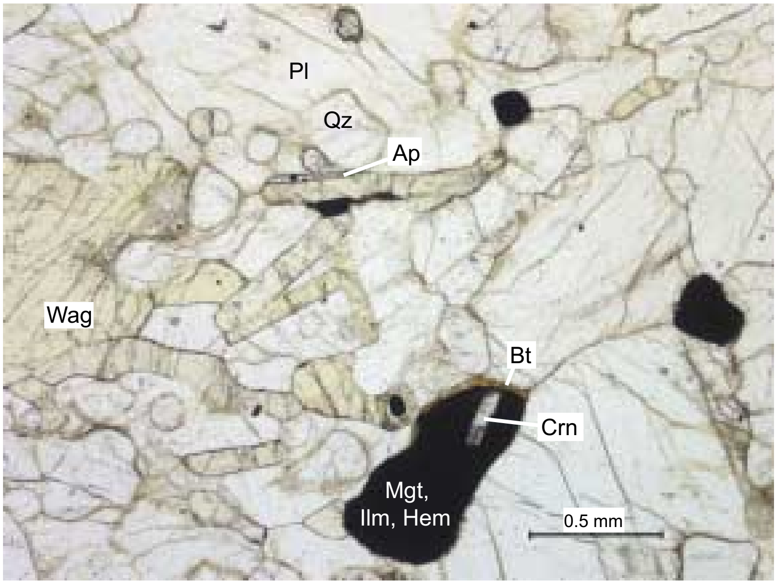

FIG. 3. Photomicrograph of wagnerite-*Ma*5*bc* (Wag, yellow and mostly tabular) in plagioclase (Pl). Secondary apatite (Ap) locally fringes wagnerite-*Ma5bc*; quartz (Qz) forms rounded grains. Mgt: magnetite, Ilm: ilmenite, Hem: hematite, Bt: biotite, Crn: corundum. Plane light.

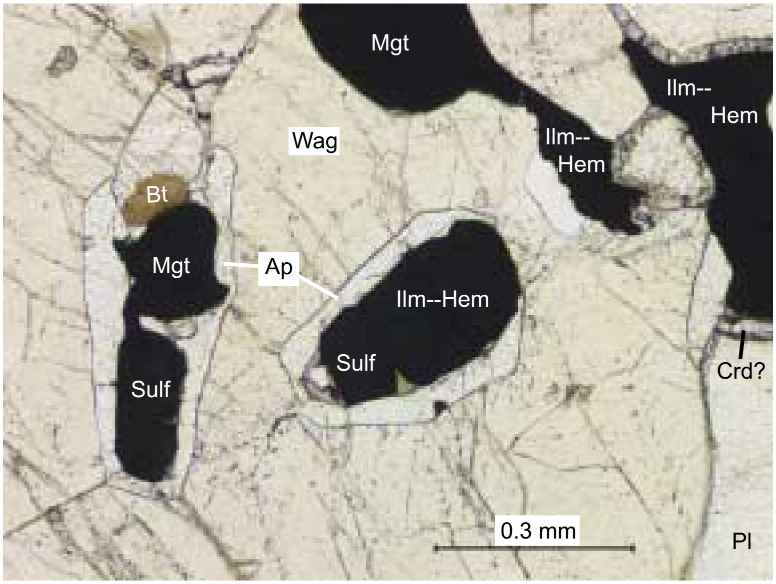

FIG. 4. Photomicrograph of wagnerite-*Ma*5*bc* (Wag) separated by rims of secondary apatite (Ap) from magnetite (Mgt), ilmenite–hematite intergrowths (Ilm–Hem), and unidentified yellow sulfide (Sulf). Bt: biotite, Pl: plagioclase, Crd: cordierite. Plane light.

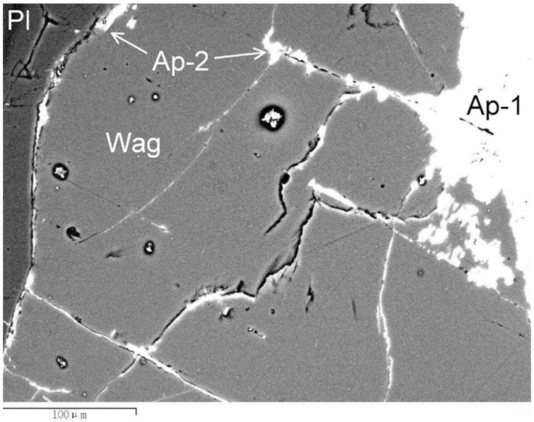

FIG. 5. Back-scattered electron image of wagnerite-*Ma*5*bc* (gray, Wag) and coarse-grained apatite (white, Ap-1). Apatite has also developed along cracks and margins of wagnerite-*Ma*5*bc* (*e.g.*, white patches, Ap–2). Pl: plagioclase (nearly black).

TABLE 3. COMPOSITION OF WAGNERITE-*Ma5bc*

	Average	Range	Formula per 4.5 O	
P_2O_5 wt%	41.39	40.95 – 41.80	P	0.991
SiO_2	0.06	0.05 – 0.08	Si	0.002
TiO_2	0.88	0.72 – 1.03	Ti	0.019
FeO	4.16	2.56 – 4.89	Fe	0.098
MnO	0.09	0.06 – 0.13	Mn	0.002
MgO	44.54	43.59 – 45.19	Mg	1.878
CaO	0.09	0.07 – 0.11	Ca	0.003
F	6.87	6.20 – 7.73	F	0.614
H_2O	2.04		OH	0.386
O=F	-2.89			
Total	97.22		Σ cations	2.993

Note: Average result of nine electron-microprobe analyses: JXA–8800A, 20 kV, 20 nA, 5~20 µm, wavelength dispersion. Standards: apatite (P, F), wollastonite (Si, Ca), rutile (Ti), hematite (Fe), Mn oxide (Mn), forsterite (Mg). All Fe as FeO. Na, Al, K, Cr below detection. H_2O calculated assuming F + OH = 1; presence of H_2O was confirmed by laser Raman spectrum analysis.

yellow. The optical orientation could not be specified. The optic axis *X* is approximately parallel to the length of the platelets so as to give negative, quasi-straight elongation when viewed down *Z* (acute bisetrix), whereas optic axis *Z* is at ~20° to the elongation, which gives inclined, positive elongation when viewed down *X* (obtuse bisectrix). Given that $Y = b$ in wagnerite and in the triplite group (*e.g.*, Palache *et al.* 1951), there is every reason to expect $Y = b$ in wagnerite-*Ma*5*bc*. In this case, $X \wedge c$ appears to be only a few degrees. The most prominent faces that result in the tabular habit could be a form {*hk*0}, *e.g.* {150}; the corresponding form in wagnerite, {021}, is prominent in some crystals of this mineral (Palache *et al.* 1951).

In general, none of the optical and physical properties listed in Table 1 can be used to distinguish wagnerite-*Ma*5*bc* from wagnerite-*Ma*2*bc* and magniotriplite because these properties depend much more on (Fe + Mn) content than on crystal structure (Fin'ko 1962, Propach 1976). X-ray diffraction is needed to identify magniotriplite and the wagnerite polytypes (see below).

The compatibility using the Gladstone–Dale relationship (Mandarino 1981) is 0.020 (excellent).

CHEMICAL COMPOSITION

Wagnerite-*Ma*5*bc* is ferroan, with minor Ti (Table 3). The presence of hydroxyl in wagnerite-*Ma*5*bc* was confirmed in a laser Raman spectrum (Fig. 6). The band near 3570 cm^{-1} represents an O–H stretching mode comparable to that reported at 3580 cm^{-1} in the infrared spectrum of OH-bearing wagnerite-*Ma*2*bc* from Miregn, Switzerland (Irouschek-Zumthor & Armbruster 1985, Chopin *et al.* 2003, and pers. commun.).

X-RAY DIFFRACTION

The measured powder pattern closely resembles the pattern for the wagnerite-*Ma*2*bc* polytype, but it does have two reflections that could be diagnostic: the (101) and (422) lines at 6.232 and 1.9129 Å, respectively (Table 4). The pattern for wagnerite-*Ma*2*bc* includes two reflections, (331) and (036), which are absent in the pattern for wagnerite-*Ma*5*bc*. Many reflections found in the pattern of wagnerite-*Ma*5*bc* are also in the calculated pattern for wagnerite-*Ma*2*bc*, although absent in the observed pattern of this polytype from Santa Fe Mountain, and thus should not be considered diagnostic for wagnerite-*Ma*5*bc*. Given the ambiguity of indexing reflections, it could prove very difficult to distinguish the two polytypes on the basis of a few reflections such as (422) in *Ma*5*bc* or (331) and (036) in *Ma*2*bc* in powder patterns (T. Armbruster, pers. commun.; see below).

Refinement of 93 lines of the powder pattern using the program UnitCell (errors given for 95% confidence level) gave *a* 9.662(2), *b* 31.702(6), *c* 11.933 (2) Å, β 108.25(2)°, *V* 3471.5(8) Å^3. The difference in unit-cell parameters obtained by single-crystal methods (Table 5) and those obtained from the powder pattern can be explained by chemical heterogeneity, particularly as the sample size in both cases was very small. In particular, the variation in F content found in the chemical analyses is nearly sufficient to account for the difference in cell volume using the relationship reported by Raade & Rømming (1986) for variation of cell volume with F/(OH + F) ratio in the solid solution between synthetic wagnerite and its hydroxyl analogue.

The X-ray-diffraction data from a single crystal of the mineral were measured by Ming Xiong and Zhesheng Ma at China University of Geosciences,

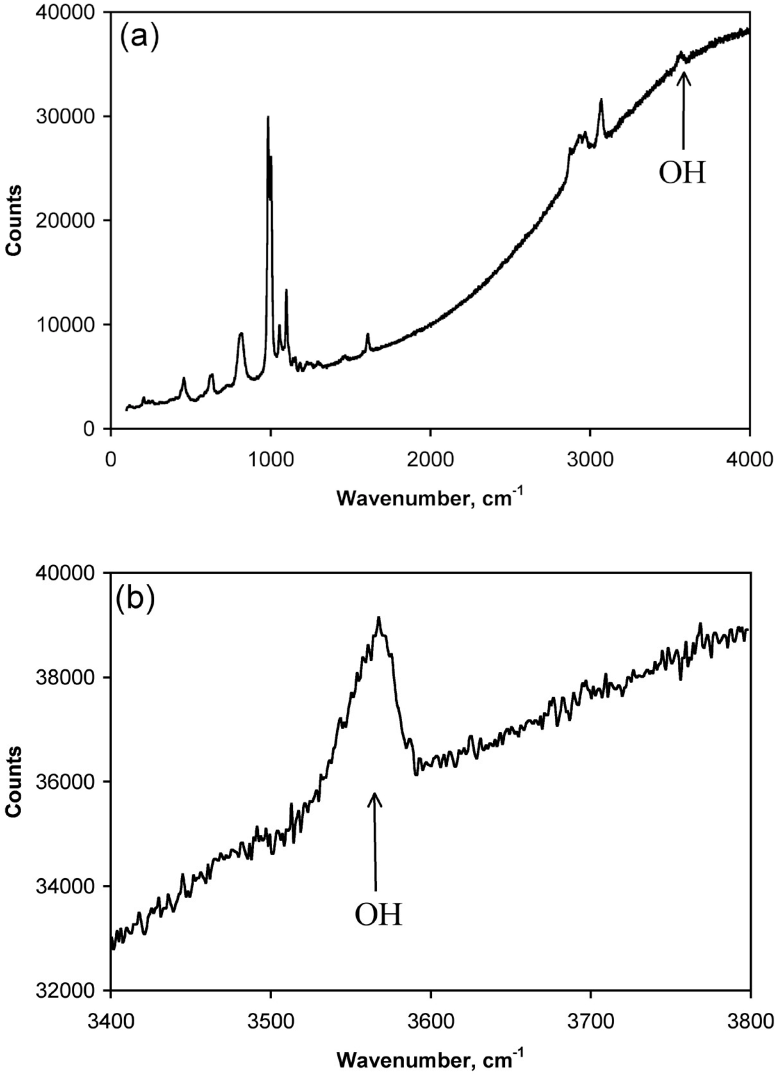

FIG. 6. Laser Raman spectrum of wagnerite-*Ma*5*bc* taken by Yan Gao at the National Gemstone Testing Center, Beijing with the instrument RENISHAW 1000, Ar laser (λ = 514 nm), power 5 mW. (a) Entire spectrum. (b) Expanded spectrum in vicinity of O–H stretching mode.

Beijing, using a Bruker Smart Apex CCD system and graphite-monochromated Mo$K\alpha$ radiation. The unit-cell parameters were obtained by least-squares refinement using 4521 reflections $[I > 2\theta(I)]$, collected in the θ interval from 2.31 to 33.47° (Table 5).

The structure of the Larsemann Hills mineral has been determined using SHELX–90 (Sheldrick 1990) and refined using SHELXL–97 (Sheldrick 1997). The atom coordinates and equivalent isotropic displacement parameters are listed in Table 6 and anisotropic displacement parameters are listed in Table 7. Bond lengths and angles are listed in Table 8. The final R index for the 4521 $[I > 2\sigma(I)]$ reflections was 0.0413. The observed and calculated structure-factors are compiled in Table 9. This table can be ordered from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada. The space group (*Ia*, no. 9) is non-centrosymmetric; no independent tests for absence of a center of symmetry were carried out.

TABLE 4. X-RAY DIFFRACTION POWDER DATA FOR WAGNERITE-*Ma5bc*, WAGNERITE-*Ma2bc*, AND MAGNIOTRIPLITE

	Wagnerite-*Ma5bc*				Wagnerite-*Ma2bc*[3]		Magnio-triplite[4]	
hkl	*d* (Å) calc.[1]	*I*/I_0 calc.[1]	*d*(Å) meas.[2]	*I*/I_o meas.[2]	*d*(Å) meas.	*I*/I_o meas.	*d*(Å) meas.	*I*/I_o meas.
040	7.910	0.02						
031	7.722	0.04						
12$\bar{1}$	7.523	0.02						
130	6.914	0.02						
101	6.225	0.3	6.232	2				
002	5.657	6.3	5.667	4	5.662	7		
051	5.525	2.2	5.526	1				
150	5.208	7.8	5.215	5	5.211	7	5.27	10
200	4.580	1.7	4.587	4				
20$\bar{2}$	4.274	1.3	4.282	3				
15$\bar{2}$	4.225	8.7	4.232	8	4.226	11	4.287	10B
25$\bar{1}$	3.825	4.5	3.828	5	3.827	5		
152	3.531	5.3	3.535	5	3.533	5	3.587	50
251	3.287	58.8	3.295	52	3.287	60	3.324	50
053	3.240	10.9	3.246	12	3.244	5		
202	3.114	67.5	3.121	59	3.114	60	3.162	70
1 10 $\bar{1}$	2.969	100	2.973	100	2.970	100	3.015	80
20$\bar{4}$	2.836	78.3	2.840	83	2.839	85	2.864	100
004	2.8285	5.2						
35$\bar{2}$	2.804	14.4	2.808	17	2.804	11		
0 10 2	2.763	6.6	2.766	11	2.766	3	2.794	60
350	2.750	31.6	2.757	28	2.748	30		
15$\bar{4}$	2.695	20.9	2.700	18	2.697	21	2.728	20
2 10 0	2.604	2.4	2.609	3				
Ma2bc: 33$\bar{1}$					2.555	5		
2 10 $\bar{2}$	2.544	6.1	2.548	6			2.576	30
1 10 $\bar{3}$	2.470	11.8	2.474	11	2.468	15	2.506	20
40$\bar{2}$	2.400	6.5	2.405	7			2.427	20
253					2.363	7		
400	2.290	4.5	2.293	7	2.289	5		
3 10 $\bar{1}$	2.255	2.9			2.251	6		
45$\bar{1}$	2.240	6.7	2.244	13	2.239	6	2.268	20B
1 10 3								
352	2.237	2.9	2.241	9				
2 10 2	2.220	10.2	2.223	9	2.220	6		
							2.223	5
25$\bar{5}$	2.196	15	2.198	15	2.197	11		
45$\bar{3}$	2.165	2.7	2.168	4				
40$\bar{4}$	2.137	4.8	2.140	5	2.137	4		
204	2.127	1.7	2.130	4				
3 10 $\bar{3}$	2.118	1.9	2.120	4			2.149	10
2 10 $\bar{4}$	2.113	6.3	2.115	6	2.114	7		
0 15 1	2.075	4	2.082	4	2.076	13		
3 10 1	2.072	14	2.076	13			2.097	30B
1 15 0	2.057	13	2.060	12	2.058	7		
1 15 $\bar{2}$	1.978	7.4	1.9803	10	1.9782	15	2.000	10
20$\bar{6}$	1.975	6	1.9768	4				
2 15 $\bar{1}$	1.932	2.2	1.9350	3				
402	1.923	11.9	1.9266	12	1.9229	11	1.951	10B
4 10 $\bar{2}$	1.913	4.7	1.9161	7				
422	1.909	1.7	1.9129	2				
1 15 2	1.891	7.3	1.8940	9				
006	1.886	5.5	1.8881	9			1.913	10B
15$\bar{6}$	1.884	9.9	1.8865	13	1.8856	18		
4 10 0	1.855	3.4	1.8579	3	1.8552	4		
2 15 1	1.850	1.1	1.8528	1				
0 15 3	1.842	1.8	1.8442	1	1.8428	3		
35$\bar{6}$	1.812	3.8	1.8140	2	1.8128	5		
2 15 $\bar{3}$	1.807	1.3	1.8087	1				
3 10 $\bar{5}$	1.791	10.5	1.7939	11	1.7918	11		
4 10 $\bar{4}$	1.771	4.3	1.7738	5	1.7720	4	1.779	10B
550	1.760	3.6	1.7641	3	1.7585	11		
3 15 $\bar{2}$	1.749	4.3	1.7528	8				
55$\bar{4}$	1.749	5.4	1.7515	11				
255	1.745	3.5	1.7488	3				
3 15 0	1.736	7.2	1.7390	7				
Ma2bc: 036					1.7368	5		
1 15 $\bar{4}$	1.722	6.5	1.7259	10	1.7233	11	1.745	15
1 10 5	1.7220	7.3	1.7246	15				
453	1.670	13.4	1.6742	8	1.6701	11	1.702	10
4 10 2	1.644	1.5	1.6456	2	1.6440	5		
5 10 $\bar{3}$	1.628	4.3	1.6302	6	1.6275	11		
2 15 3	1.625	1.5	1.6294	4				
1 15 4	1.610	1.1	1.6132	8				
0 20 0	1.5829	2.9						
3 15 2	1.5825	11.6	1.5847	17	1.5831	11	1.607	10B
206	1.578	8.9	1.5808	4				
057	1.566	4.0	1.5702	3	1.5673	4		
60$\bar{4}$	1.564	1.6	1.5685	4				
1 20 $\bar{1}$	1.5565	2.3	1.5616	2			1.579	10B
4 15 $\bar{3}$	1.5561	9.4	1.5581	15	1.5565	18		
552	1.553	11	1.5560	10	1.5526	18		
55$\bar{6}$	1.538	8.1	1.5411	6	1.5388	7	1.552	10B
0 20 2	1.524	6.3	1.5265	8	1.5253	6		
5 10 $\bar{5}$	1.504	4.2	1.5065	4	1.5054	2		
2 20 0	1.496	3.3	1.4983	3				
20$\bar{8}$	1.489	3.2	1.4911	4				
1 10 $\bar{7}$	1.487	3.8	1.4896	5				
2 20 $\bar{2}$	1.484	5.6	1.4868	5	1.4862	7		
3 10 $\bar{7}$	1.470	5.1	1.4725	4	1.4717	7		
65 $\bar{5}$	1.462	4.7	1.4638	7	1.4619	5		
35$\bar{8}$	1.433	6	1.4357	4	1.4341	4		
6 10 $\bar{2}$	1.432	1.2	1.4346	7				
60$\bar{6}$	1.425	7	1.4281	5	1.4253	5		
40$\bar{8}$	1.418	3.0	1.4203	6				
1 20 3	1.415	5	1.4192	9	1.4157	7		
008	1.414	3.3	1.4170	9				
2 20 2	1.411	1.4	1.4151	5				
3 15 $\bar{6}$	1.408	2.7	1.4118	3				
6 10 $\bar{4}$	1.402	6	1.4042	7				
4 10 4	1.397	4.8	1.3989	6	1.3982	3B		
5 15 0	1.3834	7.5	1.3850	11	1.3832	7		
2 20 $\bar{4}$	1.382	4.3	1.3837	6				
5 15 $\bar{4}$	1.378	6	1.3831	5				
3 15 4	1.374	6.8	1.3759	7	1.3747	5		
3 20 1	1.371	1.5	1.3729	2				
257	1.361	6	1.3643	3	1.3616	3		
2 10 $\bar{8}$	1.348	3	1.3500	3	1.3489	3		
1 15 6	1.3436	4	1.3458	4	1.3438	3		
4 15 3	1.339	1.1	1.3403	2				
5 10 3	1.338	1.5	1.3391	2	1.3382	3		
			1.3315	2				
2 15 $\bar{7}$					1.3256	2		
554	1.326	0.9	1.3271	3				

Note: B: broad line. [1] From single-crystal data. [2] Obtained by Fuhui Liao of College of Chemistry and Molecular Engineering at Peking University, with the instrument Bruker D8 ADVANCE using the capillary method and Cu$K\alpha_1$ radiation (λ = 1.5406 Å). Divergence slit: 2 mm. PSD fast-scan from 10.000° to 72.878° with step of 0.0144 and step time 70 s at 25°C. [3] Santa Fe Mountain, Colorado, U.S.A. (Sheridan *et al.* 1976). [4] Massif des Albères, France (Fontan 1981). Lines reported as 321 and 406 are presumed to be $\bar{3}$21 and $\bar{4}$06, corresponding to 1 10 $\bar{3}$ and 60$\bar{4}$, respectively, in the table.

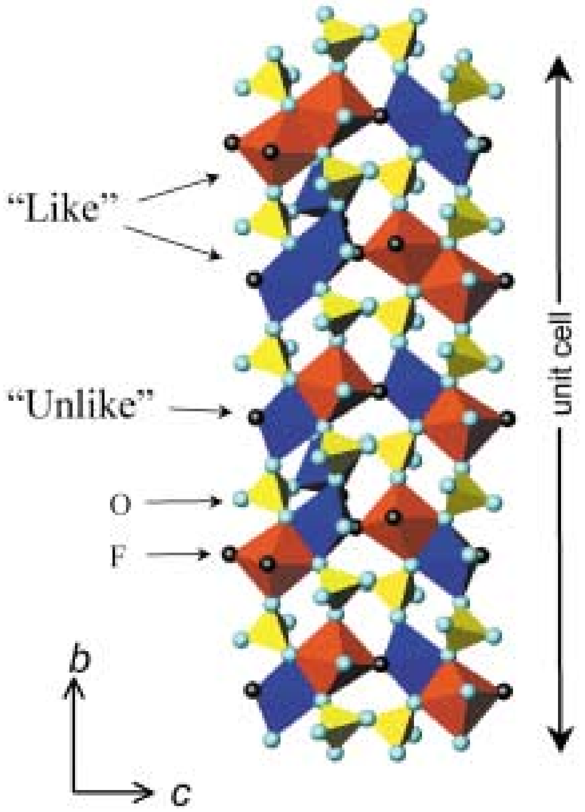

FIG. 7. Diagram of one of two *b–c* sections of the wagnerite-*Ma*5*bc* structure. Red: $MgO_4(F,OH)_2$ octahedra, blue: $MgO_4(F,OH)$ trigonal bipyramids, turquoise spheres: O, black: (F,OH); the other section is similar. "Like" and "unlike" refer to the edge-shared linkages (see text). Comparable *b–c* sections of wagnerite-*Ma*2*bc* show either all "like" or all "unlike" linkages.

TABLE 5. DATA ON THE CRYSTAL AND STRUCTURE REFINEMENT OF WAGNERITE-*Ma*5*bc*

Empirical formula	$Mg_2(PO_4)(F,OH)$	
Formula weight	165.236	
Temperature	293(2) K	
Wavelength	0.71073 Å (Mo*K*α)	
Crystal system	Monoclinic	
Space group	*Ia*	
Unit-cell dimensions	*a* 9.645(2) Å	α 90°
	b 31.659(6) Å	β 108.26(3)°
	c 11.914(2) Å	γ 90°
Volume	3455(1) $Å^3$	
Z	40	
Density (calculated)	3.177 g/cm^3	
Absorption coefficient	1.067 mm^{-1}	
F(000)	3200	
Crystal size	0.2 × 0.2 × 0.2 mm^3	
Theta range for data collection	2.31 to 33.47°	
Completeness to theta = 33.47°	94.0 %	
Index ranges	$-14 \le h \le 12$, $-48 \le k \le 41$, $-17 \le l \le 18$	
Reflections collected	14181	
Independent reflections	10580 [R(int) = 0.0242]	
Reflections [$I > 2\sigma(I)$]	4521	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10580 / 2 / 721	
Goodness-of-fit on F^2	0.795	
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0413$, $wR_2 = 0.1061$	
R indices (all data)	$R_1 = 0.0888$, $wR_2 = 0.1288$	
Absolute structure-parameter	0.14(17)	
Largest diff. peak and hole	1.739 and –1.561 $e.Å^{-3}$	

DESCRIPTION OF THE STRUCTURE AND COMPARISON WITH RELATED STRUCTURES

The structures of magniotriplite and of the two polytypes of wagnerite are frameworks built up of fairly regular PO_4 tetrahedra and distorted $MgO_4(F,OH)_n$ polyhedra (Coda *et al.* 1967, Tadini 1981, Huminicki & Hawthorne 2002); in wagnerite, the latter are $MgO_4(F,OH)_2$ octahedra and $MgO_4(F,OH)$ trigonal bipyramids in equal amounts. The structures of wagnerite-*Ma*5*bc* and wagnerite-*Ma*2*bc* differ in the linkages between these polyhedra. In wagnerite-*Ma*2*bc*, each of the four octahedra shares two F–O edges and one O–O edge with other octahedra, whereas each of the four trigonal bipyramids shares one O–O edge with a trigonal bipyramid; these O–O edges can be called "like linkages" (Figs. 7, 8). There is one exception: *M*4 shares one O–O edge with the trigonal bipyramid *M*3, *i.e.*, an "unlike linkage". The situation is similar for the 10 octahedra and trigonal bipyramids in wagnerite-*Ma*5*bc*, except that there are four "unlike linkages": *M*12, *M*14, *M*15 and *M*20 octahedra share one O–O edge with the trigonal bipyramids *M*1, *M*7, *M*2 and *M*6, respectively, *i.e.*, the proportion of "unlike linkages" is 40% in

TABLE 6. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR WAGNERITE-*Ma5bc*

Atom	*x*	*y*	*z*	U(eq)	Atom	*x*	*y*	*z*	U(eq)
Mg(1)	0.4443(3)	0.2227(1)	0.1170(2)	0.006(1)	O(11)	0.4110(7)	0.0843(2)	0.1322(5)	0.012(1)
Mg(2)	0.3471(3)	0.0223(1)	0.7797(2)	0.008(1)	O(12)	0.5949(7)	0.1119(2)	0.0334(5)	0.013(1)
Mg(3)	0.7026(3)	0.2427(1)	0.5129(2)	0.006(1)	O(13)	0.4120(6)	0.1430(2)	0.5820(5)	0.010(1)
Mg(4)	0.2050(3)	0.1427(1)	0.0097(2)	0.006(1)	O(14)	0.6402(7)	0.1683(2)	0.7366(5)	0.012(1)
Mg(5)	0.8493(3)	0.1216(1)	0.2900(3)	0.010(1)	O(15)	0.5738(6)	0.1936(2)	0.5252(5)	0.010(1)
Mg(6)	0.3520(3)	0.0772(1)	0.2841(2)	0.009(1)	O(16)	0.4211(7)	0.2161(2)	0.6527(4)	0.008(1)
Mg(7)	0.0946(3)	0.0430(1)	0.3879(3)	0.010(1)	O(17)	-0.0835(7)	0.2595(2)	0.5841(5)	0.012(1)
Mg(8)	0.0876(3)	0.0573(1)	0.8867(2)	0.006(1)	O(18)	0.1371(7)	0.2307(2)	0.7403(5)	0.011(1)
Mg(9)	0.5892(3)	0.1564(1)	0.3903(2)	0.008(1)	O(19)	0.0859(7)	0.2107(2)	0.5278(6)	0.014(1)
Mg(10)	0.9469(3)	0.1782(1)	1.1120(3)	0.010(1)	O(20)	-0.0857(6)	0.1849(2)	0.6397(5)	0.009(1)
Mg(11)	0.6881(3)	0.0517(1)	0.0042(2)	0.005(1)	O(21)	0.8752(6)	0.0400(2)	0.8180(5)	0.007(1)
Mg(12)	0.3607(3)	0.2211(1)	0.8059(2)	0.006(1)	O(22)	0.6613(7)	0.0709(2)	0.6572(5)	0.011(1)
Mg(13)	0.1895(3)	0.1531(1)	0.5075(2)	0.006(1)	O(23)	0.7001(6)	0.0895(2)	0.8673(5)	0.010(1)
Mg(14)	-0.3042(3)	0.0476(1)	0.5060(2)	0.006(1)	O(24)	0.8775(6)	0.1146(2)	0.7615(5)	0.010(1)
Mg(15)	0.4341(3)	0.0791(1)	0.5937(3)	0.013(1)	O(25)	0.3677(6)	0.0836(2)	0.7432(5)	0.013(1)
Mg(16)	0.8620(3)	0.1780(1)	0.8003(2)	0.007(1)	O(26)	0.2137(6)	0.1057(2)	0.8710(5)	0.009(1)
Mg(17)	0.6068(3)	0.1481(1)	0.8936(2)	0.006(1)	O(27)	0.1566(6)	0.1314(2)	0.6622(5)	0.007(1)
Mg(18)	-0.0670(3)	0.1226(1)	0.6011(3)	0.011(1)	O(28)	0.3834(6)	0.1576(2)	0.8232(5)	0.008(1)
Mg(19)	0.1033(3)	0.2483(1)	0.3939(2)	0.007(1)	O(29)	0.3768(7)	0.2152(2)	0.2656(5)	0.007(1)
Mg(20)	0.4292(3)	0.0217(1)	0.0912(3)	0.011(1)	O(30)	0.1961(6)	0.1891(2)	0.3650(5)	0.007(1)
P(1)	0.0144(2)	0.0196(1)	0.6221(2)	0.007(1)	O(31)	0.3766(7)	0.1402(2)	0.3190(5)	0.008(1)
P(2)	0.0136(2)	0.0803(1)	0.1237(2)	0.007(1)	O(32)	0.1651(7)	0.1717(2)	0.1523(5)	0.013(1)
P(3)	0.5165(2)	0.1208(1)	0.1228(2)	0.007(1)	O(33)	0.6557(6)	0.0314(2)	0.1593(5)	0.011(1)
P(4)	0.5138(2)	0.1805(1)	0.6250(2)	0.006(1)	O(34)	0.7095(7)	0.0083(2)	0.3692(5)	0.012(1)
P(5)	0.0163(2)	0.2208(1)	0.6234(2)	0.007(1)	O(35)	0.8715(6)	-0.0151(2)	0.2484(5)	0.014(1)
P(6)	0.7753(2)	0.0792(1)	0.7743(2)	0.007(1)	O(36)	0.8796(7)	0.0590(2)	0.3198(5)	0.010(1)
P(7)	0.2790(2)	0.1198(1)	0.7735(2)	0.008(1)	O(37)	0.8814(7)	0.2580(2)	0.3208(5)	0.008(1)
P(8)	0.2757(2)	0.1790(1)	0.2748(2)	0.007(1)	O(38)	0.7068(7)	0.2075(2)	0.3689(5)	0.008(1)
P(9)	0.7773(2)	0.0208(1)	0.2728(2)	0.008(1)	O(39)	0.8691(6)	0.1837(2)	0.2516(5)	0.011(1)
P(10)	0.7789(2)	0.2200(1)	0.2750(2)	0.007(1)	O(40)	0.6610(7)	0.2302(2)	0.1587(5)	0.012(1)
O(1)	-0.0821(7)	0.0587(2)	0.5850(6)	0.013(1)	F(1)	0.4802(5)	0.0318(1)	0.9413(4)	0.005(1)
O(2)	0.1310(7)	0.0290(2)	0.7428(5)	0.012(1)	F(2)	0.5663(6)	0.2847(1)	0.4205(4)	0.015(1)
O(3)	-0.0848(7)	-0.0173(2)	0.6362(6)	0.015(1)	F(3)	0.2263(5)	0.0149(1)	0.9805(4)	0.008(1)
O(4)	0.0885(7)	0.0087(2)	0.5309(6)	0.017(1)	F(4)	0.0651(6)	0.1834(1)	-0.0843(5)	0.018(1)
O(5)	-0.0863(7)	0.0431(2)	0.0815(5)	0.012(1)	F(5)	0.8081(6)	0.1702(2)	0.9562(4)	0.026(1)
O(6)	0.1360(7)	0.0682(2)	0.2382(5)	0.012(1)	F(6)	0.3063(6)	0.2299(2)	-0.0416(4)	0.017(1)
O(7)	-0.0753(6)	0.1171(2)	0.1498(5)	0.010(1)	F(7)	0.4909(7)	0.0706(2)	0.4366(5)	0.044(2)
O(8)	0.0774(7)	0.0931(2)	0.0269(6)	0.015(1)	F(8)	0.9844(5)	0.1303(1)	0.4431(4)	0.021(1)
O(9)	0.4204(6)	0.1601(2)	0.0862(5)	0.011(1)	F(9)	0.2347(6)	0.0840(2)	0.4722(4)	0.044(2)
O(10)	0.6323(6)	0.1288(2)	0.2461(5)	0.008(1)	F(10)	0.7381(6)	0.1180(1)	0.4783(4)	0.051(2)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

wagnerite-*Ma*5*bc versus* 25% in wagnerite-*Ma*2*bc*. This difference is evident in chains parallel to *c*, of which 60% are comprised of "unlike linkages" in wagnerite-*Ma*5*bc* (Fig. 7) *versus* 50% in wagnerite-*Ma*2*bc*, and in chains parallel to *b*, in which 20% of the linkages are "unlike" in wagnerite-*Ma*5bc *versus* 0% in wagnerite-*Ma*2*bc* (Fig. 8).

The proportion of "unlike" to "like" linkages is related to the position of (F,OH) atoms (*e.g.*, Fig. 8). The (F,OH) positions are nearly coplanar, in planes parallel to (001) in which configurations of these positions are either shaped more like a V (configuration 1) or more like a U (configuration 2) (Fig. 9). The sequence of Us and Vs in the *b* direction differs for the two minerals: in wagnerite-*Ma*2*bc*, there is a simple alternation VUVUVU or 121212, whereas in wagnerite-*Ma*5*bc*, the succession is VUVVU or 12112, and the ...VV... (...11...) sequence corresponds to the "unlike" linkage (Fig. 8). Moreover, the V and U configurations are evident in the (F,OH) positions for magniotriplite if one considers the sequences F1–F2–F1–F2 (green-red-green-red) and F2–F1–F2–F1 (red-green-red-green) in the *a* direction (white lines and circles in Fig. 9). This figure is another way to illustrate Tadini's (1981, p. 680) hypothesis for explaining the difference between magniotriplite and wagnerite-*Ma*2*bc* as the result of order–disorder in the arrangement of (F,OH) atoms. Magniotriplite can be viewed as having a disordered succession of Vs and Us (configurations 1 and 2) in the *b* direction, so that, on the average, the *F*1 and *F*2 sites appear to be 50% occupied. The presence of the 12112 succession in wagnerite-*Ma*5*bc*, together with the 1211212 and 121121212 successions in wagnerite-*Ma*7*bc* and wagnerite-*Ma*9*bc*, respectively (Chopin *et al.* 2003), extends Tadini's (1981) hypothesis to include more than one type of order at the (F,OH) positions.

TABLE 7. ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR WAGNERITE-*Ma*5*bc*

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mg(1)	0.012(2)	0.005(1)	0.003(1)	-0.001(1)	0.003(1)	0.000(1)
Mg(2)	0.002(1)	0.009(1)	0.012(1)	0.000(1)	0.001(1)	0.001(1)
Mg(3)	0.009(1)	0.005(1)	0.005(1)	0.000(1)	0.003(1)	-0.001(1)
Mg(4)	0.004(1)	0.006(1)	0.007(1)	-0.001(1)	0.001(1)	0.000(1)
Mg(5)	0.006(1)	0.009(1)	0.015(1)	-0.001(1)	0.004(1)	0.000(1)
Mg(6)	0.004(1)	0.008(1)	0.014(1)	0.001(1)	0.002(1)	-0.001(1)
Mg(7)	0.009(1)	0.012(1)	0.008(1)	0.003(1)	0.002(1)	0.004(1)
Mg(8)	0.002(1)	0.008(1)	0.009(1)	-0.001(1)	0.002(1)	0.000(1)
Mg(9)	0.007(1)	0.012(1)	0.004(1)	-0.003(1)	0.002(1)	-0.003(1)
Mg(10)	0.014(2)	0.006(1)	0.009(1)	0.000(1)	0.003(1)	0.002(1)
Mg(11)	0.002(1)	0.008(1)	0.006(1)	0.002(1)	0.003(1)	-0.002(1)
Mg(12)	0.007(1)	0.006(1)	0.006(1)	0.001(1)	0.004(1)	0.000(1)
Mg(13)	0.001(1)	0.011(1)	0.006(1)	0.003(1)	0.003(1)	0.001(1)
Mg(14)	0.004(1)	0.010(1)	0.006(1)	-0.003(1)	0.003(1)	-0.003(1)
Mg(15)	0.015(2)	0.007(1)	0.021(2)	-0.001(1)	0.012(1)	0.001(1)
Mg(16)	0.006(1)	0.007(1)	0.007(1)	-0.001(1)	0.001(1)	-0.002(1)
Mg(17)	0.007(1)	0.006(1)	0.004(1)	0.000(1)	0.001(1)	0.001(1)
Mg(18)	0.012(2)	0.005(1)	0.018(2)	-0.001(1)	0.008(1)	0.001(1)
Mg(19)	0.008(1)	0.008(1)	0.003(1)	0.000(1)	-0.001(1)	0.002(1)
Mg(20)	0.013(2)	0.007(1)	0.014(2)	0.001(1)	0.007(1)	0.000(1)
P(1)	0.007(1)	0.008(1)	0.006(1)	0.000(1)	0.003(1)	0.001(1)
P(2)	0.007(1)	0.007(1)	0.008(1)	-0.001(1)	0.005(1)	0.000(1)
P(3)	0.007(1)	0.008(1)	0.008(1)	-0.001(1)	0.005(1)	-0.001(1)
P(4)	0.006(1)	0.006(1)	0.007(1)	-0.001(1)	0.005(1)	0.000(1)
P(5)	0.008(1)	0.006(1)	0.006(1)	-0.001(1)	0.003(1)	0.000(1)
P(6)	0.008(1)	0.008(1)	0.007(1)	0.001(1)	0.002(1)	0.000(1)
P(7)	0.008(1)	0.007(1)	0.007(1)	0.001(1)	0.000(1)	-0.001(1)
P(8)	0.006(1)	0.005(1)	0.008(1)	0.000(1)	0.002(1)	0.000(1)
P(9)	0.008(1)	0.008(1)	0.006(1)	0.001(1)	0.001(1)	-0.001(1)
P(10)	0.009(1)	0.006(1)	0.006(1)	0.001(1)	0.002(1)	0.000(1)
O(1)	0.009(3)	0.015(3)	0.014(3)	0.005(2)	0.003(2)	0.002(2)
O(2)	0.011(3)	0.015(3)	0.009(3)	-0.003(2)	0.004(2)	0.001(2)
O(3)	0.017(3)	0.012(3)	0.022(3)	-0.001(2)	0.013(3)	-0.008(2)
O(4)	0.021(3)	0.015(3)	0.018(3)	0.003(2)	0.010(3)	0.007(3)
O(5)	0.007(3)	0.015(3)	0.015(3)	-0.008(2)	0.005(2)	-0.005(2)
O(6)	0.013(3)	0.011(3)	0.011(3)	0.009(2)	0.002(2)	0.000(2)
O(7)	0.016(3)	0.013(3)	0.003(2)	-0.003(2)	0.007(2)	0.001(2)
O(8)	0.018(3)	0.011(3)	0.015(3)	-0.001(2)	0.004(2)	-0.009(2)
O(9)	0.006(3)	0.015(3)	0.012(2)	0.003(2)	0.002(2)	0.007(2)
O(10)	0.011(3)	0.008(3)	0.005(2)	-0.004(2)	0.001(2)	-0.001(2)
O(11)	0.010(3)	0.010(3)	0.017(3)	-0.001(2)	0.005(2)	-0.001(2)
O(12)	0.017(3)	0.010(3)	0.010(3)	0.000(2)	0.002(2)	0.004(2)
O(13)	0.005(3)	0.016(3)	0.010(2)	-0.007(2)	0.002(2)	-0.001(2)
O(14)	0.011(3)	0.011(3)	0.016(3)	0.006(2)	0.005(2)	0.002(2)
O(15)	0.010(3)	0.009(2)	0.011(3)	-0.001(2)	0.002(2)	-0.006(2)
O(16)	0.018(3)	0.008(3)	0.000(2)	0.000(2)	0.008(2)	0.000(2)
O(17)	0.009(3)	0.015(3)	0.010(2)	0.004(2)	0.002(2)	0.005(2)
O(18)	0.012(3)	0.011(3)	0.009(3)	-0.003(2)	0.004(2)	0.000(2)
O(19)	0.021(3)	0.007(2)	0.014(3)	-0.001(2)	0.007(3)	0.003(2)
O(20)	0.013(3)	0.007(2)	0.011(3)	-0.001(2)	0.008(2)	0.000(2)
O(21)	0.008(3)	0.002(2)	0.013(2)	-0.003(2)	0.004(2)	-0.001(2)
O(22)	0.007(3)	0.018(3)	0.008(3)	0.000(2)	-0.002(2)	0.000(2)
O(23)	0.007(3)	0.017(3)	0.007(2)	0.002(2)	0.006(2)	-0.002(2)
O(24)	0.008(3)	0.010(3)	0.012(3)	0.001(2)	0.005(2)	-0.001(2)
O(25)	0.006(3)	0.007(3)	0.026(3)	0.002(2)	0.004(2)	0.002(2)
O(26)	0.007(3)	0.015(3)	0.006(2)	0.001(2)	0.006(2)	0.005(2)
O(27)	0.002(2)	0.015(3)	0.003(2)	-0.004(2)	-0.002(2)	0.004(2)
O(28)	0.012(3)	0.002(2)	0.007(2)	0.005(2)	0.000(2)	-0.002(2)
O(29)	0.009(3)	0.007(2)	0.007(3)	-0.002(2)	0.005(2)	-0.002(2)
O(30)	0.003(2)	0.011(2)	0.012(3)	0.002(2)	0.008(2)	-0.001(2)
O(31)	0.015(3)	0.001(2)	0.009(2)	-0.001(2)	0.003(2)	-0.002(2)
O(32)	0.006(3)	0.016(3)	0.015(3)	-0.001(2)	0.000(2)	0.000(2)
O(33)	0.009(3)	0.017(3)	0.006(2)	-0.004(2)	0.000(2)	0.002(2)
O(34)	0.011(3)	0.019(3)	0.009(3)	-0.002(2)	0.008(2)	-0.004(2)
O(35)	0.004(2)	0.011(3)	0.024(3)	0.004(2)	0.002(2)	0.007(2)
O(36)	0.015(3)	0.002(2)	0.013(2)	0.002(2)	0.006(2)	0.001(2)
O(37)	0.014(3)	0.003(2)	0.006(2)	0.002(2)	0.003(2)	-0.002(2)
O(38)	0.011(3)	0.012(3)	0.003(2)	-0.002(2)	0.006(2)	0.000(2)
O(39)	0.008(3)	0.004(2)	0.023(3)	0.001(2)	0.005(2)	-0.001(2)
O(40)	0.008(3)	0.017(3)	0.007(3)	-0.003(2)	-0.001(2)	-0.003(2)
F(1)	0.000(2)	0.002(2)	0.012(2)	-0.003(1)	0.002(1)	0.002(1)
F(2)	0.013(2)	0.015(2)	0.018(2)	0.008(2)	0.007(2)	-0.004(2)
F(3)	0.006(2)	0.007(2)	0.006(2)	-0.005(1)	-0.004(2)	0.000(1)
F(4)	0.009(2)	0.016(2)	0.028(3)	0.013(2)	0.007(2)	-0.006(2)
F(5)	0.032(3)	0.032(3)	0.012(2)	0.001(2)	0.005(2)	-0.011(2)
F(6)	0.018(3)	0.028(3)	0.007(2)	0.002(2)	0.009(2)	0.004(2)
F(7)	0.064(4)	0.017(2)	0.028(3)	-0.007(2)	-0.021(2)	0.016(2)
F(8)	0.030(3)	0.012(2)	0.012(2)	0.002(2)	-0.007(2)	-0.007(2)
F(9)	0.063(4)	0.023(2)	0.024(2)	0.010(2)	-0.018(2)	-0.030(2)
F(10)	0.081(4)	0.021(2)	0.020(2)	-0.015(2)	-0.028(2)	0.036(2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2 a^{*2} U_{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U_{12}]$

In contrast, F in the synthetic triplite and zwieselite end-members fully occupies only one site that is located midway between the *F*1 and *F*2 sites in magniotriplite and naturally occurring triplite (Fig. 9) (Rea & Kostiner 1972, Yakubovich *et al.* 1978), *i.e.*, these are ordered *Mabc* structures. A single, fully occupied F site is also characteristic of the synthetic end-member Cd and Cu compounds, which Rea & Kostiner (1974, 1976) found to be isostructural with triplite and zwieselite.

In triplite-group minerals, the (F,OH) sites are located at a "normal" distance from three cation sites and at a very long distance from a fourth; *e.g.*, 1.88–2.32 Å and 2.91–3.06 Å, respectively, in magniotriplite (Tadini 1981), whereas in end-member triplite and zwieselite, the single F sites are situated at 2.04–2.14 Å from two cation sites and 2.37–2.64 Å from two others. The distance between the *F*1 and *F*2 sites decreases linearly with average ionic ratio except for synthetic Fe_2PO_4F (Fig. 10a). In other words, shift of F to the single site eliminates one of the three M^{2+}–F bonds of "normal" length. Although the average M^{2+}–F distances decrease slightly with increasing ionic radius, the minimum M^{2+}–F distance increases with this average (Fig. 10b), suggesting that ionic size could be the main control on F position. Synthetic end-member zwieselite is an exception to these trends. This could be a result of Fe–F avoidance, a phenomenon well recognized in silicates (*e.g.*, Munoz 1984), whereby Fe–F bonds are energetically unfavorable. A role for Fe–F avoidance in the crystal chemistry of triplite-group minerals is also indicated by fractionation of elements between coexisting triplite-group minerals and triphylite-group minerals [Li(Fe,Mn)PO_4]: Fe is markedly fractionated into the triphylite-group minerals, whereas Mg and Mn are fractionated into the triplite group (Keller *et al.* 1994).

The above relationships cannot be extrapolated to the ordered polytypes of wagnerite. In wagnerite-*Ma*2*bc*, the *F*1–*F*2 distance would be only ~1Å (estimated from data of Coda *et al.* 1967) if both positions were occupied as in magniotriplite, *i.e.*, about the same distance

TABLE 8. BOND LENGTHS [Å] AND ANGLES [°] FOR WAGNERITE-*Ma5bc*

Mg(1)	F(6)	O(40)	O(9)	O(16)#1	O(29)					120.8(2)	O(2)
	1.954(5)	2.005(7)	2.015(7)	2.011(6)	2.083(6)				90.9(3)	89.2(2)	O(25)
O(29)	122.4(3)	112.4(3)	89.6(2)	81.1(2)				79.2(3)	114.5(3)	123.6(3)	O(3)#3
O(16)#1	90.3(2)	90.6(3)	166.4(3)				93.4(3)	166.8(3)	102.1(3)	85.9(2)	O(21)#4
O(9)	86.2(2)	102.3(3)				2.024(6)	2.021 (7)	2.014(7)	2.002(7)	1.974(5)	
O(40)	124.6(3)					O(21)#4	O(3)#3	O(25)	O(2)	F(1)	Mg(2)
Mg(3)	F(2)	O(15)	O(17)#6	O(38)	O(40)#7					96.4(3)	O(26)#2
	1.948(6)	2.026(6)	2.040(7)	2.058(6)	2.086(7)				79.6(2)	103.7(3)	O(8)
O(40)#7	85.4(3)	88.4(3)	88.8(3)	167.5(3)				135.6(3)	102.7(3)	119.8(3)	O(9)
O(38)	94.9(3)	79.4(2)	102.0(3)				86.5(3)	89.2(3)	168.7(3)	84.5(3)	O(32)
O(17)#6	118.2(3)	137.2(3)				2.071(7)	2.065(7)	2.045(6)	2.048(6)	1.947(6)	
O(15)	104.1(3)					O(32)	O(9)	O(8)	O(26)#2	F(4)	Mg(4)
Mg(5)	F(8)	O(10)	O(7)#6	O(36)	O(39)					127.4(3)	O(6)
	1.901(5)	2.004(7)	2.025(6)	2.019(6)	2.041(6)				87.8(3)	90.5(3)	O(35)#4
O(39)	89.5(2)	89.7(3)	78.4(2)	165.2(3)				167.9(3)	103.9(3)	84.9(2)	O(31)
O(36)	87.5(2)	103.9(3)	90.4(3)				91.5(3)	81.5(3)	108.9(3)	122.8(3)	O(11)
O(7)#6	119.1(3)	114.1(3)				2.073(7)	2.037(6)	2.034(6)	2.001(7)	1.902(6)	
O(10)	125.4(3)					O(11)	O(31)	O(35)#4	O(6)	F(7)	Mg(6)
Mg(7)	F(9)	O(34)#4	O(36)#9	O(4)	O(6)					104.4(2)	O(26)
	1.914(5)	2.018(7)	2.040(7)	2.038(7)	2.104(6)				137.4(3)	117.6(2)	O(21)#9
O(6)	84.1(3)	87.4(3)	90.5(3)	167.0(3)				100.2(3)	80.7(2)	96.4(3)	O(8)#5
O(4)	97.1(3)	79.8(3)	99.9(3)				168.7(3)	89.4(3)	88.2(3)	84.2(2)	O(2)
O(36)#9	120.3(3)	132.8(3)				2.090(6)	2.046(7)	2.029(6)	2.000(6)	1.976(5)	
O(34)#4	106.4(3)					O(2)	O(8)#5	O(21)#9	O(26)	F(3)	Mg(8)
Mg(9)	F(10)	O(31)	O(38)	O(15)	O(10)					87.0(3)	O(17)#10
	1.923(6)	2.023(7)	2.036(6)	2.035(6)	2.083(6)				103.1(3)	124.9(3)	O(32)#11
O(10)	82.9(2)	89.2(3)	88.1(3)	167.8(3)				91.5(3)	164.0(3)	90.0(3)	O(7)#11
O(15)	99.3(3)	99.4(3)	79.7(2)				78.8(2)	116.0(3)	88.8(3)	118.3(3)	O(39)#5
O(38)	102.7(3)	132.8(3)				2.035(7)	2.010(7)	2.017(7)	2.007(7)	1.934(6)	
O(31)	123.7(3)					O(39)#5	O(7)#11	O(32)#11	O(17)#10	F(5)	Mg(10)
Mg(11)	F(1)#2	O(23)#2	O(33)	O(5)#6	F(3)#12	O(12)					
	2.010(5)	2.054(6)	2.072(6)	2.098(7)	2.176(5)	2.179(7)				78.0(2)	O(28)
O(12)	85.4(2)	75.4(2)	86.8(3)	117.8(3)	164.4(3)				104.5(3)	161.2(3)	O(18)
F(3)#12	80.59(17)	114.0(2)	83.8(2)	74.7(2)				77.9(2)	95.4(2)	83.3(2)	F(6)#5
O(5)#6	154.0(2)	96.7(3)	89.6(3)				97.4(2)	85.1(3)	165.4(3)	96.5(2)	O(29)#7
O(33)	79.8(2)	162.0(3)				79.2(2)	176.4(3)	102.9(3)	87.9(2)	95.8(2)	O(16)
O(23)#2	100.6(2)				2.088(6)	2.090(6)	2.062(5)	2.073(7)	2.026(6)	2.033(6)	
					O(16)	O(29)#7	F(6)#5	O(18)	O(28)	F(2)#7	Mg(12)
Mg(13)	F(8)#9	O(30)	O(27)	O(13)	O(19)	F(9)					
	2.017(5)	2.063(6)	2.082(6)	2.075(7)	2.131(6)	2.295(6)				79.9(3)	O(22)#9
F(9)	79.0(2)	108.6(2)	86.5(2)	72.6(2)	163.8(3)				163.7(3)	100.8(3)	O(34)#9
O(19)	84.9(2)	75.9(3)	88.5(3)	122.8(3)				98.4(3)	88.3(3)	149.3(3)	O(1)
O(13)	150.1(3)	98.2(2)	89.7(2)				123.7(3)	76.2(3)	87.6(3)	84.4(3)	O(4)#4
O(27)	79.4(2)	164.4(3)				160.8(3)	72.5(2)	114.0(2)	82.2(2)	77.8(2)	F(10)#9
O(30)	99.4(2)				2.307(6)	2.129(7)	2.081(7)	2.087(6)	2.068(7)	2.023(6)	
					F(10)#9	O(4)#4	O(1)	O(34)#9	O(22)#9	F(7)#9	Mg(14)

as in magniotriplite (Fig. 10a). The minimum Mg–F distances are 1.951 and 1.901 Å in wagnerite-*Ma2bc* and wagnerite-*Ma5bc*, respectively, *i.e.*, similar to those in magniotriplite despite the smaller ionic radius of Mg (Fig. 10b).

STABILITY RELATIONSHIPS OF THE Mg_2PO_4F MINERALS

Factors stabilizing the various polytypes of wagnerite and magniotriplite could include compositional variables, P–T conditions, kinetics or some combination of

TABLE 8. BOND LENGTHS [Å] AND ANGLES [°] FOR WAGNERITE-*Ma5bc*

Mg(15)	F(9)	O(13)	O(3)#3	O(25)	O(22)	F(7)					
	2.018(6)	2.034(7)	2.042(7)	2.078(7)	2.098(7)	2.126(7)				78.5(2)	O(37)#7
F(7)	80.1(2)	96.6(2)	99.5(3)	175.7(3)	76.9(3)				103.7(3)	160.1(3)	O(14)
O(22)	157.0(3)	102.8(3)	87.6(3)	105.5(3)				85.1(3)	167.3(3)	96.5(2)	O(24)
O(25)	97.4(3)	86.3(3)	77.2(3)				98.1(2)	78.0(2)	92.8(2)	82.2(2)	F(5)
O(3)#3	96.4(3)	162.5(3)				178.9(3)	81.1(2)	101.2(3)	88.1(3)	98.6(3)	O(20)#6
O(13)	79.6(2)				2.137(6)	2.094(6)	2.073(7)	2.056(7)	2.043(6)	2.017(6)	
					O(20)#6	F(5)	O(24)	O(14)	O(37)#7	F(4)#11	Mg(16)
Mg(17)	F(5)	O(12)#5	O(28)	O(14)	O(23)	F(2)#7					
	1.977(6)	2.054(7)	2.075(7)	2.097(6)	2.127(7)	2.207(5)				80.5(2)	O(1)
F(2)#7	78.5(2)	111.3(2)	73.1(2)	85.3(2)	164.8(3)				166.4(3)	96.1(2)	O(20)
O(23)	87.4(2)	76.5(2)	120.0(3)	86.8(3)				86.9(3)	101.8(3)	155.2(3)	O(27)
O(14)	79.6(3)	163.3(3)	91.4(2)				77.7(2)	98.7(2)	93.5(2)	77.5(2)	F(8)#9
O(28)	150.9(3)	95.4(3)				179.3(2)	103.0(3)	81.3(2)	86.4(3)	101.8(3)	O(24)#9
O(12)#5	100.9(3)				2.154(6)	2.107(5)	2.068(6)	2.046(6)	2.032(7)	1.993(6)	
					O(24)#9	F(8)#9	O(27)	O(20)	O(1)	F(10)#9	Mg(18)
Mg(19)	F(6)#7	O(19)	O(37)#9	O(18)#1	O(30)	F(4)#7					
	1.989(6)	2.039(7)	2.066(7)	2.066(6)	2.152(6)	2.221(5)				83.87(19)	F(1)#2
F(4)#7	78.2(2)	114.8(2)	73.5(2)	82.4(2)	163.6(3)				98.2(2)	79.5(2)	O(5)#3
O(30)	87.5(2)	76.0(2)	119.4(2)	87.1(3)				164.1(3)	96.8(2)	96.9(2)	O(11)
O(18)#1	79.7(2)	162.8(3)	90.5(3)				85.6(3)	102.5(3)	78.8(2)	162.7(3)	O(33)
O(37)#9	151.1(2)	95.1(3)				101.6(3)	79.7(2)	85.2(3)	176.4(3)	95.7(2)	O(35)#4
O(19)	102.3(3)				2.125(7)	2.101(7)	2.062(7)	2.055(6)	2.021(5)	1.999(5)	
					O(35)#4	O(33)	O(11)	O(5)#3	F(1)#2	F(3)#2	Mg(20)
P(1)	O(4)	O(1)	O(2)	O(3)						109.0(3)	O(8)
	1.516(7)	1.527(7)	1.552(7)	1.552(6)					109.5(3)	108.8(4)	O(7)
O(3)	110.5(4)	107.5(4)	109.7(4)					109.2(3)	110.9(4)	109.5(4)	O(6)
O(2)	109.9(4)	108.2(4)					1.546(6)	1.538(6)	1.521(7)	1.504(6)	
O(1)	111.0(4)						O(6)	O(7)	O(8)	O(5)	P(2)
P(3)	O(12)	O(9)	O(11)	O(10)						108.1(3)	O(13)
	1.514(6)	1.531(6)	1.567(7)	1.562(6)					106.6(3)	110.7(3)	O(16)
O(10)	108.9(3)	109.1(3)	110.0(3)					110.7(3)	110.3(3)	110.3(3)	O(14)
O(11)	113.0(3)	105.8(4)					1.544(6)	1.537(6)	1.523(6)	1.534(6)	
O(9)	110.1(4)						O(14)	O(16)	O(13)	O(15)	P(4)
P(5)	O(19)	O(18)	O(17)	O(20)						109.4(4)	O(23)
	1.525(7)	1.543(6)	1.540(6)	1.555(6)					112.3(3)	109.9(4)	O(24)
O(20)	112.6(3)	111.4(3)	105.1(4)					105.4(3)	108.1(3)	111.6(3)	O(21)
O(17)	108.6(4)	109.6(4)					1.556(6)	1.533(6)	1.537(6)	1.504(6)	
O(18)	109.4(4)						O(21)	O(24)	O(23)	O(22)	P(6)
P(7)	O(27)	O(25)	O(28)	O(26)						108.3(4)	O(29)
	1.519(6)	1.538(6)	1.556(6)	1.551(6)					111.4(3)	110.2(3)	O(30)
O(26)	109.7(3)	110.4(3)	107.6(3)					108.9(3)	105.7(3)	112.3(3)	O(31)
O(28)	112.2(3)	108.7(3)					1.552(6)	1.537(6)	1.531(6)	1.532(7)	
O(25)	108.2(3)						O(31)	O(30)	O(29)	O(32)	P(8)
P(9)	O(33)	O(35)	O(36)	O(34)						107.5(4)	O(40)
	1.524(6)	1.538(6)	1.549(6)	1.540(6)					111.5(3)	108.4(4)	O(37)
O(34)	109.2(4)	111.5(3)	107.5(3)					109.2(3)	109.6(4)	110.7(3)	O(38)
O(36)	112.1(3)	107.3(4)					1.542(6)	1.545(6)	1.526(7)	1.520(6)	
O(35)	109.3(4)						O(38)	O(37)	O(40)	O(39)	P(10)

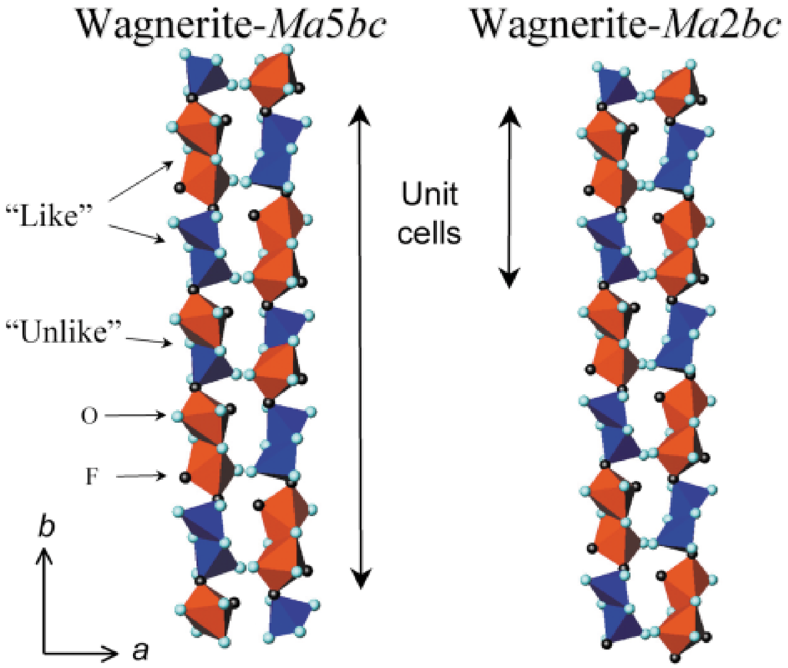

FIG. 8. Diagram comparing chains of Mg polyhedra parallel to *b* in wagnerite-*Ma*5*bc* and wagnerite-*Ma*2*bc*, based on data from this paper and Coda *et al.* (1967), respectively. Red: $MgO_4(F,OH)_2$ octahedra, blue: $MgO_4(F,OH)$ trigonal bipyramids, turquoise spheres: O, black: (F,OH). "Like" and "unlike" refer to the edge-shared linkages (see text). The juxtaposition of two type-1 configurations (Fig. 9) is associated with the "unlike" linkage in wagnerite-*Ma*5*bc*.

the three. Potentially critical compositional variables are the ratios F/OH, Mg/Fe, and Fe/Mn. The importance of F/OH is most obvious in the anion composition of triploidite-group *versus* triplite-group minerals. Fluorine clearly favors the disordered configuration, so that only highly magnesian compositions are ordered (Table 2). The wagnerite polytypes are the only F-dominant members of the triploidite group; its Fe- and Mn-dominant analogues (respectively wolfeite and triploidite) are OH-dominant, a marked contrast with the triplite group (Strunz & Nickel 2001). The reason for this difference probably lies in the different geometries of the F^- ion and the OH^- unit, a subject beyond the scope of this paper.

The average radius of the *M* cations is probably the most important factor in stabilizing the triplite-group *Mabc* structure *versus* the ordered triploidite-group structure (generally *Ma*2*bc*) where F is greatly dominant over OH. An average ionic radius (based on ionic radii of Shannon 1976) between 0.76 Å [magniotriplite from Hållsjöberget and Albères, calculated from data of Henriques (1956) and Fontan (1981), respectively] and 0.73 Å [wagnerite from Benson mines and Kyakhta, calculated from the data of Jaffe *et al.* (1992) and Fin'ko (1962), respectively, or ≥86% of the Mg end-member] divides the stability ranges of the disordered *Mabc* structures (*e.g.*, magniotriplite) from the ordered *Ma*2*bc* and higher-order structures (wagnerite). That is, there is no compositional overlap between magniotriplite and the wagnerite polytypes in terms of the *M* cations. Nonetheless, temperature also could play a role, *i.e.*, heating an ordered *Ma*2*bc* (or higher order) structure should eventually transform it into the disordered *Mabc* structure. Up to four polymorphs of synthetic wagnerite have been reported, but none could be quenched (*e.g.*, Berak & Tomczak 1965). By running differential thermal analyses on well-crystallized end-member wagnerite, Auh (1970) and Auh & Hummel (1974) found a small thermal effect at 1255°C (apparently at $P = 1$ bar) during heating and cooling, which they cited as evidence for a single polymorphic inversion. This heat effect might be due to the ordering of F without a polymorphic transformation.

Less obvious are the conditions favoring formation of wagnerite-*Ma*5*bc* *versus* wagnerite-*Ma*2*bc* or other polytypes of wagnerite. The very limited data on syn-

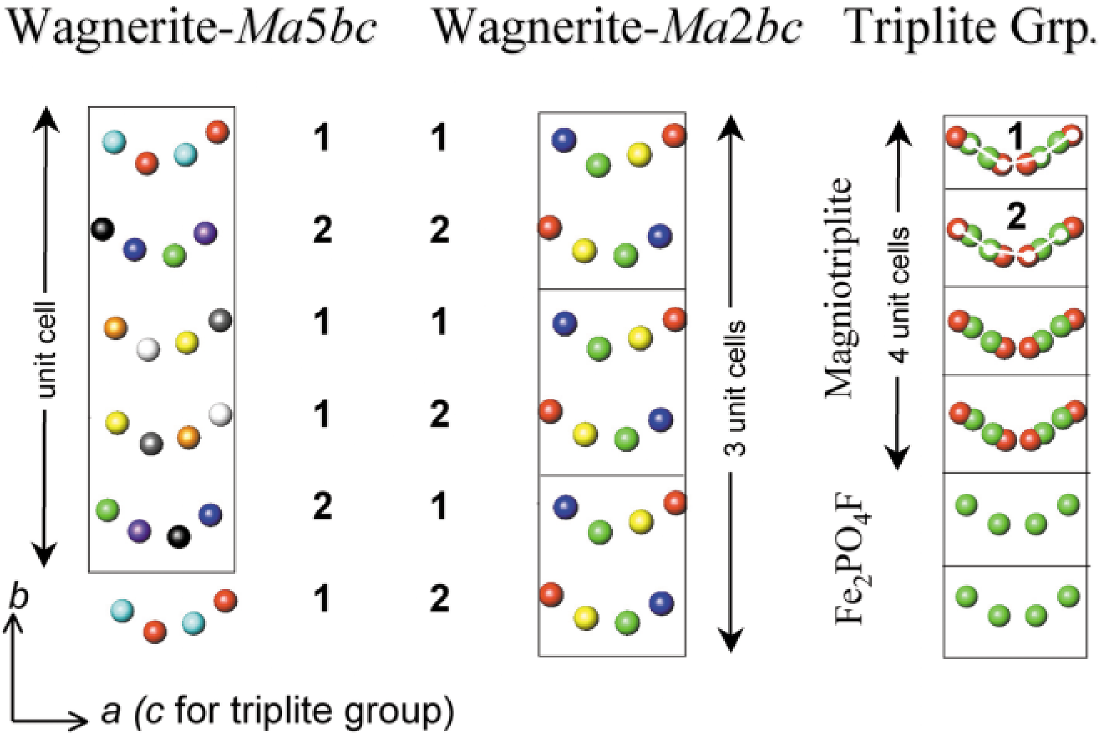

FIG. 9. Configuration of F sites in wagnerite-*Ma*5*bc*, wagnerite-*Ma*2*bc*, magiotriplite and synthetic end-member zwieselite, Fe_2PO_4F (n.b.: *c* in triplite-group minerals corresponds to *a* in wagnerite-*Ma*5*bc* and wagnerite-*Ma*2*bc*), based on data from this paper, Coda *et al.* (1967), Tadini (1981), and Yakubovich *et al.* (1978), respectively. Individual F sites are represented by different colors (*cf.* Fig. 8); those in magniotriplite are only half occupied. Two possible configurations are indicated by heavy lines and white, filled circles in the diagram for magniotriplite.

thetic wagnerite suggest that higher-order polytypes form at higher temperatures than the *Ma*2*bc* polytype (Table 10). This suggestion is not inconsistent with the limited data on natural systems, but the amphibolite-facies sample from Star Lake, Manitoba would be an exception if the polytype were confirmed to be *Ma*5*bc* or a higher order, as the powder data suggest. Data are too few to assess possible roles of the ratios Fe/Mg and F/OH, or another compositional variable such as TiO_2. In compiling Table 10, we note that identifications of polytype by single-crystal refinements are few, so powder X-ray patterns also had to be used, which adds to the difficulty in assessing the relationship between polytype and conditions of crystallization. Thomas Armbruster (pers. commun.) notes that all polytypes of wagnerite produce an X-ray powder pattern that is governed by a pseudo-translation along *b* of ~6.34 Å, whereas the reflections responsible for the F distribution that determine polytype are weak. In the case of wagnerite-*Ma*2*bc*, all reflections with $k = 2n$ are strong and those for $k = 2n + 1$ are weak. In principle, an indexed powder pattern would allow determination of the polytype, but in practice, there is ambiguity in the correct indexing of the weak "superstructure" reflections.

Another possibility is that many $M^{2+}{}_2PO_4F$ compounds originally crystallized in the disordered state, and only magnesian varieties subsequently ordered on cooling, *i.e.*, Mn and other large cations, as well as Cu^{2+} and Fe^{2+}, inhibit ordering on cooling. Only wagnerite that formed in low-temperature environments, *e.g.*, at Werfen, Austria, first crystallized as an ordered polytype. This alternative interpretation is suggested by the presence of the disordered magniotriplite in relatively low-temperature environments (granitic pegmatites, amphibolite-facies rocks), whereas the highly ordered polytypes of wagnerite can be found in relatively high-temperature environments or synthesized at relatively high temperatures (Table 10). One would expect the converse, because disorder generally increases with increasing temperature. The 1255°C temperature reported by Auh & Hummel (1974) for the inversion in end-member wagnerite is too high to be relevant to most

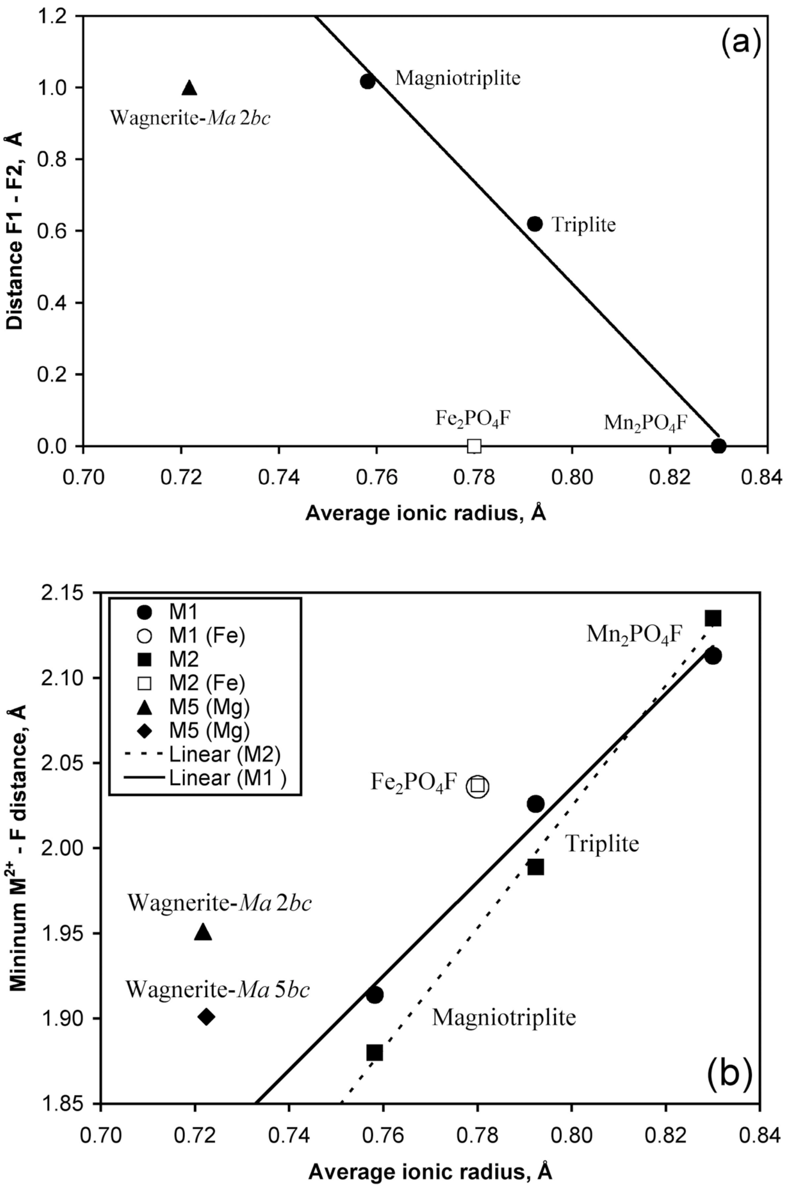

FIG. 10. Variation of distance between partially occupied *F*1 and *F*2 sites (a) and minimum cation – F distance (b) with average ionic radius of the *M* cation (based on the ionic radii of Shannon 1976) in minerals and synthetic analogues of the triplite group and wagnerite, based on the data of Coda *et al*. (1967), Waldrop (1969), Rea & Kostiner (1972), Yakubovich *et al.* (1978), Tadini (1981), and our findings. Lines are least-squares fits excluding Fe_2PO_4F and wagnerite. The *F*1–*F*2 distance given for wagnerite-*Ma*2*bc* has been estimated from the F positions reported by Coda *et al*. (1967).

TABLE 10. POLYTYPE IDENTIFICATION OF WAGNERITE REPORTED IN THE LITERATURE[1]

Locality	Polytype identification	Conditions	References
		Ma2bc	
Werfen, Austria	SREF[1]: absence of F disorder	Greenschist facies	Hegemann & Steinmetz (1927), Coda *et al.* (1967), T. Armbruster (pers. commun.)
Miregn, Central Alps, Switzerland	SREF	Amphibolite facies	Irouschek-Zumthor & Armbruster (1985), Chopin *et al.* (2003)
Santa Fe Mountain, Colorado, U.S.A.	Precession photography, Powder: $k = 2n + 1$ lines present[2]	Amphibolite facies	Sheridan *et al.* (1976)
Dora Maira, Western Alps, Italy	SREF	$700 < T < 750$°C, $P \sim 30$ kbar	Brunet *et al.* (1998), Chopin *et al.* (2003)
Synthetic, Mg_2PO_4OH–Mg_2PO_4F solid solution	SREF for Mg_2PO_4OH Assumed for F-bearing compositions as powder patterns are similar for the entire F–OH range	$500 < T < 650$°C, $2 < P < 7$ bar	Raade & Rømming (1986), G. Raade (pers. commun.)
		Ma5bc	
Larsemann Hills, Antarctica	SREF	$750 < T < \sim 860$°C, $P \approx 6$–7 kbar	This paper
		Ma7bc* and *Ma9bc	
Reynolds Ranges, Australia	SREF	$750 < T < 800$°C, $P \approx 4$–5 kbar	Vry & Cartright (1994), Chopin *et al.* (2003)
		Possibly *Ma5bc* or higher order	
Star Lake, Manitoba	Powder: $k = 2n + 1$ lines absent[2]	Amphibolite facies	Leroux & Ercit (1992)
Synthetic, F–Mg end member	Powder: $k = 2n + 1$ lines absent[3]	$850 < T < 1100$°C, $P \sim 1$ bar	Auh (1970), Auh & Hummel (1974)

Note: [1] This table lists those samples of wagnerite for which the evidence for polytype identification is reasonably certain, the best evidence being SREF (single-crystal refinement). [2] Reflection at 5.66 Å (200) is present; Sheridan *et al.* (1976) cited it as diagnostic for distinguishing wagnerite (in this case, the *Ma2bc* polytype) from magniotriplite. [3] Based on our indexing of the pattern reported by Auh (1970).

occurrences of wagnerite, but perhaps it is lowered by Fe and Mn substitution for Mg or by increased pressure (or both), so that in complex natural systems, wagnerite could have crystallized as the disordered *Mabc* polytype at geologically reasonable temperatures.

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