

WARWICKITE FROM ST. LAWRENCE COUNTY, NEW YORK: MINERAL ASSOCIATION, CHEMICAL COMPOSITION, CATION ORDERING, AND SPLITTING OF THE WARWICKITE *M1* SITE

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ABSTRACT

Warwickite has been discovered in the Edwards and Balmat #3 mines in the Balmat-Edwards mining district, St. Lawrence County, New York, located in the Adirondack Lowlands. The samples from the two mines are similar in chemistry and atomic arrangement but differ chemically from previously described samples; they are among the most Fe-poor samples described to date. The warwickite in the Edwards Mine sample occurs as 1–2 mm-diameter green crystals associated with pink spinel, forsterite, phlogopite, and pyrite in an impure dolomitic marble, whereas warwickite in the specimens from the Balmat #3 mine, approximately 10 km distant, occurs as brown to amber colored, slender, elongate, millimeter-size crystals in a calcitic marble in association with pink spinel, phlogopite, anhydrite, pyrite, and galena. Chemical analyses of the two specimens by electron microprobe show similar empirical formulas of $(\text{Mg}_{1.43}\text{Ti}_{0.36}\text{Al}_{0.18}\text{Cr}^{3+}_{0.02}\text{Zr}_{0.01})_{\Sigma 2.00}\text{B}_{0.98}\text{O}_4$ (Edwards Mine) and $(\text{Mg}_{1.39}\text{Ti}_{0.40}\text{Al}_{0.18}\text{Cr}^{3+}_{0.01}\text{Zr}_{0.01}\text{Fe}^{2+}_{0.01})_{\Sigma 2.00}\text{B}_{0.94}\text{O}_4$ (Balmat mine). The atomic arrangement of a specimen from each mine was determined, and the high-precision refinements provide new insight into the warwickite structure. The *M1* site in warwickite is split into two sites to accommodate two occupants with differing bonding requirements; the *M1* site contains Mg and the *M1'* site hosts Ti, with the two sites being separated by approximately 0.2 Å. The optimized structural formula for both warwickite samples is similar to $[\text{M}^1(\text{Mg}_{0.84}\text{Al}_{0.14}\text{Ti}_{0.02}^{4+})_{2.74}\text{M}^{1'}(\text{Ti}_{0.91}^{4+}\text{Mn}_{0.08}^{2+}\text{Mg}_{0.01})_{1.30}]_{\Sigma 4.04}\text{M}^2(\text{Mg}_{0.86}\text{Al}_{0.10}\text{Ti}_{0.04}^{4+})_{4.00}\text{B}_4\text{O}_{16}$, demonstrating ordering of Mg at *M1* and *M2* and Ti at *M1'*. The site-splitting demonstrates how divalent Mg and tetravalent Ti can exist at a site in solid solution by ordering the two cations at split sites.

Keywords: warwickite, St. Lawrence County, New York, USA, crystal structure, site-splitting.

INTRODUCTION

Warwickite, a Mg-Ti borate $[(\text{Mg},\text{Ti},\text{Fe},\text{Cr},\text{Al})_2\text{O}(\text{BO}_3)_4]$, was first described from the Franklin Marble, town of Warwick, Orange County, New York (Shepard 1838). At this locality, warwickite occurs as slender, dark colored prisms associated with chondrodite, spinel, forsterite, dravite, pyrite, magnetite, and graphite. Shepard (1839) reported the first chemical composition of the mineral, unfortunately incorrect

because the analyzed mineral was altered. Hunt (1851) investigated another warwickite crystal from the type locality but made the same error as Shepard, analyzing an impure specimen. He considered the mineral to be a new species and name it “enceladite”. More precise and complex compositions were presented by Smith (1874) and Bradley (1909). Later researchers studied the crystal morphology (Des Cloiseaux 1874) and, more recently, the atomic arrangement (Takeuchi *et al.* 1950, Moore & Araki 1974, Bigi *et al.* 1991). It should

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be noted that the Fe-rich warwickite, $\text{Mg}(\text{Fe}^{3+}, \text{Al})\text{O}(\text{BO}_3)$, studied by Bigi *et al.* (1991) was subsequently recognized as a new species and was named yuanfuliite (Appel *et al.* 1999).

Grew *et al.* (2017, Appendix 3), in a detailed compendium of boron-bearing minerals, listed the currently confirmed occurrences of warwickite and the references to those occurrences. Seven localities, including the Edwards Mine, are listed, and the additional occurrence from the Balmat #3 mine described herein yields eight confirmed localities for the phase. The reader is referred to Grew *et al.* (2017), particularly Appendix 3, for the most complete bibliography of warwickite references.

Warwickite has the idealized chemical formula $(\text{Mg}_{1.5}\text{Ti}_{0.5})\text{O}(\text{BO}_3)$ and an orthorhombic atomic arrangement. Warwickite from the type locality has the composition $(\text{Mg}_{1.33}\text{Ti}_{0.34}\text{Al}_{0.21}\text{Fe}^{3+}_{0.12})_{\Sigma 2.0}(\text{BO}_3)\text{O}$, deviating relatively little from the ideal endmember $(\text{Mg}_{1.5}\text{Ti}_{0.5})\text{O}(\text{BO}_3)$. In this paper we report two new occurrences of essentially Fe-free warwickite in marble from the Edwards Mine (Lupulescu *et al.* 2014) and the Balmat #3 mine, St. Lawrence County, New York. We present descriptions, mineral associations, chemical compositions, and crystal structure refinements for warwickite from two specimens. The structure refinements demonstrate for the first time the splitting of the *M1* site into two sites to preferentially accommodate Mg and Ti and illustrate details of the warwickite atomic arrangement not offered previously.

REGIONAL GEOLOGY

The Edwards Mine (−75.26706, 44.33092; Lupulescu *et al.* 2014) and the Balmat #3 mine (−75.4023, 44.26665), coordinates as WGS 84, are in the Balmat-Edwards mining district, St. Lawrence County, New York, and are separated by *ca.* 10 km. The two mines where warwickite has recently been found are in the Adirondack Lowlands, the northwestern part of the Grenville-age Adirondack Mountains (1.0–1.3 Ga). The Lowlands are well known for zinc and talc mines, and thus are one of the best-studied regions of the Grenville province.

The Adirondack Lowlands domain is separated from the Adirondack Highlands domain by a deformation zone known as the Carthage-Colton Mylonite Zone (Geraghty *et al.* 1981, Streepey *et al.* 2001). Compared to the Highlands, bedrock of the Lowlands includes a significant proportion of supracrustal rocks that display a well-established stratigraphy. Sequences of shallow-water carbonates and evaporites (now marbles and layers of anhydrite overlain by talc-tremolite schists of

the Upper Marble Formation) overlie a sequence of siliciclastic and volcanoclastic sediments (now metapelites, metapsamites, and leucogneisses; Carl 1988, Chiarenzelli *et al.* 2012). The clastic sequence, in turn, overlies another carbonate-dominated sequence known as the Lower Marble Formation (now composed of marbles, calc-silicates, quartzites, and tourmalinites; Brown 1983, Brown & Ayuso 1984, Slack *et al.* 1984, Chiarenzelli *et al.* 2011). Detrital U-Pb zircon data from the Lowlands metasedimentary rocks suggest deposition of sediments in a back-arc basin (Trans-Adirondack basin) with the margin in the southern Adirondack Highlands (Chiarenzelli *et al.* 2015, 2017). The supracrustal rocks were deformed and metamorphosed under peak conditions of the upper amphibolite facies (Buddington 1939) during the Shawinigan Orogeny (*ca.* 1.19–1.14 Ga; Corrigan 1995, Rivers 2008).

A suite of igneous rocks intruded the metasedimentary units in the Lowlands between 1.15 and 1.2 Ga (Heumann *et al.* 2006, Chiarenzelli *et al.* 2010). The Antwerp-Rossie granitic suite is the oldest of these igneous rocks (Buddington 1939) and was followed by many other granitic rocks displaying A-type characteristics (Peck & Valley 2004 and references therein).

A variety of metamorphosed mafic and ultramafic rocks are scattered throughout the lithological units of the Lowlands. The largest is the Pyrites Complex, which occurs as an enclave in the Lower Marble Formation and has been interpreted to be a tectonically emplaced slab of oceanic crust and upper mantle material from the Trans-Adirondack back-arc basin (Chiarenzelli *et al.* 2009, 2011). Beside the Pyrites Complex, small intrusions, dikes, and irregular bodies of mafic rocks, in places up to 200 m thick, are found within the Popple Hill gneiss (Carl 2000). The Upper Marble Formation is intruded by the Balmat Gabbro and contains small enclaves and layers of mafic amphibolites.

The Edwards and Balmat sedimentary exhalative (SEDEX) Zn deposits are hosted by the Upper Marble Formation. After decades of exploration and mining, 16 lithological subunits have been distinguished in the Balmat deposit; the sulfide ore bodies are within subunits 6, 11, and 14. Subunits 6 and 11 both overlie a layer of pink-lavender anhydrite. Subunit 13 has a talc-tremolite-anthophyllite lithology and hosts the major talc deposits in the region. The Edwards Zn deposit is structurally above subunit 16 (Chamberlain *et al.* 2017 and references therein).

SAMPLE LOCATION AND SPECIMEN DESCRIPTIONS

The warwickite specimens described in this report are from the New York State Museum mineral

collection. Specimen NYSM 13164 is from the Edwards Mine and specimen SC 16469 is from the Balmat #3 mine; however, information on the precise collection location within each mine is missing. As the two specimens were accessioned into the mineral collection at different times, and donated by different individuals, it is difficult to assess the validity of the location information provided. However, because NYSM 13164 was collected and donated by one of the mine geologists, there is more confidence in the reported occurrence of warwickite at the Edwards Mine locality.

NYSM 13164. Edwards Mine warwickite occurs as 1–2 mm-diameter green crystals associated with pink spinel, forsterite, phlogopite, and pyrite in an impure dolomitic marble. Some of the warwickite crystals are altered to an unknown yellow mineral phase(s). The spinel crystals are scattered throughout the specimen, and phlogopite forms small crystal clusters. Forsterite and spinel display bright yellow and red fluorescence under short-wave and long-wave UV light, respectively.

SC 16469. In the Balmat #3 mine, brown to amber colored, slender, elongate, millimeter-size warwickite crystals occur in a calcitic marble in association with pink spinel, phlogopite, anhydrite, pyrite, and galena. Warwickite with spinel grains form a centimeter-wide band in the middle of the specimen. Forsterite and spinel display the same fluorescence as in the NYSM 13164 specimen; phlogopite is lime-green under short-wave UV light.

EXPERIMENTAL METHODS

Electron microprobe analysis

Several millimeter-size warwickite crystals were mounted in epoxy, polished, coated with carbon, and analyzed by wavelength dispersive X-ray spectrometry in the electron microprobe facility at the Earth and Environmental Sciences Department, Rensselaer Polytechnic Institute (RPI), Troy, New York. Specimen NYSM 13164 was analyzed in 2010 with a JEOL 733 Superprobe under operating conditions of 15 kV accelerating voltage, 40 nA beam current, and a 20 μ m beam diameter. The standards used were ilmenite (Fe 219.4 cps/nA), chromite (Cr 120.6 cps/nA, Mg 111.4 cps/nA, Al 83.8 cps/nA), rutile (Ti 1244.4 cps/nA), tephroite (Mn 293.2 cps/nA), and zircon (Zr 123.3 cps/nA).

Specimen SC 16469 was analyzed in 2018 with a CAMECA SX 100 electron microprobe (also in the Earth and Environmental Sciences Department, RPI), under conditions of 15 kV, 20 nA, 20 μ m beam diameter, and using the following standards: kyanite (Al 526.6 cps/nA), synthetic fayalite (Fe 338.0 cps/

TABLE 1. ELECTRON MICROPROBE COMPOSITIONS OF BALMAT AND EDWARDS WARWICKITE

Oxide	NYSM 13164	SC 16469
FeO	0.01	0.34
Cr ₂ O ₃	0.91	0.55
TiO ₂	21.89	24.04
MnO	0.14	0.13
Al ₂ O ₃	6.96	6.91
ZrO ₂	0.76	0.66
MgO	43.63	42.60
V ₂ O ₃	0.00	0.32
B ₂ O ₃ *	25.70	24.45
Total	100.00	100.00

* B₂O₃ by difference. Empirical formulae:

Edwards (Mg_{1.43}Ti_{0.36}Al_{0.18}Cr³⁺_{0.02}Zr_{0.01}) Σ _{2.00}B_{0.98}O₄

Balmat (Mg_{1.39}Ti_{0.40}Al_{0.18}Cr³⁺_{0.01}Zr_{0.01}Fe²⁺_{0.01}) Σ _{2.00}B_{0.93}O₄

nA), tephroite (Mn 311.2 cps/nA), rutile (Ti 1192.0 cps/nA), V₂O₃ (V 1166.0 cps/nA), chromite (Cr 902.1 cps/nA), zircon (Zr 269.4 cps/nA), synthetic forsterite (Mg 422.5 cps/nA), and kyanite (Si 254.3 cps/nA). The data were reduced using a ZAF correction routine. The results are given in Table 1.

Crystal structure

X-ray diffraction data were collected with a Bruker Apex II CCD single-crystal diffractometer at the University of Vermont using graphite-monochromated MoK α radiation. For each sample, data were collected for a redundant sphere of reciprocal space (average redundancy \approx 9.75) and were integrated and corrected for Lorentz and polarization factors and absorption using the Bruker Apex2 package of programs. The atomic arrangement was refined in space group *Pnma*, on *F*², with SHELXL-97 (Sheldrick 2015) using neutral atom scattering factors and full-matrix least-squares, minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$ with no restraints. All atoms were refined with anisotropic temperature factors; an extinction coefficient was also refined. After initial refinements of the structure, the splitting of the M1 site into M1 and M1' was obvious in both crystals. In the final refinements including those split sites they were not constrained to sum to 1.00 because the presence of minor elements other than Mg and Ti might cause errors in the site occupant assignments, but in retrospect that was not necessary, as the atom sum of the two sites in the two crystals added to 1.01 and 1.02 in samples NYSM 13164 and SC 16469, respectively.

Complete details of crystal data and data collection are contained in Table 2, and atomic positions and

TABLE 2. CRYSTAL DATA AND DETAILS OF DATA COLLECTION FOR BALMAT AND EDWARDS WARWICKITE

	Edwards	Balmat
Unit cell dimensions	$a = 9.2130(5) \text{ \AA}$ $b = 3.0845(2) \text{ \AA}$ $c = 9.3595(5) \text{ \AA}$	$a = 9.2159(2) \text{ \AA}$ $b = 3.08460(10) \text{ \AA}$ $c = 9.3557(3) \text{ \AA}$
Volume	265.97(3) \AA^3	265.958(13) \AA^3
Space Group	<i>Pnma</i>	<i>Pnma</i>
θ Range	3.10 to 32.99°	3.10 to 33.09°
Index Ranges	$-13 \leq h \leq 14$ $-4 \leq k \leq 4$ $-13 \leq l \leq 14$	$-14 \leq h \leq 13$ $-4 \leq k \leq 4$ $-14 \leq l \leq 14$
Reflections collected	5465	5435
Independent reflections	558 [$R(\text{int}) = 0.0133$]	559 [$R(\text{int}) = 0.0126$]
Absorption correction	multi-scan	multi-scan
Solution method	direct methods	direct methods
Solution program	SHELXS-97 (Sheldrick 2015)	SHELXS-97 (Sheldrick 2015)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick 2015)	SHELXL-97 (Sheldrick 2015)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$
Data/restraints/params	558 / 0 / 49	559 / 0 / 48
Goodness-of-fit on F^2	1.102	1.084
Final R indices	534 data; $I > 2\sigma(I)$, $R1 = 0.0149$, $wR2 = 0.0431$	552 data; $I > 2\sigma(I)$, $R1 = 0.0137$, $wR2 = 0.0378$
Weighting scheme	all data, $R1 = 0.0158$, $wR2 = 0.0443$ $w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 0.0264P]$ where $P = (F_o^2 + 2F_c^2)/3$	all data, $R1 = 0.0138$, $wR2 = 0.0379$ $w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 0.0546P]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction coefficient	0.0400(50)	0.0670(50)
Largest diff. peaks	0.273 and -0.272 e\AA^{-3}	0.243 and -0.253 e\AA^{-3}

equivalent isotropic displacement parameters are given in Table 3; bond lengths are contained in Table 4. A list of observed and calculated structure factors and Crystallography Information Files (CIF) for the two structures may be obtained from The Depository of Unpublished Data on the MAC website (documents Lupulescu CM58, 19–00046)¹.

RESULTS

Chemical composition

Table 1 gives analyses of both warwickite specimens under study. Although the analyses of the two specimens are similar, we note that there are large differences between the chemical compositions of samples NYSM 13164 and SC 16469 (Table 1) and the compositions of warwickite from the type locality and the published literature. In particular, our samples are Fe-poor compared to previously described warwickites. Titanium concentrations are comparable to the Ti amount in the warwickite from the type locality (Moore & Araki 1974).

Crystal structure

The atomic arrangement of warwickite, (Mg,Ti,Fe,Cr,Al)₂O(BO₃), was first determined by Takeuchi *et al.* (1950) using visual intensity estimates of X-ray diffractions. Subsequent to that work, Moore & Araki (1974) described the structure in detail and related the warwickite structure to those of wightmanite and pinakiolite, describing the topology of the three atomic arrangements as “3 Å wallpaper structures”. A more recent refinement of the structure was provided by Bigi *et al.* (1991), who described the structure of particularly Fe- and Cr-rich samples of warwickite from Jumilla, Spain; their work did not provide quantitative details of site occupancy. Synthetic warwickite was examined by Kawano & Yamane (2011), who compared their refinement details to those of Moore & Araki (1974). Here we provide the results of crystal structure refinements of samples NYSM 13164 and SC 16469 from the Adirondack Lowlands. The structure refinements quantitatively elucidate the site preference of minor elements in the phase and demonstrate for the first time the splitting of the M1 site in warwickite to accommodate both Mg and Ti, two disparate ions that jointly occupy the M1 site.

¹ <http://mineralogicalassociation.ca/>

TABLE 3. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC ATOMIC DISPLACEMENT PARAMETERS

Sample	Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq)	Occ.
13164	<i>M1</i>	0.1237(5)	1/4	0.5735(4)	0.0072(6)	Mg _{0.68(2)} □ _{0.32}
16469		0.1235(6)	1/4	0.5738(4)	0.0080(6)	Mg _{0.69(2)} □ _{0.31}
13164	<i>M1'</i>	0.1041(5)	1/4	0.5662(4)	0.0056(3)	Ti _{0.33(1)} □ _{0.67}
16469		0.1044(5)	1/4	0.5667(4)	0.0061(3)	Ti _{0.33(2)} □ _{0.67}
13164	<i>M2</i>	0.10356(3)	1/4	0.18960(3)	0.00654(11)	Mg _{1.00}
16469		0.10332(3)	1/4	0.18938(3)	0.00665(10)	Mg _{1.00}
13164	<i>O1</i>	0.02085(7)	1/4	0.86507(7)	0.01321(17)	O _{1.00}
16469		0.02134(7)	1/4	0.86493(7)	0.01327(16)	O _{1.00}
13164	<i>O2</i>	0.24931(7)	1/4	0.75009(6)	0.01190(16)	O _{1.00}
16469		0.24951(7)	1/4	0.74992(7)	0.01173(16)	O _{1.00}
13164	<i>O3</i>	0.23572(6)	1/4	0.00725(6)	0.01028(16)	O _{1.00}
16469		0.23588(6)	1/4	0.00710(6)	0.01020(15)	O _{1.00}
13164	<i>O4</i>	0.01141(7)	1/4	0.38393(6)	0.01052(16)	O _{1.00}
16469		0.01145(7)	1/4	0.38403(6)	0.01044(15)	O _{1.00}
13164	<i>B1</i>	0.16720(10)	1/4	0.87514(8)	0.00783(19)	B _{1.00}
16469		0.16767(9)	1/4	0.87498(8)	0.00778(18)	B _{1.00}

The principles of the warwickite atomic arrangement have been established; here we comment on the details that were revealed in our high-precision results from the two crystal structure refinements but do not repeat the earlier structure descriptions. For a detailed recounting of the principles of the warwickite atomic arrangement the reader is referred to Moore & Araki (1974).

In the warwickite atomic arrangement, the Mg²⁺ and Ti⁴⁺ cations are distributed between two octahedra, *M1* and *M2*. Moore & Araki (1974) noted that Mg is dominant at both the *M1* and *M2* sites, but the Ti is accommodated solely at the *M1* site; thus, *M1* accommodates two ions with disparate bond distances. We found that the *M1* site is split into two distinct sites, which we denote as *M1* and *M1'*, such that the *M1* site principally accommodates Mg cations and the *M1'* site

contains Ti⁴⁺ cations; both sites are 4c positions in space group *Pnma*, in (*x*, 1/4, *z*) positions, and they are separated by ~0.2 Å. During final refinements for both samples, without the split *M1* sites, we noted that the final difference maps were not featureless. When sample NYSM 13164 was modeled without an *M1'* site, the *R1* value was 2.38% and the largest peak (0.52 e⁻/Å³) was located 0.74 Å from *M1*; when *M1* was split into *M1* and *M1'*, the *R1* value dropped to 1.49% and the highest difference peak was 0.27 e⁻/Å³. Similarly, in sample SC 16469 we observed that the highest peak (0.49 e⁻/Å³) was 0.65 Å from *M1* with an *R1* value of 2.25%, which reduced to *R1* = 1.37% with the highest difference peak of 0.24 e⁻/Å³ after being modeled with an *M1'* site. The ratio of occupancy of *M1*:*M1'* was similar for the two samples (NYSM 13164, 2.74:1.30; SC 16469, 2.76:1.31). When refining the atomic

TABLE 4. SELECTED BOND LENGTHS IN NEW YORK WARWICKITES (Å)

Sample	13164	16469	13164	16469
<i>M1</i> -			<i>M1'</i> -	
O2	2.018(5)	2.016(5)	O4	1.908(4)
O4(×2)	2.021(3)	2.020(3)	O4(×2)	1.931(2)
O4	2.053(5)	2.054(5)	O2	2.180(4)
O3(×2)	2.107(3)	2.109(3)	O3(×2)	2.205(3)
Mean	2.055	2.055	Mean	2.060
<i>M2</i> -			B-	
O1(×2)	1.9885(4)	1.9891(4)	O1	1.352(1)
O4	2.0072(6)	2.0083(6)	O3	1.3883(9)
O3	2.0965(7)	2.0978(6)	O2	1.394(1)
O2(×2)	2.1299(5)	2.1305(4)	Mean	1.378
Mean	2.057	2.058		1.377

arrangement with the $M1'$ site included, we noted that the best results came when $M1$ was modeled with an Mg occupant and $M1'$ was modeled with Ti, a site assignment that was subsequently confirmed by the site analysis using OccQP (Wright *et al.* 2000). Bond-valence sums for Mg and Ti confirmed the site preferences of Mg for the $M1$ site and Ti for the split $M1'$ site. Although the average bond lengths of the two samples are similar (Table 4), the shortest bond in the $M1'$ site is distinctly shorter than in $M1$, 1.91 *versus* 2.02 Å, providing a more suitable bonding environment for Ti at $M1'$. However, despite this site preference, we notice that Mg is overbonded at the $M1$ site and Ti is underbonded at $M1'$, suggesting further disorder of surrounding oxygen atoms, which was not modeled.

The warwickites from St. Lawrence County, New York, contain significant Al; the amount of the substituent Al^{3+} raises the question of where the ion resides. The final cation occupancy of the $M1$, $M1'$, and $M2$ sites was modeled using OccQP (Wright *et al.* 2000). The results of the OccQP refinement illustrated that sample NYSM 13164 has the structural formula $[^{M1}(Mg_{0.84}Al_{0.14}Ti_{0.02}^{4+})_{2.74}^{M1'}(Ti_{0.91}^{4+}Mn_{0.08}^{2+}Mg_{0.01})_{1.30}]_{\Sigma 4.06}^{M2}(Mg_{0.86}Al_{0.10}Ti_{0.04}^{4+})_{4.00}B_4O_{16}$, and sample SC 16469 has a similar structural formula of $[^{M1}(Mg_{0.83}Al_{0.14}Ti_{0.03}^{4+})_{2.76}^{M1'}(Ti_{0.97}^{4+}Mn_{0.02}^{2+}Fe_{0.01}^{2+})_{1.31}]_{\Sigma 4.06}^{M2}(Mg_{0.85}Al_{0.10}Ti_{0.05}^{4+})_{4.00}B_4O_{16}$. Although our work quantifies the site occupancies of the octahedral sites in warwickite for the first time, the site preferences are in good agreement with the qualitative conclusions of Moore & Araki (1974).

SUMMARY AND CONCLUSIONS

Warwickite from the Balmat-Edwards mining district occurs in the Upper Marble Formation, and the mineral association is like that in marbles and skarns; the mineral association suggests that it is the product of Grenville-age, regional metamorphism. The elements contributing to the formation of warwickite (magnesium and titanium) are probably from the host impure dolomitic marble of the Upper Marble Formation; the boron is probably derived from the evaporitic layers also found within the marble.

Based on published chemical compositions of warwickite, Bigi *et al.* (1991) suggested the possibility of Cr and Fe^{3+} endmembers of the warwickite group. Yuanfuliite was ultimately found in the Zhuanmiao boron deposit in China (Huang & Wang 1994) and described in detail by Appel *et al.* (1999) as the Fe^{3+} endmember of the warwickite group.

From crystal structure refinements, we conclude that the $M1$ site in warwickite is split into two octahedral sites, $M1$ and $M1'$, which are occupied by Mg and Ti cations, respectively; both sites are 4c

positions in the space group $Pnma$ and are separated by ~ 0.2 Å. When the structure of each sample was modeled with the split $M1$ site ($M1$ and $M1'$), superior $R1$ values were achieved ($R1 = 1.49\%$ for NYSM 13164 and $R1 = 1.37\%$ for SC 16469) and the difference maps were featureless. This site-splitting in the warwickite crystal structure was confirmed through site occupancy optimization, which demonstrated that the Mg is ordered at the $M1$ site and the Ti is ordered at the $M1'$ site. Although the site-splitting is found in $Mg_3TiO_2(BO_3)_2$, warwickite, it will not necessarily be observed in minerals such as yuanfuliite, in which the ($MgFe^{3+} \rightarrow Mg_{1.5}Ti_{0.5}$) substitution occurs, due to the greater similarity in charge and radius between the occupying ions of the $M1$ site.

Such site-splitting as observed in warwickite is to be expected in any compound with mixed-ion sites that contain ions that are not identical in their bonding behavior; every substituent atom will seek its ideal position within a site to satisfy its bond-valence requirements, subject to the constraints of the coordinating ligands. Whether such site-splitting can be detected is dependent on the quality of the data used to determine the structure and the distance between the split sites, and not a question of whether it will occur, as has been found in numerous mineral structure studies to date.

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