

Beltrandoite, a new root-name in the högbomite supergroup: the Mg end-member magnesiobeltrandoite-2N3S

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Abstract: Magnesiobeltrandoite-2N3S, ideally $\text{Mg}_6\text{Al}_{20}\text{Fe}_2^{3+}\text{O}_{38}(\text{OH})_2$, is a new member of the högbomite supergroup of minerals. It occurs in magnesian chloritites of a metamorphosed layered mafic complex in the Etna-Levaz continental slice, middle Valtourneche, Aosta Valley, Italy. Magnesiobeltrandoite-2N3S grows in a fine-grained chlorite matrix associated as inclusions to relict pre-Alpine hercynite spinels and dolomite in cm- to dm-long darker boudins, which are cut by corundum + clinoclase ± dolomite veins. It occurs as subhedral to euhedral black crystals (~50–400 μm), dark reddish-brown in thin section. It shows dark brown streak and vitreous lustre. It is brittle, with no cleavage observed and uneven fracture. Mohs hardness ≈ 6–6½. $D_{\text{calc}} = 3.93 \text{ g} \cdot \text{cm}^{-3}$. It shows no fluorescence under UV radiation and no cathodoluminescence. The mineral is optically uniaxial (–) with an estimated mean refractive index of ca. 1.80. Pleochroism is weak with ϵ = deep reddish brown (along c axis) and ω = reddish brown (⊥ c). Absorption is E > O. The Raman spectrum shows a weak and strongly polarized broad OH-characteristic absorption centred at 3364 cm^{-1} . Electron microprobe analysis combined with Synchrotron Mössbauer source spectrometry yielded the following empirical formula based on 40 anions per formula unit (pfu) $[\text{Al}_{18.36}\text{Mg}_{3.96}\text{Fe}_{2.52}^{2+}\text{Fe}_{2.08}^{3+}\text{Ti}_{0.56}\text{Cr}_{0.40}\text{Zn}_{0.06}\text{V}_{0.03}^{3+}\text{Mn}_{0.02}]_{\Sigma 28}\text{O}_{38}(\text{OH})_2$. The ideal formula is $\text{Mg}_6\text{Al}_{20}\text{Fe}_2^{3+}\text{O}_{38}(\text{OH})_2$. The eight strongest lines in the X-ray powder diffraction pattern are [$d_{\text{obs}}/\text{\AA}$ (I) (hkl)]: 2.858 (42) (1 1 0), 2.735 (51) (1 0 7), 2.484 (46) (0 1 8), 2.427 (100) (1 1 5), 1.568 (29) (1 2 8), 1.514 (30) (0 2 12), 1.438 (42) (2 0 13), and 1.429 (72) (2 2 0). The crystal structure of magnesiobeltrandoite-2N3S [$P\bar{3}m1$, $a = 5.7226(3)$, $c = 23.0231(9)$ Å, $V = 652.95(5)$ Å³] was refined from X-ray single-crystal data to $R1 = 0.022$; it is isostructural with magnesiöhögbomite-2N3S.

Key-words: magnesiobeltrandoite-2N3S; new mineral; crystal-structure refinement; electron microprobe analysis; chemical formula; högbomite supergroup; Valtourneche; Aosta Valley; Italy.

1. Introduction

The högbomite-supergroup comprises a series of complex oxide minerals related to the spinel-group minerals. It includes the högbomite, nigerite, and taaffeite groups, which form polysomatic series composed of spinel (S) and nolanite (N) modules (Armbruster, 2002). The spinel module has $\text{T}_2\text{M}_4\text{O}_8$ composition and the nolanite module $\text{TM}_4\text{O}_7(\text{OH})$, where T and M represent tetrahedrally and octahedrally coordinated cations, respectively. The nolanite module in nigerite and högbomite minerals has the formula $\text{TM}_4\text{O}_7(\text{OH})$ whereas in taaffeite minerals it is modified (N') and has the formula BeTM_4O_8 . The

composition and classification of these minerals depend on the composition of the nolanite module (that determines the root-name), the composition of the spinel module (that determines the prefix) and the polysomatic sequence of N and S modules (that sets the suffix).

Regarding the root-names, the dominance of the tetravalent cation in the nolanite module identifies högbomite from nigerite: if Ti-bearing, they are classified with the root-name högbomite; if Sn-bearing, they are classified with the root-name nigerite. If Be occupies a tetrahedral position close to the site occupied by hydrogen in the nolanite module of nigerite- and högbomite-group minerals, the root-name is taaffeite and the relevant mineral species are nominally anhydrous.

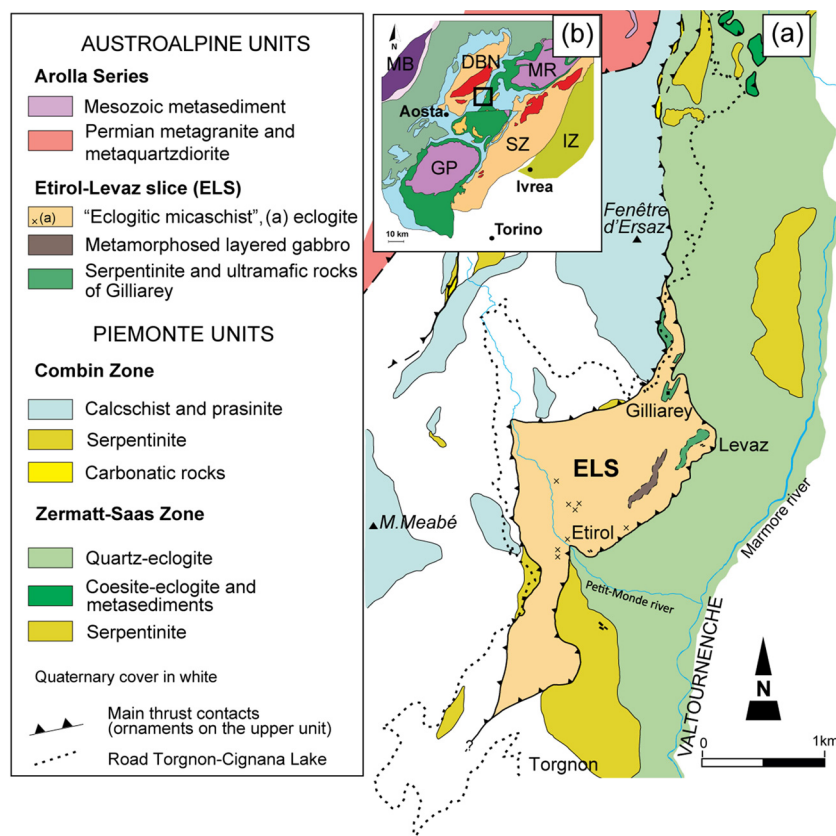


Fig. 1. (a) Geotectonic map of the continental Etnol-Levaz slice (ELS), Torgnon, Valtournenche, Valle d'Aosta region, Italy and the adjoining units of the Piemonte Zone. (b) Simplified tectonic map of the northwestern Alps with location of the portion enlarged in (a). Ivrea Zone (IZ), Sesia Zone (SZ), Dent Blanche Nappe (DBN): in red the Upper Tectonic Units of II-DK in SZ and of Valpelline Series of DBN. Gran Paradiso (GP) and Monte Rosa (MR). Mont Blanc Massif (MB).

Regarding the prefix, it depends upon the composition of the spinel module. Up to now, all members of the supergroup have modules of aluminous spinels (spinel, hercynite or gahnite). Therefore, the prefixes magnesio-, ferro- and zinco- are assigned on the basis of the cation defining the spinel module (Mg, Fe and Zn, respectively).

Different polysomes constitute different mineral species and thus a hyphenated suffix defining the polysome in terms of nolanite and spinel modules is added to define the species. There are ten known or modelled polysomatic combinations of nolanite and spinel modules (see Table 1 in Shimura *et al.*, 2012). Different polytypes of polysomatic sequences have also been described (e.g. magnesiotaafeite-2N²S, Malcherek & Schlüter, 2016).

In the Etnol-Levaz continental slice of the middle Valtournenche, Aosta Valley, magnesian chloritite layers occur in a metamorphosed mafic complex. In some chloritites, rare relict mineral aggregates were found that contain, in addition to a green spinel, a brown mineral determined as "högbomite" on the basis of its optical characteristics (Regis *et al.*, 2015). However, a deeper and more accurate re-examination based on EMPA analyses combined with a single-crystal X-ray study allowed identifying this mineral as a new member of the högbomite supergroup, isostructural with magnesiohög-

bomite-2N3S. Shimura *et al.* (2012) reported that "... högbomite-group minerals are defined as $Ti > Sn$. The corresponding Ti-free samples should be classified into a newly defined group in close relation with högbomite and nigerite groups". The new phase is Ti-poor, Sn-free and has Fe^{3+} -dominant over Ti at the M5 octahedron of the nolanite module and for this reason deserved a new root-name. The proposed root-name beltrandoite honours Marco Beltrando (1978–2015), geologist and petrologist at the Department of Earth Sciences of the University of Torino, for his sound contributions to the evolution of the Alpine orogeny. During his too short but very brilliant career, he obtained very important scientific results, such as the recognition of hyper-extended margins in the collisional belt of the Western Alps and the heating-cooling cycles in rift systems. He was able to connect structural geology and tectonics with petrology, geochronology and stratigraphy. His great ability to link the observations at the micro-scale to those at the meso- and macro-scale allowed him to shed new light on the evolution of both extensional and collisional systems. His new and original ideas have made him one of the leaders of a new generation of Alpine geologists. It is very sad that Marco's life and brilliant career terminated so suddenly in the place where he felt best, in his beloved mountains.

Table 1. Analytical data (wt%) for magnesiobeltrandoite-2N3S (average of 55 spot analyses).

	Mean	Range	SD	Standard ^c
MgO	10.43	9.33–11.11	0.45	Olivine
ZnO	0.34	0.14–0.52	0.07	Rhodonite
NiO	0.09	0–0.16	0.04	NiAs
MnO	0.23	0.15–0.32	0.03	Rhodonite
FeO	11.80	10.83–14.18	0.69	Fayalite
Fe ₂ O ₃ ^a	10.83	9.66–12.13	0.57	
Al ₂ O ₃	61.10	59.41–63.50	0.81	Almandine
Cr ₂ O ₃	1.98	1.23–3.19	0.32	Cr
V ₂ O ₃	0.15	0.09–0.25	0.03	V
TiO ₂	2.91	1.14–4.49	0.26	Ilmenite
H ₂ O ^b	1.18	1.16–1.19	0.01	
Total	100.90			

^a By charge balance and 28 cations pfu.^b By stoichiometry assuming 2 (OH) pfu.^c K α line used.

The average composition of the spinel modules in this new species has dominant aluminium and has Mg > Fe²⁺, thus, conforming to the högbomite nomenclature (Armbruster, 2002), the new name “beltrandoite” is prefixed by “magnesio” (as dominant element of the spinel module) and suffixed by “-2N3S” to represent the alternate spinel (S) and nolanite (N) modules ($c = 23.0$ Å). The new mineral and the name were approved in November 2016 (IMA No. 2016-073) by the IMA Commission on New Minerals, Nomenclature and Classification. The holotype material (a thin section and a 2 mm-thick rock chip) is deposited in the mineralogical collections of the Museo Regionale di Scienze Naturali di Torino, Sezione di Mineralogia, Petrografia e Geologia, via Giovanni Giolitti 36, 10123 Torino, Italy, catalogue number M/U17182.

2. Occurrence

The sample containing magnesiobeltrandoite-2N3S was collected by our colleague Marco Gattiglio (University of Torino) along the stream “Marmore” of the middle Valtournenche (Valle d’Aosta, Italy; ~N 45°49’36”; E 7°34’51”) in the debris underneath the Etirol-Levaz slice (Fig. 1).

The Etirol-Levaz slice (ELS; see Fig. 1) is a lens-like continental fragment, sandwiched between the overlying blueschist- to greenschist-facies Combin zone and the underlying eclogite-facies Zermatt-Saas zone, both derived from the Mesozoic Piemonte-Liguria Ocean (Kienast, 1983; Ballèvre *et al.*, 1986; Dal Piaz *et al.*, 2015). It was interpreted as an extensional allochthon derived from the Adriatic continental margin and stranded inside the Piemonte-Liguria oceanic domain during Jurassic rifting (Dal Piaz *et al.*, 2001; Beltrando *et al.*, 2010; Rubatto *et al.*, 2011; Regis *et al.*, 2015). The slice consists of pre-Alpine, most likely Variscan, amphibolite- to granulite-facies gneisses, micaschists and metabasics,

locally very well preserved as to both fabric and mineralogy (Kienast, 1983; Ballèvre *et al.*, 1986). During the Early Tertiary subduction, the ELS rocks were overprinted by Alpine eclogite-facies metamorphism and converted to garnet-phengite micaschist (“eclogitic micaschist”), minor fine-grained phengite orthogneiss and paragneiss with small pods of eclogite locally retrogressed to prasinite (Regis, 2007; Fassmer *et al.*, 2016). In the central portion of the ELS, a lens-like body of a layered coronitic metagabbro with cumulus structures has been reported (Kienast, 1983; Ballèvre *et al.*, 1986). The studied rock, containing the högbomite-like minerals, has been proved by two of us (DR and RC) to derive from the layered metagabbro, where it occurs as massive chloritite bands, most likely after primary spinel pyroxenites (Regis *et al.*, 2015). The chloritite locally contains cm- to dm-long darker boudins with relict green spinel + a brown högbomite-looking mineral, cut by corundum + chlorite ± dolomite veins.

The Alpine reaction coronas developed in the metagabbro around clinopyroxene, orthopyroxene and spinel were investigated in detail by Kienast (1983). Based on chemical compositions and microstructures of major phases, the author suggested that the layered metagabbro underwent an Alpine high-pressure metamorphic overprint at about 550 °C and 15–16 kbar. More recent thermobarometric studies of the high-pressure Alpine assemblage (garnet + omphacite + phengite + rutile) of ELS eclogites (Regis, 2007; Fassmer *et al.*, 2016) have shown two stages of garnet + omphacite growth during the prograde to peak P - T path. The metamorphic HP peak was constrained at ~560 °C and ~24 kbar (Regis, 2007; Fassmer *et al.*, 2016).

3. Experimental methods

3.1. Electron-microprobe analysis (EMPA)

Two thin sections, DB402, and DB321, were obtained from the same rock chip; one includes a corundum vein, and the other the rock matrix. A preliminary study of the chemistry of the minerals present in thin section was carried out by backscattered electron imaging and energy-dispersive spectrometry (EDS) at the Department of Earth Sciences, University of Turin. The measurements were executed with a Cambridge S-360 SEM equipped with Oxford Instruments Inca Energy 200 EDS spectrometer and X-Act3 SDD detector, operating at an acceleration voltage of 15 kV and beam current of 1 nA. Elemental maps of K α spectral lines were obtained with SmartMap Option of Inca Energy 200 Oxford Instruments operating at 15 kV and 1 nA.

Chemical analyses were later carried out by wavelength-dispersive X-ray spectrometry (WDS) with the JEOL 8200 Super Probe at the Department of Earth Sciences, University of Milan, operating at an accelerating voltage of 15 kV, a specimen current of 5 nA, and a beam diameter of 1 μ m. Minerals and synthetic compounds were used as standards (element, spectral line): olivine (Fe, K α), rhodonite (Zn and Mn, K α), NiAs (Ni,

Table 2. Hyperfine parameters derived from the SMS spectrum of magnesiobeltrandoite-2N3S.

	Component/ colour in Fig. 3	Coordination/ Rel. distribution (%)	CS ^a (mm/s)	QS ^b (mm/s)	Area (%)	FWHM ^c (mm/s)
Fe ²⁺ /Fe _{tot} = 54%	Fe ²⁺ (red)	T sites ^d /14(5)	0.81(2)	0.98(5)	8(1)	0.12(5)
	Fe ²⁺ (orange)	M sites ^e /86(3)	1.10(5)	1.02(8)	46(2)	0.50(4)
Fe ³⁺ /Fe _{tot} = 46%	Fe ³⁺ (blue)	T sites/83(4)	0.29(2)	0.58(4)	38(1)	0.25(2)
	Fe ³⁺ (cyan)	M sites/17(5)	0.49(2)	0.54(4)	8(1)	0.10(5)

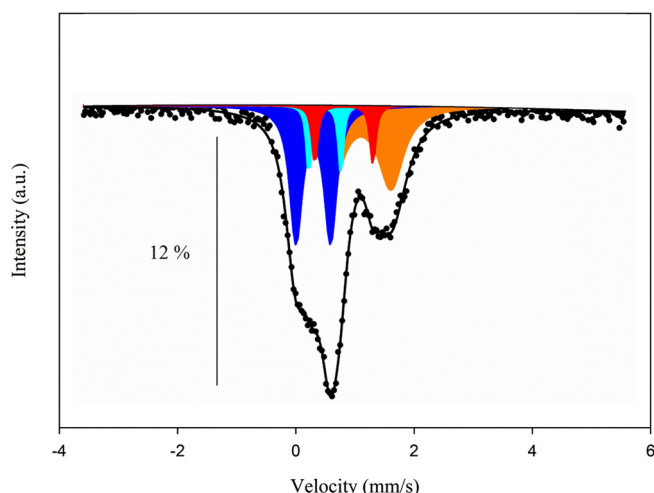
^a CS: centre shift relative to α -Fe.^b QS: quadrupole splitting.^c FWHM: full width at half maximum including the source linewidth.^d T site: tetrahedral site.^e M site: octahedral site.

Fig. 2. Room-temperature SMS spectrum of magnesiobeltrandoite-2N3S. Solid circles, experimental data; continuous black line, full transmission integral fit. Four quadrupole doublets were used to fit the spectrum: in blue Fe³⁺ in tetrahedral coordination; cyan, Fe³⁺ in octahedral coordination; red, Fe²⁺ in tetrahedral coordination; orange, Fe²⁺ in octahedral coordination. Percentage on the left indicates the relative absorption.

$K\alpha$), fayalite (Fe, $K\alpha$), almandine (Al, $K\alpha$), Cr ($K\alpha$), V ($K\alpha$), ilmenite (Ti, $K\alpha$). Corrections to the raw data were made with the $\varphi\rho Z$ procedure (Pouchou & Pichoir, 1985). Representative average analyses of the minerals present in the sample are reported in Table S1a–e in Supplementary Material linked to this article and freely available on the GSW website of the journal: <http://eurjmin.geoscienceworld.org/>. The composition of magnesiobeltrandoite-2N3S corresponds to an average of 55 data points (Table 1). H₂O was calculated on the basis of two OH groups pfu. Tin, Si, P, Ni, Ca, Na, K, were not present in the spectra. The empirical formula of magnesiobeltrandoite-2N3S calculated on the basis of 28 cations and 40 (O + OH) pfu (Fe²⁺/Fe³⁺ by charge balance) is [Al_{18.36}Mg_{3.96}Fe_{2.52}Fe_{2.08}Ti_{0.56}Cr_{0.40}Zn_{0.06}V_{0.03}³⁺Mn_{0.02}]_{Σ28}O₃₈(OH)₂. The ideal formula is Mg₆Al₂₀Fe₂³⁺O₃₈(OH)₂, which requires Al₂O₃ = 70.84, MgO = 16.80, Fe₂O₃ = 11.11, H₂O = 1.25, total 100 wt%.

3.2. Synchrotron Mössbauer source spectroscopy

Synchrotron Mössbauer spectroscopy (SMS) was performed at the Nuclear Resonance Beamline ID18 (Rüffer & Chumakov, 1996) using the nuclear monochromator as described by Potapkin *et al.* (2012) at the European Synchrotron Radiation Facility (ESRF), Grenoble. The SMS provides ⁵⁷Fe resonant radiation at 14.4 keV within a bandwidth of ~6 neV, which is tunable in energy over a range of about ±0.6 μ eV. In contrast to radioactive sources, the beam emitted by the SMS can be focused and it is fully resonant and up to 99% polarized. The SMS spectra were collected during operation in multibunch mode (7/8 + 1 filling) with the beam focused to a spot size of roughly 15 × 15 μ m² using Kirkpatrick-Baez bending mirrors. The SMS linewidth was controlled before and after each sample measurement using K₂Mg⁵⁷Fe(CN)₆, whose Mössbauer spectrum consists of a single line, and the velocity scale was calibrated using 25 μ m thick natural α -iron foil. The SMS spectrum was collected for ~12 h from a single crystal previously checked using X-ray single-crystal diffraction to exclude the presence of possible inclusions of different species. The spectrum was fitted using the program MossA with the full transmission integral and a Lorentzian-squared source line shape (Prescher *et al.*, 2012) and is reported in Fig. 2. The spectrum was fitted using four components corresponding to Fe³⁺ and Fe²⁺ in tetrahedral and octahedral position. Observed hyperfine parameters agree well with observed values for Fe²⁺ and Fe³⁺ in these coordination environments and are reported in Table 2. The refined Fe³⁺/Fe_{total} ratio is 46(2)%.

3.3. Raman spectroscopy

The Raman spectrum of magnesiobeltrandoite-2N3S (Fig. 3) was obtained using a micro/macro Jobin Yvon Mod. LabRam HRVIS, equipped with a motorized x-y stage and an Olympus microscope. The backscattered Raman signal was collected with 50× objective for a non-oriented crystal. The 532.11 nm line of a frequency doubled Nd-YAG laser and the 632.81 line of a He–Ne laser was used as excitation; laser power was controlled by

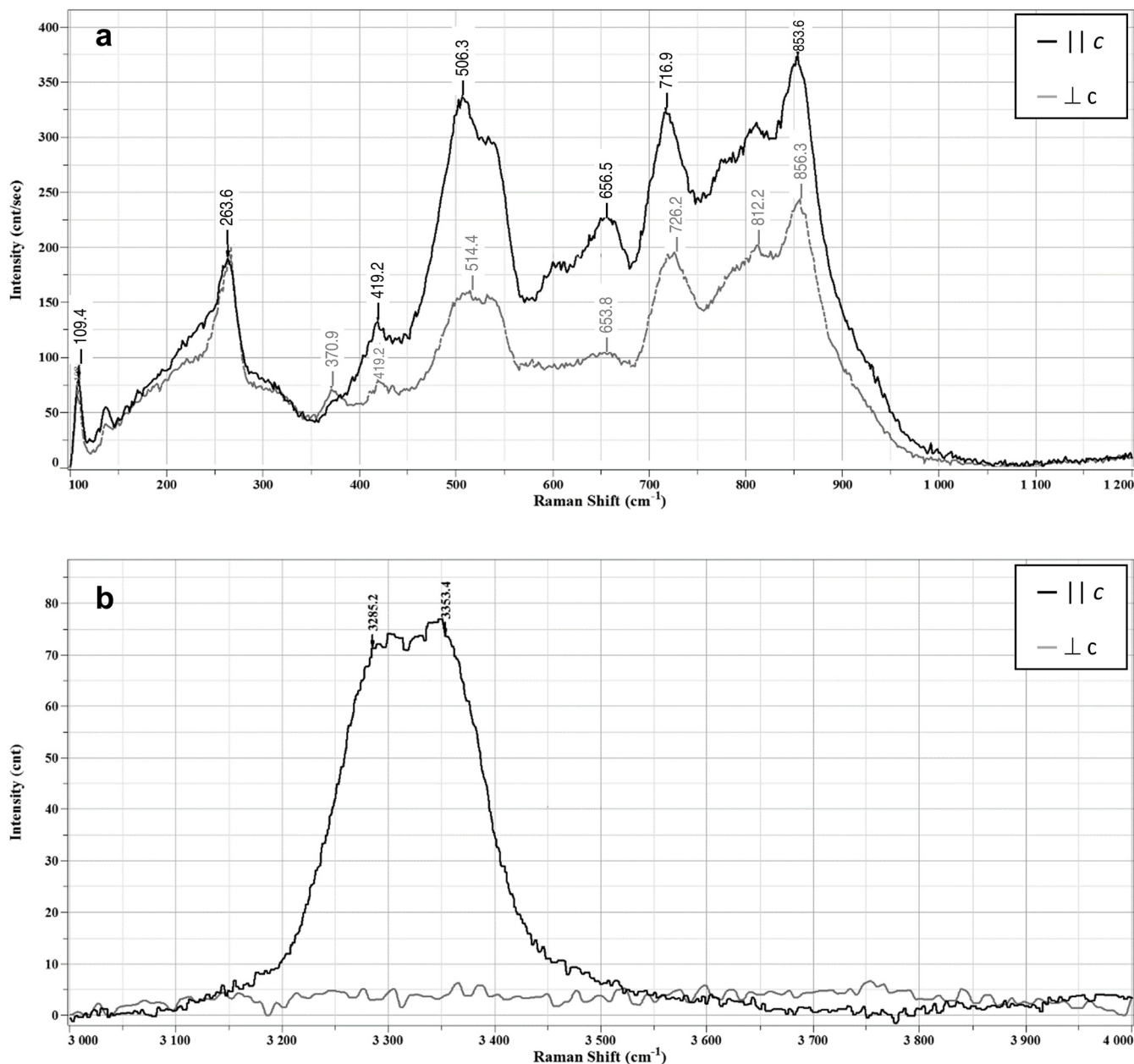


Fig. 3. Raman spectra of magnesiobeltrandoite-2N3S in the 100–1200 cm^{-1} region (a) and between 3000 and 4000 cm^{-1} (b).

means of a series of density filters. The minimum lateral and depth resolution was set to few μm . The system was calibrated using the 520.6 cm^{-1} Raman band of silicon before each experimental session. The spectra were collected with multiple acquisitions (5–20) with single counting times ranging between 10 and 20 s. The spectrum was recorded using the LabSpec 5 program (2004, 2005) from 100 to 4000 cm^{-1} and the results of the spectroscopic analysis are reported below.

3.4. X-ray powder diffraction

X-ray powder diffraction data were calculated from the structure data with XPow (Downs *et al.*, 1993) and are reported in Table 3. Experimental data were obtained on a

powdered sample using an Oxford Ruby, Gemini Ultra diffractometer equipped with a CCD area detector at CrisDi (Interdepartmental Centre for the Research and Development of Crystallography, Torino, Italy) with graphite-monochromatized $\text{CuK}\alpha$ radiation, and are also reported (in Å) in Table 4. Refined cell parameters using GSAS (Larson & Von Dreele, 1994) are $a = 5.7164(1)$, $c = 22.9702(8)$ Å, $V = 650.03(2)$ Å³.

3.5. Single-crystal structural refinement (SREF)

A prismatic crystal was carved with a needle from the chlorite matrix of DB321 rock chip. Single-crystal X-ray studies were carried out on a crystal of 0.080 mm $\times$ 0.060 mm $\times$ 0.020 mm using an Oxford Xcalibur Ruby Gemini

Table 3. X-ray powder diffraction data for magnesiobeltrandoite-2N3S. The eight strongest reflections are reported in bold.

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>I</i> _{obs}	<i>I</i> _{calc}
0	0	5	4.594	4.605	9.4	6.6
0	1	2	4.546	4.552	11.7	10.3
1	0	3	4.157	4.163	5.4	7.3
0	1	5	3.367	3.373	8.6	8.0
1	0	6	3.028	3.034	10.8	12.9
1	1	0	2.858	2.861	42.2	43.8
1	0	7	2.735	2.740	51.2	45.6
0	1	8	2.484	2.489	45.9	38.9
1	0	8	2.484	2.489	23.0	9.1
0	2	1	2.461	2.464	12.3	12.0
1	1	5	2.427	2.430	100.0	100.0
0	2	2	2.420	2.423	27.8	26.7
0	2	4	2.273	2.276	7.7	6.3
0	2	6	2.079	2.082	20.2	15.4
2	0	6	2.079	2.082	22.0	15.3
0	2	7	1.976	1.979	12.3	9.8
2	0	7	1.976	1.979	16.2	14.5
0	1	13	1.664	1.668	5.3	4.6
3	0	0	1.650	1.652	6.0	6.3
2	1	7	1.625	1.628	21.1	17.2
0	2	11	1.596	1.599	5.5	5.4
1	2	8	1.568	1.570	29.0	21.7
2	1	8	1.568	1.570	11.1	8.2
0	3	5	1.553	1.555	12.8	12.3
3	0	5	1.553	1.555	15.4	10.3
0	2	12	1.514	1.517	29.6	21.9
0	2	13	1.438	1.441	11.1	11.4
2	0	13	1.438	1.441	42.2	30.9
2	2	0	1.429	1.431	71.8	61.2
2	0	14	1.368	1.370	13.9	7.1
3	1	8	1.239	1.240	9.1	6.4
4	1	5	1.052	1.053	6.8	5.7
1	4	5	1.052	1.053	7.7	5.0
4	0	12	1.039	1.041	5.7	4.9
0	4	13	1.014	1.015	17.0	8.1

Note: Reflections with $I_{\text{rel}} > 5\sigma(I_{\text{rel}})$ are listed.

Table 4. Parameters for X-ray data collection and crystal-structure refinement of magnesiobeltrandoite-2N3S crystal.

Diffractometer	Xcalibur Ruby Gemini Ultra
X-ray radiation	Mo K α (0.71073 Å)
Temperature	293(2) K
Crystal size (mm)	0.08 × 0.05 × 0.02
Space group	$P\bar{3}m1$
Unit-cell dimensions (Å)	$a = 5.7226(3)$ $c = 23.0231(9)$
Cell volume (Å ³)	652.95(5)
Refined formula	Mg _{5.13} Fe _{4.83} Al ₁₈ O ₃₈ (OH) ₂
<i>Z</i>	1
Completeness	98.5%
Average redundancy	8.2
Reflections collected	11966
θ -range for data collection (°)	3.54–40.91
Index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-41 \leq l \leq 36$
Unique reflections	1721
Reflections $> 2\sigma(I)$	1626
R_{int}	0.0340
R_{σ}	0.0195
Number of least-squares parameters	94
Goodness-of-fit on F^2	1.111
$R1$, $I > 2\sigma(I)$	0.0219
$R1$, all data	0.0242
w $R2$ (on all F^2)	0.0603
Extinction coefficient	0.0019(7)
Largest diff. peak and hole	0.513 and $-0.555 \text{ e} \cdot \text{\AA}^{-3}$
$\Delta\rho_{\text{min}}$ ($-\text{e} \cdot \text{\AA}^{-3}$)	0.55 [0.93 Å from O3]
$\Delta\rho_{\text{max}}$ ($\text{e} \cdot \text{\AA}^{-3}$)	0.51 [0.77 Å from M6]

Ultra diffractometer equipped with a CCD area detector at CrisDi (Interdepartmental Centre for the Research and Development of Crystallography, Torino, Italy) with graphite-monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The sample-to-detector distance was 5.3 cm. A total of 394 exposures (step = 1° , time/step = 63.2 s), covering a full reciprocal sphere with a redundancy of about 8 was used. Data were integrated and corrected for Lorentz and polarization background effects, using the package CrysAlisPro, Agilent Technologies, Version 1.171.37.31 (release 14-01-2014 CrysAlis171.36.24). Refinement of the unit-cell parameters was based on 4873 measured reflections, and gave the following lattice parameters: $a = 5.7226(3)$, $c = 23.0231(9) \text{ \AA}$, $V = 652.95(5) \text{ \AA}^3$. The $c:a$ ratio calculated from the unit-cell parameters is 4.023. The data were corrected for absorption using the multi-scan method (SCALE3 ABSPACK) with a d_{min} of $0.54 \text{ \AA}$. The structure was refined trigonal, space group $P\bar{3}m1$, starting from the

atom coordinates of magnesiöhögbomite-2N3S (Hejny & Armbruster, 2002). Ionized atom scattering curves were used for all atoms, which were refined with anisotropic displacement parameters. The scattering curve for ionized aluminium was used in all octahedral M sites but M5. For the M5 site the scattering curves of both Mg^{2+} and Fe^{2+} were used with the restraint of complementary full occupancy. The latter approach was adopted for all tetrahedral sites in the structure. Hydrogen was localized as a maximum at *ca.* 1 Å of the anion site O4 in the Fourier difference maps and it was added to the model fixing the observed atom coordinates and restraining the isotropic displacement using a riding motion model. Twinning by reticular merohedry (twin fraction 50.5(1):49.5(1)) was observed as reflection on (001). At convergence $R1$ was 0.0222 for 1626 reflections with $F_o > 4\sigma(F_o)$ and 0.0242 for all 1721 data. Parameters for X-ray data collection and crystal-structure refinement are reported in Table 4. Atom

Table 5. Atoms, site occupancies, fractional atom coordinates, and equivalent isotropic displacement parameters ($\text{\AA}^2$) for the studied magnesiobeltrandoite-2N3S crystal.

Site	Refined occ.	x	y	z	* U_{eq}
M1	Al 1.037(7)	0	0	0	0.004(1)
T2	Fe ²⁺ 0.480(5)/ Mg ²⁺ 0.520(5)	1/3	−1/3	−0.0257(1)	0.007(1)
M3	Al 1.019(4)	0.3380(1)	0.1690(1)	−0.1016(1)	0.005(1)
T4	Fe ²⁺ 0.211(5)/ Mg ²⁺ 0.789(5)	1/3	−1/3	−0.1736(1)	0.004(1)
M5	Fe ²⁺ 0.875(6)/ Mg ²⁺ 0.125(6)	−1/3	−2/3	−0.2162(1)	0.004(1)
M6	Al 1.110(4)	0.1641(1)	0.3282(1)	−0.2962(1)	0.005(1)
T7	Fe ²⁺ 0.469(5)/ Mg ²⁺ 0.531(5)	1/3	2/3	0.3699(1)	0.006(1)
M8	Al 1.028(5)	−1/3	−2/3	0.3995(1)	0.005(1)
T9	Fe ²⁺ 0.386(5)/ Mg ²⁺ 0.614(5)	0	0	0.4241(1)	0.006(1)
M10	Al 1.044(4)	0	1/2	1/2	0.005(1)
O1		−0.2962(2)	−0.1481(1)	−0.0535(1)	0.008(1)
O2		−1/3	−2/3	−0.0590(1)	0.008(1)
O3		0.5098(1)	−0.5098(1)	−0.1491(1)	0.009(1)
O4		0	0	0.1450(1)	0.008(1)
O5		−0.1638(1)	0.1638(1)	−0.2545(1)	0.007(1)
O6		1/3	−1/3	−0.2535(1)	0.007(1)
O7		0.4808(1)	−0.4808(1)	−0.3473(1)	0.009(1)
O8		0	0	−0.3396(1)	0.006(1)
O9		−0.1856(1)	0.1856(1)	0.4532(1)	0.005(1)
O10		1/3	−1/3	0.4554(1)	0.006(1)
H		0	0	0.1912	0.009

* The temperature factor has the form $\exp(-T)$ where $T = 8\pi^2 U(\sin(\theta)/\lambda)^2$ for isotropic atoms.

coordinates, anisotropic displacement parameters and main interatomic distances ($\text{\AA}$) and geometrical parameters are reported in Tables 5, S2 and 6, respectively. The CIF file is provided in the Supplementary Material linked to this article.

4. Appearance and physical properties

The holotype sample containing magnesiobeltrandoite-2N3S is a thin section (Fig. 4). The subhedral to euhedral prismatic crystals ($\sim 50\text{--}400\ \mu\text{m}$), moderately elongated parallel to **c**, are included in green spinel relics and associated in the matrix together with chlorite and dolomite, and locally show fractures filled with dolomite + clinochlore $\pm$ corundum. The mineral is dark reddish-brown in thin section. It shows dark brown streak and vitreous lustre. It is brittle, with no cleavage observed and uneven fracture. Mohs hardness is estimated as 6–6½ by analogy to h  gbomite. Density could not be measured because of small grain size and occasional chlorite and magnesite inclusions. The calculated density using the measured cell volume and empirical formula is $3.93\ \text{g}\cdot\text{cm}^{-3}$. Magnesiobeltrandoite-2N3S is unreactive and insoluble in HCl, HNO₃, and H₂SO₄. It shows no fluorescence under UV radiation and no cathodoluminescence. The mineral is optically uniaxial (−). The mean refractive index ($n_{\text{ave}} \sim 1.80$) was obtained from the Gladstone–Dale relationship (Mandarino, 1979, 1981), using the empirical formulae and calculated densities. The estimated values for the refractive indices are well beyond our available experimental range. Dispersion was not determined, but not observed under

crossed polarizers and in conoscopic interference figures. Pleochroism is weak with ϵ = deep reddish brown (along **c** axis) and ω = reddish brown ($\perp$ **c**). Absorption is $E > O$.

5. Results and discussion

5.1. Mineral chemistry of the assemblage

The minerals of the hosting chloritite are chlorite-group minerals, green spinel, magnesite, dolomite, calcite, Fe-bearing corundum and magnesiobeltrandoite-2N3S (Figs. 5 and 6a), while in the corundum- and dolomite-bearing veins green spinel and magnesiobeltrandoite-2N3S are absent. Locally, Cr-rich magnetite, ilmenite with limited pyrophanite solid solution and pyrite are also observed in the matrix (type analyses of oxides are reported in Table S1a) and in alteration rims of relict phases (in particular magnesiobeltrandoite-2N3S) (Figs. 6b and 7a).

Regarding green spinel, core compositions are close to Sp₅₉Hc₄₁ with a strong Fe²⁺ zoning (Fig. 7b) that can reach Sp₄₂Hc₅₈ in the rim of small grains in the matrix or even Sp₃₀Hc₇₀. Rims are also slightly enriched in Cr. Locally, even Cr-richer compositions are observed associated to retrogression of magnesiobeltrandoite-2N3S, with composition Sp₃₁Hc₆₉ (locally up to Sp₁₃Hc₈₇) or close to corundum veins, where composition is still more hercynite-rich (Sp₂₀Hc₈₀). The Cr-rich spinel close to the veins contains also trace amounts of V (Table S1b). Large grains of hercynitic spinel are fractured and cracks are filled by dolomite (Table S1c) and diasporite (Table S1a).

Table 6. Main interatomic distances (Å) and geometrical parameters for magnesioeltrandoite-2N3S.

T2–O1 (×3)	1.9443(12)	M1–O1 (×6)	1.9164(11)
T2–O2	1.950(2)	⟨M1–O⟩	1.9164
⟨T2–O⟩	1.946	V (Å ³)	9.20
V (Å ³)	3.78	σ^2	51.72
σ^2	0.08	λ	1.0136
λ	1.000		
		M5–O3 (×3)	2.1917(12)
T4–O3 (×3)	1.8377(13)	M5–O5 (×3)	1.8972(12)
T4–O6	1.8381(18)	⟨M5–O⟩	2.0444
⟨T4–O⟩	1.8378	V (Å ³)	10.99
V (Å ³)	3.18	σ^2	83.32
σ^2	2.94	λ	1.0295
λ	1.0008		
		M6–O5 (×2)	1.8875(8)
T7–O7 (×3)	1.9146(12)	M6–O6	1.9439(9)
T7–O10	1.9688(18)	M6–O7 (×2)	1.9712(8)
⟨T7–O⟩	1.9281	M6–O8	1.9097(10)
V (Å ³)	3.66	⟨M6–O⟩	1.9285
σ^2	15.41	V (Å ³)	9.40
λ	1.0038	σ^2	40.77
		λ	1.0118
T9–O9 (×3)	1.9572(11)		
T9–O8	1.9453(18)	M8–O7 (×3)	1.8922(11)
⟨T9–O⟩	1.9542	M8–O9 (×3)	1.9159(11)
V (Å ³)	3.83	⟨M8–O⟩	1.9040
σ^2	0.34	V (Å ³)	9.04
λ	1.0001	σ^2	47.12
		λ	1.0125
M3–O1 (×2)	1.9303(8)		
M3–O2	1.9009(11)	M10–O9 (×4)	1.9018(7)
M3–O3 (×2)	1.9331(8)	M10–O10 (×2)	1.9448(9)
M3–O4	1.9506(10)	⟨M10–O⟩	1.9161
⟨M3–O⟩	1.9297	V (Å ³)	9.22
V (Å ³)	9.44	σ^2	44.39
σ^2	36.76	λ	1.0119
λ	1.0098		
		O4–H	1.0645(17)
		O4–H...O5	2.1810(12)
		O4–H–O5	131.89(3)°

* Mean quadratic elongation (λ) and the angle variance (σ^2) were computed according to Robinson *et al.* (1971).

Carbonates in the matrix are dolomite and magnesite with limited Fe substitution (Table S1c). Dolomite in corundum veins may have higher Fe²⁺ (Mn) and trace amounts of V. Calcite was occasionally observed in cracks in spinel and may be secondary.

Chlorites in the matrix show sharp zonation (Figs. 6a, 6b, 7a and 7b) with enrichment of Fe and depletion of Si. The rims correspond to Fe-bearing aluminous clinocllore (previously classified with the name “corundophilite” and “ripidolite”, now discarded; Bayliss 1975, Table S1d). Charge balance demonstrates that chlorite has no Fe³⁺.

Magnesioeltrandoite-2N3S shows limited zonation with slighter Ti-richer cores but never reaching h gbo-mitic compositions. A chemical profile is reported in Table S1e. Fe³⁺/Fe_{total} was estimated assuming 2 (OH) pfu and charge balance. The values reported in Table S1e agree fairly well with SMS data (see below). Most of the

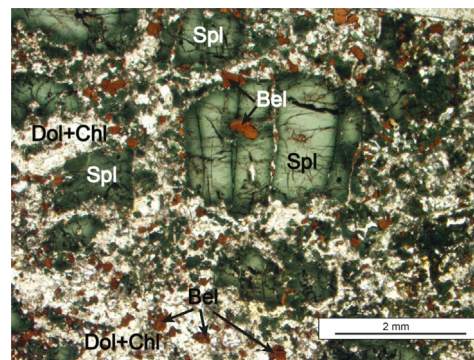


Fig. 4. Relict pre-Alpine high-*T* green spinel (Spl) with magnesioeltrandoite-2N3S (reddish brown, Bel) in a matrix composed of a fine-grained aggregate of chlorite + dolomite (white, Dol + Chl) + magnesioeltrandoite-2N3S (brown, Bel) ± corundum.

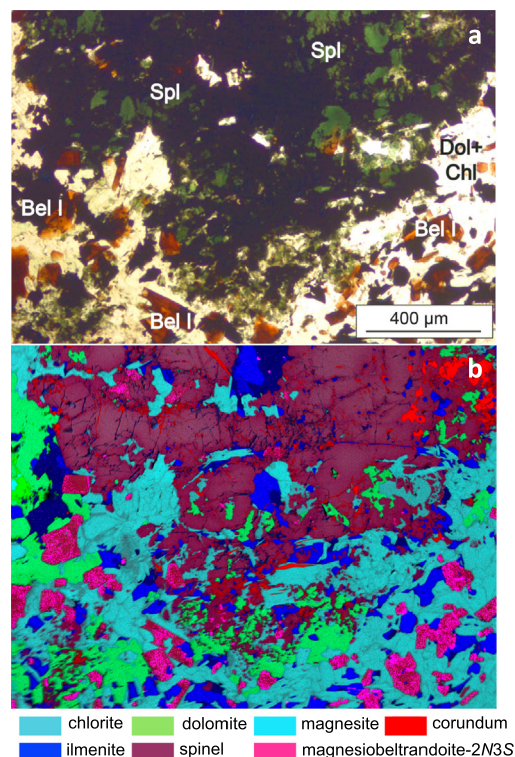


Fig. 5. Transmitted plane-polarized light (a) and composite X-ray fluorescence map (b) obtained by merging the elemental maps of MgK , AlK , CaK  and TiK  in the area reported in (a). The red areas indicated as corundum may include diaspore.

grains of magnesioeltrandoite-2N3S show incipient alteration to clinocllore even richer in Fe and Al than the rims of crystals in the matrix (Fig. 7a, Table S1d). In Fig. 8 the chemical variability of magnesioeltrandoite-2N3S of Valtournenche is plotted in a modified version of the (Ti + Sn)– R²⁺– R³⁺ diagram of h gbo-mite group minerals of Shimura *et al.* (2012). Figure 8 also reports the composition of magnesioh gbo-mite-2N3S by Hejny &

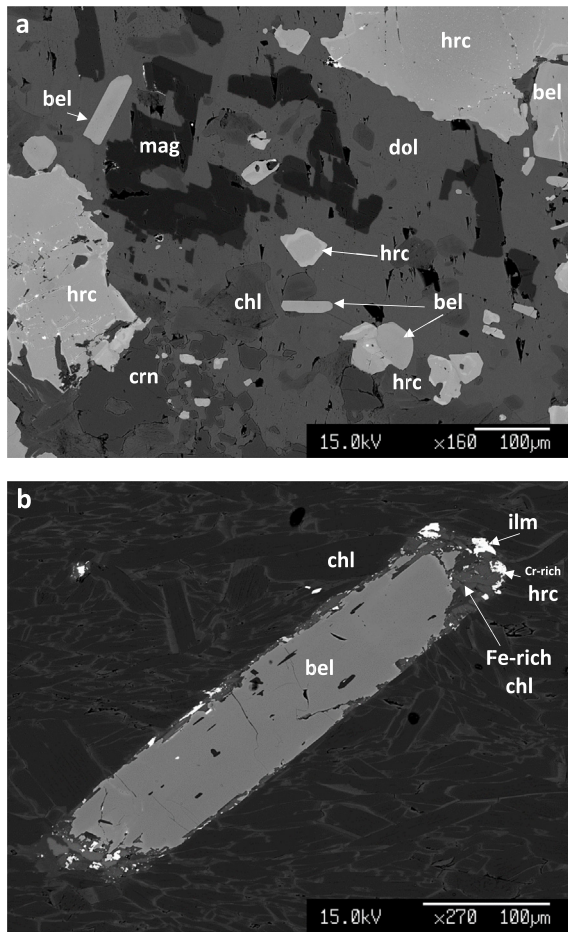


Fig. 6. (a) Backscattered-electron (BSE) image of a carbonate-rich zone of the matrix, showing the relation between relict spinel-hercynite grains with a brighter hercynitic rim (hrc) and coeval magnesiobeltrandoite-2N3S (bel) crystals dispersed in a zoned chlorite matrix. At the centre, magnesite cores are included in zoned dolomite. In the lower part of the image, a corundum grain is in contact with hercynite. (b) Magnesiobeltrandoite-2N3S crystal showing incipient alteration to Fe-rich aluminous clinocllore, ilmenite and chromium-rich hercynite. In the matrix, clinocllore shows sharp zoning to Fe and Al richer rims.

Armbruster (2002) for comparison. The compositions plotting below the R^{4+} (Ti, Sn) = 1 line cannot be classified as högbomite or nigerite because in those compositions neither Ti nor Sn are dominant in the M5 octahedron of the nolanite module.

The mineral assemblages and microstructural relationships in both the metagabbro and the chloritite indicate that the rocks experienced a complex polymetamorphic evolution. On the basis of microstructures, Regis *et al.* (2015) concluded that the pre-Alpine destabilization of green spinel, beltrandoite and magnesite led to extensive chloritization of the cumulate layers and development of the matrix assemblage Mg-chlorite + dolomite ± corundum; this stage followed the Permian high- T metamorphic evolution. The crystallization of magnesiobeltrandoite-2N3S predates the formation of the crosscutting Crn + Dol + Mg-Chl veins during the Alpine evolution.

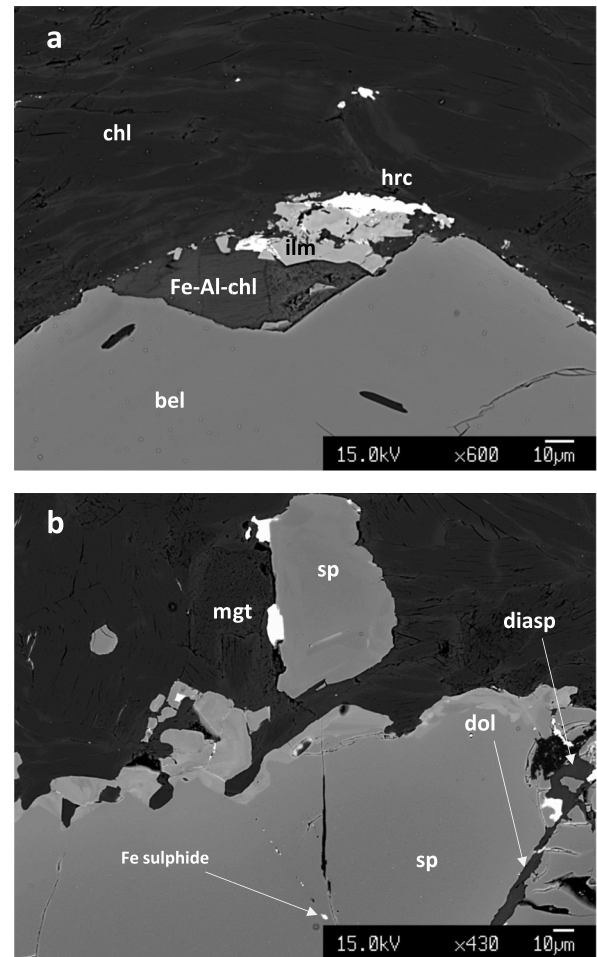


Fig. 7. BSE images showing (a) a detail of the incipient alteration of magnesiobeltrandoite-2N3S (bel) to Fe-Al-rich clinocllore + ilmenite + Cr-rich hercynite, and (b) the Fe-richer zoned rims in spinel grains, cracks filled by dolomite and diasporite.

5.2. Raman spectrum of magnesiobeltrandoite-2N3S

The strongest peak positions in the Raman spectrum of magnesiobeltrandoite-2N3S (Fig. 3a) are observed at 854, 717, 506, and 264 cm^{-1} . Minor bands are also present at 812, 657, 419, 371 and 109 cm^{-1} . Some of the bands are polarized; in particular, the band at 657 cm^{-1} is weaker in the spectrum collected with polarization perpendicular to the length of the crystal.

A weak and polarized band centred at 3364 cm^{-1} (Fig. 3b) corresponds to an O–H bond parallel to c axis, indicating that magnesiobeltrandoite-2N3S is an OH-bearing mineral. A corresponding band was found at 3350 cm^{-1} in magnesiohögbomite-2N3S by Hejny & Armbruster (2002) by FTIR.

The Raman spectra of magnesiobeltrandoite-2N3S present differences with those reported by Shimura *et al.* (2012) for magnesiohögbomite-2N4S, and the “Ti-free högbomite” of Tsunogae & Santosh (2005). For instance, “Ti-free högbomite” of Tsunogae & Santosh (2005) has strong and medium bands at 855, 808, 670, 384 and 263 cm^{-1} , not very different from those found in magnesiobeltrandoite-2N3S. However, “Ti-free högbomite”

Table 7. Refined site-scattering and assigned site-populations for magnesiobeltrandoite-2N3S.

	Al	Mg	Fe ²⁺	Fe ³⁺	Ti ⁴⁺	V ³⁺	Cr ³⁺	Mn ²⁺	Zn	Σ_{cat}	s.s.cal.	s.s.obs.	Δ	$\langle R-O \rangle_{\text{obs}}$	$\langle R-O \rangle_{\text{calc}}$	Δ
M1	0.91			0.02		0.03	0.04			1.00	13.94	13.48	-0.46	1.916	1.917	-0.001
T2	0.15	0.43	0.39						0.03	1.00	36.30	37.45	1.15	1.946	1.950	-0.004
M3	0.89	0.08		0.01			0.02			1.00	79.62	79.48	-0.14	1.930	1.925	0.005
T4	0.62	0.24	0.06	0.08						1.00	29.16	29.92	0.76	1.838	1.842	-0.004
M5		0.07	0.17	0.47	0.28			0.01		1.00	47.78	48.49	0.71	2.044	2.034	0.010
M6	0.88			0.11			0.01			1.00	87.24	86.61	-0.63	1.929	1.922	0.007
T7	0.20	0.38	0.36	0.06						1.00	36.16	37.13	0.97	1.928	1.934	-0.006
M8	0.97						0.03			1.00	26.66	26.73	0.07	1.904	1.911	-0.007
T9	0.04	0.62	0.28	0.06						1.00	33.60	34.81	1.21	1.954	1.962	-0.008
M10	0.96						0.04			1.00	40.32	40.71	0.39	1.916	1.911	0.005
Σ^*	18.37	3.96	2.52	2.08	0.56	0.03	0.40	0.02	0.06	28.00	430.78	434.81				

* Sums taking into account site multiplicity.

Notes: s.s.cal. = calculated site scattering (in electrons per formula unit, epfu); s.s.obs. = observed site scattering (in electrons per formula unit, epfu); Δ = difference; $\langle R-O \rangle_{\text{obs}}$ = observed mean bond length (in Å); $\langle R-O \rangle_{\text{calc}}$ = calculated mean bond length (in Å).

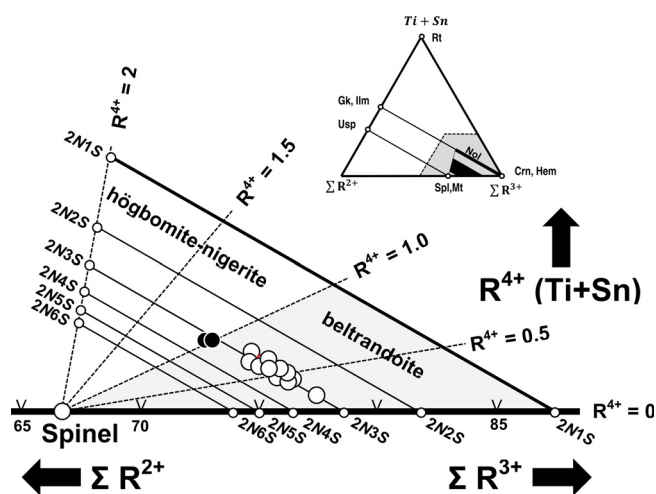


Fig. 8. (Ti + Sn)– ΣR^{2+} – ΣR^{3+} diagram of hōgbomite supergroup minerals (Shimura *et al.*, 2012); (b) close-up of the area for hōgbomite-group minerals. Open circles are the analyses of magnesiobeltrandoite-2N3S from Valtournenche. Filled circles are the hōgbomite analyses of Hejny & Armbruster (2002). Crn = corundum, hem = hematite; spl = spinel; mt = magnetite; usp = ulvöspinel; ilm = ilmenite; gk = geikielite; rt = rutile; nol = nolanite; hgb = hōgbomite.

mite” also shows peaks at 764, 556, 447, 421 and 317 cm^{-1} , which are absent in the Raman spectrum of magnesiobeltrandoite-2N3S. Differences are due perhaps to a different structure, although it is worth noting that the sample reported by Tsunogae & Santosh (2005) is richer in Al and Mg. Magnesiohōgbomite-2N4S has bands at 872, 780, 709, 659, 489, 419, 302, 263, 217, 142 and 104. Some are coincident with bands present in the spectrum reported in Fig. 3a, some others not.

5.3. Crystal-chemistry of magnesiobeltrandoite-2N3S

Magnesiobeltrandoite-2N3S is isostructural with magnesiohōgbomite-2N3S: there are ten symmetrically independent cation sites and ten anion sites. Cation sites are four

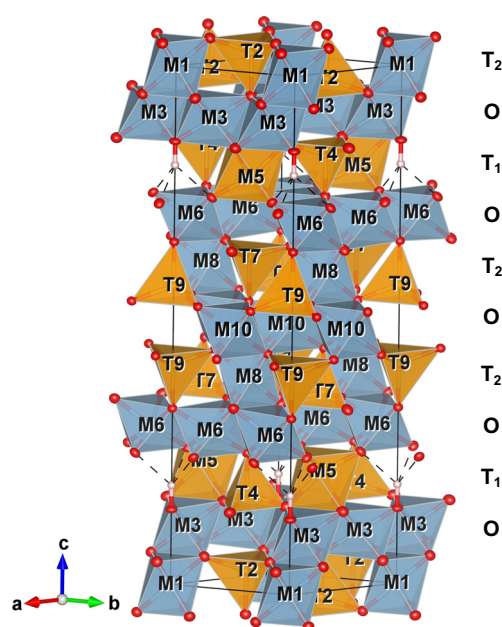


Fig. 9. Detail of the magnesiobeltrandoite-2N3S structure showing Al-dominant octahedra in light blue and (Fe+Mg+Ti) dominant tetrahedra and octahedra in orange. Site labels have been reported. Oxygen sites in red. Thermal displacement ellipsoids shown at 95% probability. The O-layers of octahedrally coordinated cations (M) and T₂-layers of tetrahedrally (T) and octahedrally (M) coordinated cations in spinel module as well as O-layers and T₁-layers of nolanite module are also shown. Plot obtained using Vesta 3 (Momma & Izumi, 2011).

tetrahedra and six octahedra. Two octahedral sites (M3 and M5) and one tetrahedral site (T4) belong to the nolanite modules, while four octahedral sites (M1, M6, M8 and M10) and three tetrahedral sites (T2, T7 and T9) correspond to spinel modules (Fig. 9). Following Hejny & Armbruster (2002), the nolanite modules are composed by a T₁-layer of tetrahedrally (T4) and octahedrally (M5) coordinated atoms and an O-layer built by octahedrally (M3) coordinated sites; the spinel module is composed by

Table 8. Bond-valence values* for structural sites of magnesiobeltrandoite-2N3S.

	M1	T2	M3	T4	M5	M6	T7	M8	T9	M10	H	Σ
O1	0.501 $\times 6\downarrow$	0.518 $\times 3\downarrow$	0.465 $\times 2\downarrow$									1.948
O2		0.510 $\times 3\rightarrow$	0.502									2.017
O3			0.462 $\times 2\downarrow$	0.635 $\times 3\downarrow$	0.319 $\times 3\downarrow$							1.878
III O4			0.441 $\times 3\rightarrow$								0.590	1.913
O5					0.702 $\times 3\downarrow$	0.549 $\times 2\downarrow$					0.133 $\times 3\downarrow$	1.933
O6				0.635		0.472 $\times 3\downarrow$						2.050
O7						0.439 $\times 2\downarrow$	0.563 $\times 3\downarrow$	0.524 $\times 3\downarrow$				2.121
O8						0.517 $\times 3\rightarrow$			0.515			2.066
O9								0.492 $\times 3\downarrow$	0.499 $\times 3\downarrow$	0.512 $\times 4\downarrow$		2.015
O10							0.516			0.457 $\times 2\downarrow$		1.859
BVS	3.006	2.064	2.797	2.540	3.063	2.964	2.175	3.048	2.012	2.961	0.989	
f.c.	3.000	2.150	2.900	2.700	3.030	3.000	2.260	3.000	2.100	3.000	1.000	

* Bond-valence parameters from Brown (1981).

Notes: BVS=bond valence sum; f.c.=formal charge; anion sites coordination reported only for coordination other than IV.

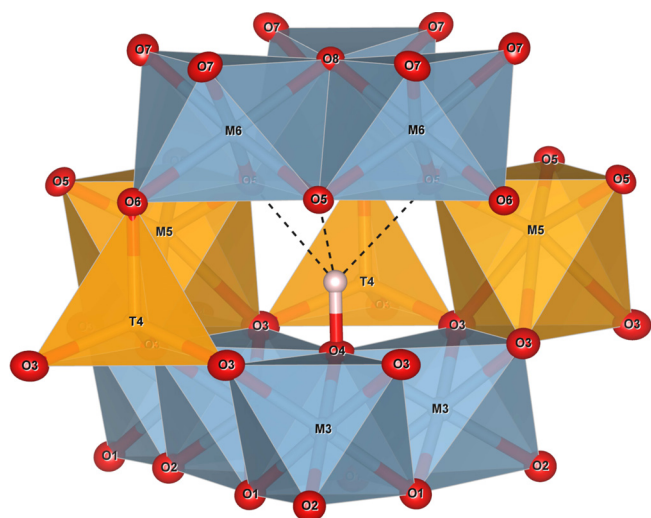


Fig. 10. Detail of the magnesiobeltrandoite-2N3S structure showing Al octahedra in light blue and (Fe+Mg+Ti) bearing tetrahedra and octahedra in orange. Plot obtained using Vesta 3 (Momma & Izumi, 2011).

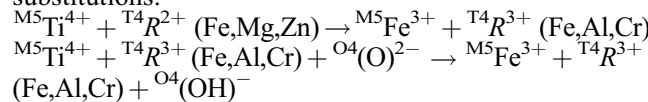
T₂-layers of tetrahedrally (T2, T7 and T9) and octahedrally (M1 and M8) coordinated atoms and an O-layer built by octahedrally (M1 and M10) coordinated sites (Fig. 9).

The largest octahedra and the smaller tetrahedron in the structure are found in the nolanite module, as previously described by Hejny & Armbruster (2002) for magnesioböhmite-2N3S. Considering the chemical composition reported in Table 1, the observed sites scattering (s.s._{obs.}) and mean bond lengths (values taken from Lavinia *et al.*, 2002 and Shannon, 1976), site assignment was calculated and is reported in Table 7. Calculations were done manually, changing site occupancies until reaching the minimum delta values reported in the last column of Table 7. This site assignment implies that a large amount of Fe³⁺ is dominantly ordered in the M5 site of the nolanite module (0.94 apfu), while some Fe³⁺ is present in the tetrahedral sites of the nolanite module (T4,

0.16 apfu) and in the T7 and T9 sites of the T₁-layer of the spinel modules (0.12 apfu each site), as well as in octahedral sites of the spinel modules (up to 0.74 apfu). This site distribution implies a total of 0.4 apfu of tetrahedral Fe³⁺ versus 1.68 octahedral Fe³⁺, i.e. a 24%, which agrees fairly well with the relative areas obtained by SMS spectroscopy (21(1)%, Table 2). Regarding Fe²⁺, it is mostly ordered in tetrahedral sites. Only 0.34 Fe²⁺ apfu is ordered in the two octahedral M5 sites pfu of the nolanite modules, which implies a 14% of octahedral Fe²⁺. This assignment compares also fairly well with the 17% observed by SMS (Table 2). This agreement further supports the site assignment.

The assigned composition of M5 site (Fe_{0.47}³⁺Ti_{0.28}Fe_{0.17}²⁺Mg_{0.07}) implies that the dominant element of the dominant charge is Fe³⁺. This is in good agreement with the observed bond-valence incidence per site calculated with structural data (Table 8), which sees a bond valence incidence of 3.063 v.u. at the M5 site. Slight overbonding is observed for anion site O7, which is related to a very distorted environment for T7 and a particularly small M8 site (occupied almost only by Al). Significant underbonding is observed for O3 and O10 that might reflect cation disorder at the bonded sites T4, M5 and T7 (Table 7) that both anions coordinate.

The entrance of Fe³⁺ as dominant species at M5, the site where Ti and Sn are located in högbomite and nigerite, respectively, can be obtained through two charge-balanced substitutions:



The first substitution assumes complete hydrogenation in the nolanite module and therefore minimum amount of Fe³⁺; this is the one that has been chosen for formula calculation. The second one assumes that the entrance of Ti⁴⁺ at the M5 site promotes dehydrogenation, and therefore yields maximum possible oxidation for Fe. However, without a direct estimation of the oxidation state of Fe or the H content it is not possible to confirm the presence of the second substitution. In addition, the

Table 9. The högbomite supergroup (references are given in brackets).

Högbomite supergroup (Mills <i>et al.</i> , 2009) $N \times \text{TM}_4\text{O}_7(\text{OH}) \cdot S \times \text{T}_2\text{M}_4\text{O}_8$ (theoretical composition)			
Högbomite group	Nigerite group	Taaffeite group	“Beltrandoite group”(*)
Ferrohögbomite-2N2S (1)(2)(3)(4)(5)	Ferronigerite-2N1S (1)(4)(14)(15)(16)(17)(18)	Ferrotaafeite-2N'2S (1)(4)(23)(24)(25)(26)	Magnesiobeltrandoite-2N3S ⁽³²⁾
Magnesiohögbomite-2N2S (1)(2)(3)(4)(5)	Ferronigerite-6N6S (1)(4)(14)(15)(16)(19)(20)	Ferrotaafeite-6N'3S ⁽¹⁾⁽⁴⁾⁽²³⁾⁽²⁷⁾⁽²⁸⁾⁽²⁹⁾	
Magnesiohögbomite-2N3S (1)(2)(4)(6)	Magnesionigerite-2N1S (1)(4)(14)(15)(16)(19)(21)(22)	Magnesiotaaffeite-2N'2S (1)(4)(23)(26)(27)(29)(30)(31)	
Magnesiohögbomite-2N4S (1)(7)	Magnesionigerite-6N6S (1)(4)(14)(15)(16)(19)(21)(22)	Magnesiotaaffeite-6N'3S (1)(4)(23)(25)(27)(29)(30)	
Magnesiohögbomite-6N6S ⁽¹⁾⁽²⁾⁽⁴⁾⁽⁶⁾⁽⁸⁾			
Zincöhögbomite-2N2S ⁽¹⁾⁽²⁾⁽⁴⁾⁽⁶⁾⁽⁹⁾⁽¹⁰⁾			
Zincöhögbomite-2N6S ⁽¹⁾⁽²⁾⁽⁴⁾⁽¹¹⁾⁽¹²⁾⁽¹³⁾			

*Because magnesiobeltrandoite-2N3S is the only mineral in the relevant group, it should be classified as “Unassigned member of the högbomite supergroup”.

References: (1) Armbruster (2002); (2) McKie (1963); (3) Gatehouse & Grey (1982); (4) Hejny & Armbruster (2002); (5) Hejny *et al.* (2002); (6) Gavelin (1916); (7) Shimura *et al.* (2012); (8) Schmetzer & Berger (1990); (9) Armbruster (1998); (10) Ockenga *et al.* (1998); (11) Moleva & Miasnikov (1952); (12) Yalçin *et al.* (1993); (13) Armbruster *et al.* (1998); (14) Bannister *et al.* (1947); (15) Jacobson & Webb (1947); (16) Burke *et al.* (1977); (17) Arakcheeva *et al.* (1995); (18) Yang *et al.* (2013); (19) Peacor (1967); (20) Grey & Gatehouse (1979); (21) Chen *et al.* (1989a); (22) Chen *et al.* (1989b); (23) Anderson *et al.* (1951); (24) Peng & Wang (1963); (25) Nuber & Schmetzer (1983); (26) Yang *et al.* (2012); (27) Hudson *et al.* (1967); (28) Burke & Lustenhouwer (1981); (29) Schmetzer (1983); (30) Bernhard *et al.* (2008); (31) Moor *et al.* (1981); (32) this work.

M5 octahedron is not coordinated with O4 anion, which coordinates M3 octahedron, but both M3 and M5 octahedra share three O3 oxygen sites, and bond strength at the O4 site can be compensated through these shared O sites (Fig. 10). The results of SMS spectrometry thus confirm that the formula assuming full hydration of the O4 sites is the right one.

The ideal formula of magnesiobeltrandoite-2N3S can be obtained considering the ideal composition of the involved modules, *i.e.* two “nolanitic” modules of composition $\text{TAl}^{\text{M}}(\text{Fe}^{3+}\text{Al}_3)\text{O}_7(\text{OH})$ (since Al^{3+} instead of Fe^{3+} is dominant in T4 site) plus three spinel modules ($\text{T}^{\text{Mg}_2}\text{MAl}_4\text{O}_8$), separating the contribution to tetrahedral and octahedral sites as $\text{T}^{\text{Mg}_2}(\text{Mg}_6\text{Al}_2)^{\text{M}}(\text{Al}_{18}\text{Fe}_2^{3+})\text{O}_{38}(\text{OH})_2$, or in a simplified form as $\text{Mg}_6\text{Al}_{20}\text{Fe}_2^{3+}\text{O}_{38}(\text{OH})_2$.

6. Relation to other species

Magnesiobeltrandoite-2N3S, $\text{Mg}_6\text{Al}_{20}\text{Fe}_2^{3+}\text{O}_{38}(\text{OH})_2$ is a new member of the högbomite supergroup (Mills *et al.*, 2009) and the first “nolanitic” Fe^{3+} -dominant member (Table 5). This magnesiobeltrandoite-2N3S is very rich in Fe^{2+} ($\text{Mg} > \text{Fe}^{2+}$ only for 0.10 apfu); a “ferrobeltrandoite-2N3S” most probably occurs in nature. It is worth noting that the amount of Fe^{2+} calculated on the assumption that there are 2 (OH) per formula unit is the maximum amount. The possibility of dehydrogenation (related or not to the Ti content) could only increase the Fe^{3+} and therefore lower further the Fe^{2+} content. Ti-

poor högbomite (Grew *et al.*, 1987; Tsunogae & Santosh, 2005) was already found although no indication of the polysome was provided.

The spinel module of magnesiobeltrandoite-2N3S is basically a spinel, with minor hercynitic molecule. Up to now, all members of the supergroup have modules of aluminous spinels (spinel, hercynite or gahnite). Therefore, the prefix is assigned on the basis of the cation defining the spinel module. The discovery of members with a spinel module corresponding to non-aluminous spinels (*i.e.*, Fe or Cr) would probably require a second prefix.

Recently, an official description of the new borate mineral mengxianminite $[(\text{Ca}, \text{Na})_2\text{Sn}_2(\text{Mg}, \text{Fe})_3\text{Al}_8[(\text{BO}_3)(\text{BeO}_4)\text{O}_6]_2]$ from Xianghualing skarn, Hunan Province, China, has been approved by IMA-CNMNC (Rao *et al.*, 2016). This mineral is supposedly related to the högbomite supergroup of minerals and would be better classified as a taaffeite because of the presence of two Sn apfu in the nolanitic module. However, the presence of B at the T sites of the nolanite modules opens new issues in the nomenclature of the högbomite supergroup.

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References

- Anderson, B.W., Payne, C.J., Claringbull, G.F., Hey, M.H. (1951): Taaffeite, a new beryllium mineral, found as cut gemstone. *Mineral. Mag.*, **29**, 765–772.
- Arakcheeva, A.V., Pushcharovskii, D.Yu., Rastsvetaeva, R.K., Kashaev, A.A., Nadezhina, T.N. (1995): Crystal structure of nigerite-6H. *Crystallogr. Rep.*, **40**, 639–644.
- Armbruster, T. (1998): Zincohögbomite-8H from Samos (Greece): crystal structure, polysomatism and polytypism in högbomite related structures. *Schweiz. Miner. Petrogr. Mitt.*, **78**, 461–468.
- (2002): Revised nomenclature of högbomite, nigerite, and taaffeite minerals. *Eur. J. Mineral.*, **14**, 389–395.
- Armbruster, T., Bermanec, V., Zebec, V., Oberhänsli, R. (1998): Titanium and iron poor zincohögbomite-16H, $\text{Zn}_{14}(\text{Al}, \text{Fe}^{3+}, \text{Ti}, \text{Mg})_8\text{Al}_{24}\text{O}_{62}(\text{OH})_2$, from Nezilovo, Macedonia: occurrence and crystal structure of a new polysome. *Schweiz. Miner. Petrogr. Mitt.*, **78**, 469–477.
- Ballèvre, M., Kienast, J.-R., Vuichard, J.P. (1986): La nappe de la Dent-Blanche (Alpes occidentales): deux unités austroalpines indépendantes. *Eclogae Geol. Helv.*, **79**, 57–74.
- Bannister, F.A., Hey, M.H., Stadler, H.P. (1947): Nigerite, a new tin mineral. *Mineral. Mag.*, **28**, 129–136.
- Bayliss, P. (1975): Nomenclature of the trioctahedral chlorites. *Can. Mineral.*, **13**, 178–180.
- Beltrando, M., Rubatto, D., Manatschal, G. (2010): From passive margins to orogens: the link between ocean-continent transition zones and (ultra)high-pressure metamorphism. *Geology*, **6**, 559–562.
- Bernhard, F., Hauzenberger, C., Walter, F., Kristiansen, R. (2008): Pseudosinhalite, magnesiotaaffeite-6N3S and magnesiotaaffeite-2N2S as replacement products of spinel in dolomite marble from Stubenberg, Styria, Austria. *Can. Mineral.*, **46**, 1195–1205.
- Brown, I.D. (1981): The bond-valence method: an empirical approach to chemical structure and bonding. in “Structure and bonding in crystals”, M. O’Keeffe, A. Navrotsky, eds. Academic Press, New York, **Vol. II**, 1–30.
- Burke, E.A.J. & Lustenhouwer, W.J. (1981): Pehrmanite, a new beryllium mineral from Rosendal Pegmatite, Kemiö Island, southwestern Finland. *Can. Mineral.*, **19**, 311–314.
- Burke, E.A.J., Lof, P., Hazebroek, H.P. (1977): Nigerite from the Rosendal pegmatite and aplites, Kemiö Island, Southwestern Finland. *Bull. Geol. Soc. Finland*, **49**, 151–157.
- Chen, J., Yang, G., Pan, Z., Shi, N., Peng, Z. (1989a): Discovery and study of pengzhizhongite-6H: a new mineral. *Acta Mineral. Sin.*, **9**, 20–24 (in Chinese).
- Chen, J., Shi, Y., Pan, Z., Peng, Z. (1989b): The crystal structure and crystal chemistry of a new mineral, pengzhizhongite-6H. *Earth Sci. J. China Univ. Geosci.*, **14**, 413–422 (in Chinese).
- Dal Piaz, G.V., Cortiana, G., Del Moro, A., Martin, S., Pennacchioni, G., Tartarotti, P. (2001): Tertiary age and paleostructural inferences of the eclogitic imprint in the Austroalpine outliers and Zermatt-Saas ophiolite, western Alps. *Int. J. Earth Sci.*, **90**, 668–684.
- Dal Piaz, G.V., Bistacchi, A., Gianotti, F., Monopoli, B., Passeri, L., Schiavo, A., Bertolo, D., Bonetto, F., Ciarapica, G., Dal Piaz, G., Gouffon, Y., Massironi, M., Ratto, S., Toffolon, G. (2015): Note illustrative della Carta Geologica d’Italia alla scala 1:50.000. Sheet 070, Monte Cervino, 431 p.
- Downs, R.T., Bartelmehs, K.L., Gibbs, G.V., Boisen Jr. M.B. (1993): Interactive software for calculating and displaying X-ray or neutron powder diffractometer patterns of crystalline materials. *Am. Mineral.*, **78**, 1104–1107.
- Fassmer, K., Obermüller, G., Nagel, T.J., Kirst, F., Froitzheim, N., Sandmann, S., Miladinova, I., Fonseca, R.O.C., Munker, C. (2016): High-pressure metamorphic age and significance of eclogite-facies continental fragments associated with oceanic lithosphere in the Western Alps (Etirol-Levaz Slice, Valtour-nenche, Italy). *Lithos*, **252–253**, 145–159.
- Gatehouse, B.M. & Grey, I.E. (1982): The crystal structure of högbomite-8H. *Am. Mineral.*, **67**, 373–380.
- Gavelin, A. (1916): Über Högbomit. *Bull. Geol. Inst. Univ. Upps.*, **15**, 289–316.
- Grew, E.S., Abraham, K., Medenbach, O. (1987): Ti-poor högbomite in kornepurine-cordierite-sillimanite rocks from Ellammankovilpatti, Tamil Nadu, India. *Contrib. Mineral. Petrol.*, **95**, 21–31.
- Grey, I.E. & Gatehouse, B.M. (1979): The crystal structure of nigerite-24R. *Am. Mineral.*, **64**, 1255–1264.
- Hejny, C. & Armbruster, T. (2002): Polysomatism in högbomite: the crystal structures of 10T, 12H, 14T, and 24R polysomes. *Am. Mineral.*, **87**, 277–292.
- Hejny, C., Gnos, E., Grobety, B., Armbruster, T. (2002): Crystal chemistry of the polysome ferrohögbomite-2N2S, a long-known but newly defined mineral species. *Eur. J. Mineral.*, **14**, 957–967.
- Horiba Jobin Yvon (2004, 2005): LabSpec software for Raman spectroscopic data analysis, acquisition and manipulation. Version 5.64.15. HORIBA Jobin Yvon SAS, Villeneuve d’Ascq, France.
- Hudson, D.R., Wilson, A.F., Threadgold, I.M. (1967): A new polytype of taaffeite—a rare beryllium mineral from the granulites of central Australia. *Mineral. Mag.*, **36**, 305–310.
- Jacobson, R. & Webb, J.S. (1947): The occurrence of nigerite, a new tin mineral in quartz-sillimanite-rocks from Nigeria. *Mineral. Mag.*, **28**, 118–128.
- Kienast, J.-R. (1983) Le métamorphisme de haute pression et basse température (éclogites et schistes bleus): données nouvelles sur la pétrologie des roches de la croûte océanique subductée et des sédiments associés. PhD Thesis, No. 83-49, Université Pierre et Marie Curie, Paris 6, 532 p.
- Larson, A.C. & Von Dreele, R.B. (1994): General Structure Analysis System (GSAS). Los Alamos National Laboratory Report LAUR, 86-748.
- Lavinia, B., Salviulo, G., Della Giusta, A. (2002): Cation distribution and structure modelling of spinel solid solutions. *Phys. Chem. Minerals*, **29**, 10–18.
- Malcherek, Th. & Schlüter, J. (2016): Crystal structure of Cr-bearing $\text{Mg}_3\text{BeAl}_8\text{O}_{16}$, a new polytype of magnesiotaaffeite-2N2S. *Acta Crystallogr.*, **E72**, 1060–1063.
- Mandarino, J.A. (1979): The Gladstone-Dale relationship. Part III. Some general applications. *Can. Mineral.*, **17**, 71–76.
- (1981): The Gladstone-Dale relationship. Part IV. The compatibility concept and its application. *Can. Mineral.*, **19**, 441–450.
- McKie, D. (1963): The högbomite polytypes. *Mineral. Mag.*, **33**, 563–580.
- Mills, S.J., Hatert, F., Nickel, E.H., Ferraris, G. (2009): The standardisation of mineral group hierarchies: application to recent nomenclature proposals. *Eur. J. Mineral.*, **21**, 1073–1080.
- Moleva, V.A. & Myasnikov, V.S. (1952): Högbomite and its variety, zinc högbomite. *Dokl. Akad. Nauk SSSR*, **83**, 733–736 (in Russian).
- Momma, K. & Izumi, F. (2011): VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.*, **44**, 1272–1276.

- Moor, R., Oberholzer, W.F., Gübelin, E. (1981): Taprobanite, a new mineral of the taaffeite-group. *Schweiz. Miner. Petrogr. Mitt.*, **61**, 13–21.
- Nuber, B. & Schmetzer, K. (1983): Crystal structure of ternary Be–Mg–Al oxides: taaffeite, $\text{BeMg}_3\text{Al}_8\text{O}_{16}$, and musgravite, $\text{BeMg}_2\text{Al}_6\text{O}_{12}$. *Neues Jb. Miner. Monath.*, **1983**, 393–402.
- Ockenga, E., Yalçin, Ü., Medenbach, O., Schreyer, W. (1998): Zincohögbomite, a new mineral from eastern Aegean metabauxites. *Eur. J. Mineral.*, **10**, 1361–1366.
- Peacor, D.R. (1967): New data on nigerite. *Am. Mineral.*, **52**, 864–866.
- Peng, C.C. & Wang, K.J. (1963): Discovery of a compact structure with 8-layers. Crystal structure analysis of taaffeite. *Sci. Sin.*, **12**, 276–278 (in Russian). [M.A. 16-609].
- Potapkin, V., Chumakov, A.I., Smimov, G.V., Celse, J.P., Rüffer, R., McCammon, C., Dubrovinsky, L. (2012): The ^{57}Fe Synchrotron Mössbauer Source at the ESRF. *J. Synchrotron Radiat.*, **19**, 559–569.
- Pouchou, J.L. & Pichoir, F. (1985): “PAP” ($\phi\rho Z$) procedure for improved quantitative microanalysis. in “Microbeam analysis”, J.T. Armstrong, ed. San Francisco Press, San Francisco, CA, USA, 104–106.
- Prescher, C., McCammon, C., Dubrovinsky, L. (2012): MossA: a program for analyzing energy-domain Mössbauer spectra from conventional and synchrotron sources. *J. Appl. Crystallogr.*, **45**, 329–331.
- Rao, C., Hatert, F., Dal Bo, F., Wang, R., Gu, X., Baijot, M. (2016): Mengxianminite, IMA 2015-070. CNMNC Newsletter No. 29, February 2016, 200. *Mineral. Mag.*, **80**, 199–205.
- Regis, D. (2007) The Austroalpine slice of Etnol-Levaz (Valtournenche, Valle d’Aosta): new data on the prograde metamorphic path and eclogite-facies peak. Unpublished MSc Thesis, University of Torino, 98 p. (in Italian).
- Regis, D., Cossio, R., Compagnoni, R. (2015): Alpine corundum-bearing veins from the Etnol-Levaz austroalpine continental slice (Valtournenche, Aosta, Italy). *Rend. Online Soc. Geol. Ital.*, **37**, 57–60.
- Robinson, K., Gibbs, G.V., Ribbe, P.H. (1971): Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science*, **172**, 567–570.
- Rubatto, D., Regis, D., Hermann, J., Boston, K., Engi, M., Beltrando, M., McAlpine, S.R.B. (2011): Yo-yo subduction recorded by accessory minerals in the Italian Western Alps. *Nat. Geosci.*, **4**, 338–342.
- Rüffer, R. & Chumakov, A.I. (1996): Nuclear-resonance beamline at ESRF. *Hyperfine Interact.*, **97**, 589–604.
- Schmetzer, K. (1983): Crystal chemistry of natural Be–Mg–Al-oxides: taaffeite, taprobanite, musgravite. *Neues Jb. Miner. Abh.*, **146**, 15–28.
- Schmetzer, K. & Berger, A. (1990): Lamellar iron-free högbomite-24R from Tanzania. *Neues Jb. Miner. Mh.*, **1990**, 401–412.
- Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.*, **A32**, 751–767.
- Shimura, T., Akai, J., Lazic, B., Armbruster, T., Shimizu, M., Kamei, A., Tsukada, K., Owada, M., Yuhara, M. (2012): Magnesio-högbomite-2N4S: a new polysome from the central Sør Rondane Mountains, East Antarctica. *Am. Mineral.*, **97**, 268–280.
- Tsunogae, T. & Santosh, M. (2005): Ti-free högbomite in spinel- and sapphirine-bearing Mg–Al rock from the Palghat-Cauvery shear zone, southern India. *Mineral. Mag.*, **69**, 937–949.
- Yalçin, Ü., Schreyer, W., Medenbach, O. (1993): Zn-rich högbomite formed from gahnite in the metabauxites of the Menderes Massif, SW Turkey. *Contrib. Mineral. Petrol.*, **113**, 314–324.
- Yang, Z., Ding, K., De Fourestier, J.D., Mao, Q., Li, H. (2012): Ferrotaaffeite-2N’2S, a new mineral species, and the crystal structure of Fe^{2+} -rich magnesiotaaffeite-2N’2S from the Xianghualing tin-polymetallic ore field, Hunan Province, China. *Can. Mineral.*, **50**, 21–29.
- Yang, Z., De Fourestier, J.D., Ding, K., Li, H. (2013): Li-bearing ferronigerite-2N1S from the Xianghualing tin-polymetallic ore field, Hunan Province, China. *Can. Mineral.*, **51**, 913–919.

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