

Hydroxycalciumicrolite, $\text{Ca}_{1.5}\text{Ta}_2\text{O}_6(\text{OH})$, a new member of the microlite group from Volta Grande pegmatite, Nazareno, Minas Gerais, Brazil

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[Received 4 January 2015; Accepted 11 May 2016; Associate Editor: Ian Graham]

ABSTRACT

Hydroxycalciumicrolite, $\text{Ca}_{1.5}\text{Ta}_2\text{O}_6(\text{OH})$ is a new microlite-group mineral found in the Volta Grande pegmatite, Nazareno, Minas Gerais, Brazil. It occurs as isolated octahedral and as a combination of octahedral and rhombic dodecahedral crystals, up to 1.5 mm in size. The crystals are yellow and translucent, with a white streak and vitreous to resinous lustre. The mineral is brittle, with a Mohs hardness of 5–6. Cleavage is not observed and fracture is conchoidal. The calculated density is 6.176 g cm^{-3} . Hydroxycalciumicrolite is isotropic, $n_{\text{calc.}} = 2.010$. The infrared and Raman spectra exhibit bands due to O–H stretching vibrations. The chemical composition determined from electron microprobe analysis ($n = 13$) is (wt.%): Na_2O 0.36(8), CaO 15.64(13), SnO_2 0.26(3), Nb_2O_5 2.82(30), Ta_2O_5 78.39(22), MnO 0.12(2), F 0.72(12) and H_2O 1.30 (from the crystal structure data), $\text{O} = \text{F} - 0.30$, total 99.31(32), yielding an empirical formula, $(\text{Ca}_{1.48}\text{Na}_{0.06}\text{Mn}_{0.01})_{\Sigma 1.55}(\text{Ta}_{1.88}\text{Nb}_{0.11}\text{Sn}_{0.01})_{\Sigma 2.00}\text{O}_{6.00}[(\text{OH})_{0.76}\text{F}_{0.20}\text{O}_{0.04}]$. Hydroxycalciumicrolite is cubic, with unit-cell parameters $a = 10.4205(1) \text{ Å}$, $V = 1131.53(2) \text{ Å}^3$ and $Z = 8$. It represents a pyrochlore supergroup, microlite-group mineral exhibiting $P4_332$ symmetry, instead of $Fd\bar{3}m$. The reduction in symmetry is due to long-range ordering of Ca and vacancies on the A sites. This is the first example of such ordering in a natural pyrochlore, although it is known from synthetic compounds. This result is promising because it suggests that other species with $P4_332$ or lower-symmetry space group can be discovered and characterized.

KEYWORDS: hydroxycalciumicrolite, $\text{Ca}_{1.5}\text{Ta}_2\text{O}_6(\text{OH})$, pyrochlore supergroup, microlite group, crystal structure, Raman spectra, infrared spectrum.

Introduction

HYDROXYCALCIOMICROLITE, $\text{Ca}_{1.5}\text{Ta}_2\text{O}_6(\text{OH})$, from the Volta Grande pegmatite, Nazareno, Minas Gerais, Brazil, is a new mineral (IMA 2013-073) named according to the nomenclature system for the pyrochlore supergroup of minerals approved by

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<https://doi.org/10.1180/minmag.2016.080.116>

IMA-CNMNC (Atencio *et al.*, 2010). The general formula of the pyrochlore-supergrupp minerals is $A_{2-m}B_2X_{6-w}Y_{1-n}$, where $m = 0$ to 1.7, $w = 0$ to 0.7, $n = 0$ to 1 (Lumpkin and Ewing, 1995). In hydroxycalciummicrolite, the *A*, *B* and *Y* sites are dominated by Ca, Ta and OH, respectively. The type material is deposited in the Museu de Geociências, Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil, registration number DR917. Part of the cotype sample has been deposited at the University of Arizona Mineral Museum, RRUFF Project (<http://ruff.info/R130269>).

Occurrence, physical properties, chemical composition and vibrational spectroscopy

Hydroxycalciummicrolite occurs as an accessory phase in the Volta Grande pegmatite (21°10'08.6" S 44°36'01.3"W), Nazareno, Minas Gerais, Brazil. The pegmatites of Volta Grande field, intrusive into Archaean amphibolites (tholeiitic metabasalts), are probably related to the Transamazonian-cycle age Ritópolis granite, which is contemporaneous with the Tabuões trondhjemitic, dated by Quéméneur and Vidal (1989) at 1931 ± 20 Ma. The ore extraction process in the Volta Grande mine has been described by Heinrich (1964). In the past the kaolinized pegmatite was hauled by scraper to a hopper where it was washed by means of hoses into a series of sluice boxes in which kaolinite and mica were almost entirely removed along with most of the quartz particles. The residuum of quartz and heavy minerals was further concentrated by washing and then dried before shipment to the separation plant. The concentrate was separated magnetically and electrostatically into fractions: (1) cassiterite; (2) 'tantalite'; (3) 'microlite' ('djalmaita'); and (4) ilmenite + 'garnet'. Some papers on the Volta Grande pegmatites present no paragenetic data as they have been based on these minerals concentrates (e.g. Guimarães, 1950; Francesconi, 1972; Francesconi *et al.*, 1976). Several minerals were identified in the concentrates: albite, almandine, 'amphibole', beryl, bityite, brookite, cassiterite, epidote, fluorite, fluorapatite, gahnite, goethite, hematite, ixiolite, 'lepidolite', magnetite, microcline, 'microlite' monazite-(Ce), muscovite, 'pyrochlore', quartz, rutile, samarskite-(Y), spodumene, tantalite-(Mn), 'tourmaline', 'varlamoffite', xenotime-(Y) and zircon. Hydroxycalciummicrolite (10 crystals) was separated from an old concentrate, labelled

'djalmaita', from the Museu de Geociências, Universidade de São Paulo, without the details of donor registration. Hydrokenomicrolite (Andrade *et al.*, 2013a) and fluorcalciummicrolite (Andrade *et al.*, 2013b) are also from the same concentrate. So no paragenetic data can be presented for these minerals. Information concerning mineralogical parageneses were summarized by Pires and Cabral (1998). The pegmatites of the Rio da Mortes tin district (Rolff, 1948) were first investigated by Guimarães and Guedes (1944, 1946), who recorded the following mineralogical distribution in outcrops of the pegmatite along its strike from Rio das Mortes towards Fazenda Volta Grande, after which the pegmatite bodies were collectively named: 80 m of cm-sized crystals of spodumene and feldspars, 300 m of coarse-grained cassiterite, muscovite and quartz, followed by 30 m of mm-sized crystals of lepidolite. Relics of spodumene enclosed in quartz and microcline, or in a micaceous aggregate, were found in the spodumene-poor zones. These authors proposed two stages of pegmatite formation: (1) calcic-sodic stage, marked by crystallization of oligoclase, to which cassiterite and spodumene are probably related; and (2) a potassic stage, responsible for the formation of microcline and muscovite, both along with quartz, at the expense of oligoclase and spodumene, respectively. Spodumene may be replaced by quartz with formation of lepidolite (Guimarães 1948, 1950). The paragenetic relations amongst ore (opaque) minerals were established by Guimarães (1950). He concluded that tantalite was contemporaneous with cassiterite; 'uranmicrolite' formed later, as indicated by the inclusion of cassiterite grains in the latter. Further textural evidence demonstrated that replacement of tantalite by microlite occurred (Peixoto and Guimarães, 1953). Whether tantalite altered to microlite or 'uranmicrolite' was attributed to the local availability of uranium in the hydrothermal solution (Belezkij, 1956; Guimarães and Belezkij, 1956). A similar paragenetic sequence in two stages was proposed by Heinrich (1964): (1) magmatic, with quartz, muscovite, microcline, spodumene, sodic plagioclase, cassiterite and tantalite as main phases; and (2) hydrothermal, characterized by lepidolite and microlite, and barium microlite (which is intergrown with microlite and replaces it). He considered that several of the pegmatite bodies were the result of two or more periods of injection of pegmatite-forming magma. The calcic-sodic stage advanced by Guimarães and Guedes (1944) was not recognized by Heinrich (1964); however,

Francesconi (1972) characterized the existence of the calcic-sodic stage, and attributed it to a final alkaline stage (K, Li, Rb, Cs) forming lepidolite, bityite, microlite and zircon (now metamict). Although Heinrich (1964) stated that nearly all pegmatites are either unzoned or indistinctly zoned, the distribution of spodumene, lepidolite and muscovite recorded by Guimarães and Guedes (1944, 1946) is suggestive of zoning of the bodies. At the Volta Grande mine, a well-defined lepidolite-spodumene boundary can be traced along ore bodies (Pires and Pires 1992). Internal zoning in the pegmatites has been reported by Quéménéur (1987). The Volta Grande pegmatites present a particular zonation. This consists of an aplitic zone of fine-grained albite in the border, which wraps a principal mass of granitoid composed of spodumene, quartz, albite, microcline and muscovite. At the centre of this granitoid zone, a lenticular layer (0.5 to 3 m thick) exists, composed of large spodumene crystals and intergranular quartz. In the central part, the ore bodies also contain compact lepidolite lenses. These pegmatites are mined for tin and tantalum and are characterized by their enrichment in rubidium (0.8% Rb_2O on average in the bulk composition). A contact aureole is well-developed and affects the wall rock amphibolite to a thickness of 2 to 3 m. This aureole does not contain tourmaline, and contains two distinct facies: a thin layer of zinnwaldite glimmerite (2 cm thick, locally with some pockets >100 cm thickness), and a facies with holmquistite and scattered zinnwaldite of 1 to 3 m thick that passes into fresh amphibolite (Quéménéur and Lagache, 1994). No propylitic alteration was observed (Quéménéur and Lagache, 1999). Data on the microlite-group minerals were obtained by Pinto (2000). Hafnium from the Volta Grande pegmatite was described by Pereira *et al.* (2002, 2003, 2004).

Hydroxycalciumicrolite occurs as isolated octahedral and as a combination of octahedral and rhombic dodecahedral crystals, up to 1.5 mm in size (Fig. 1). The mineral is yellow and translucent, with a white streak and vitreous to resinous lustre. The mineral is colourless under plane-polarized light. No anomalous anisotropy was noted. It is non-fluorescent under short- and long-wave ultraviolet light. It does not exhibit cathodoluminescence under an electron microprobe beam. The mineral is brittle, with a Mohs' hardness of 5–6 and conchoidal fracture. Cleavage was not observed. The calculated density is 6.176 g cm^{-3} , based on the empirical formula and unit-cell parameters obtained from the single-crystal X-ray diffraction



FIG. 1. Hydroxycalciumicrolite crystal from Nazareno, Minas Gerais, Brazil.

data. Optically, the mineral is isotropic. The refractive index calculated from the Gladstone-Dale relationship is $n_{\text{calc.}} = 2.010$ (higher than that of readily available immersion liquids).

The chemical composition of hydroxycalciumicrolite was determined using a CAMECA SX50 electron microprobe (25 kV, 20 nA, 1 μm beam diameter) with a dwell (peak) time of 20 s (10 s on backgrounds) for all elements. Investigation using back-scattered electrons (BSE) (Fig. 2) showed that the sample is homogenous and wavelength-dispersive spectroscopy was used (Jercinovic *et al.*, 2012) to determine the presence of trace elements (< 0.1 wt%) with a detection limit of 0.03 wt%. The standards included albite (Na), diopside (Ca), cassiterite (Sn), LiNbO_3 (Nb), LiTaO_3 (Ta), rhodonite (Mn) and MgF_2 (F), yielding an

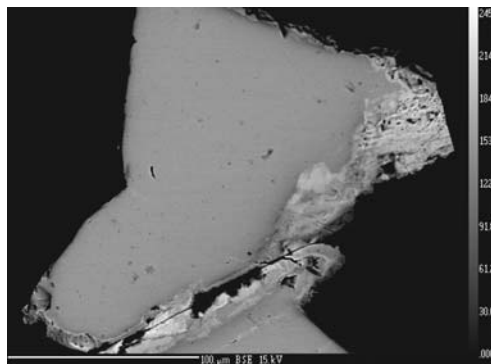


FIG. 2. Backscattered electron image of the hydroxycalciumicrolite grain analysed in this study.

TABLE 1. Powder X-ray diffraction data for hydroxycalciumicrolite (indexed with $a = 10.4280(8)$ Å)* and for fluorcalciumicrolite (Andrade *et al.*, 2013*b*) (indexed with $a = 10.417(1)$ Å)*.

Hydroxycalciumicrolite			Fluorcalciumicrolite					
I_{rel}	$d_{\text{meas.}}(\text{Å})$	$d_{\text{calc.}}(\text{Å})$	I_{rel}	$d_{\text{meas.}}(\text{Å})$	$d_{\text{calc.}}(\text{Å})$	h	k	l
1	7.367	7.374				1	1	0
100	6.025	6.021	59	5.997	6.014	1	1	1
1	4.661	4.664				2	1	0
1	4.255	4.257				2	1	1
<1	3.677	3.687				2	2	0
15	3.145	3.144	83	3.138	3.141	3	1	1
73	3.010	3.010	100	3.005	3.007	2	2	2
7	2.606	2.607	29	2.602	2.604	4	0	0
2	2.391	2.392	14	2.389	2.390	3	3	1
7	2.006	2.007	23	2.004	2.005	5	1	1
7	2.006	2.007				3	3	3
8	1.843	1.843	23	1.841	1.8415	4	4	0
4	1.762	1.763	13	1.760	1.7608	5	3	1
2	1.591	1.590	25	1.589	1.586	5	3	3
5	1.572	1.572	17	1.571	1.5704	6	2	2
4	1.505	1.505	24	1.504	1.5036	4	4	4
2	1.460	1.460				1	5	5
2	1.460	1.460	21	1.459	1.4587	1	1	7
2	1.358	1.358	7	1.356	1.3562	1	3	7
2	1.358	1.358				3	5	5

*Calculated data were obtained using *CELLCALC* software (Miura, 2003).

The strongest lines are given in bold.

average composition (wt.%) (13 points in one grain) of Na₂O 0.36(8), CaO 15.64(13), SnO₂ 0.26(3), Nb₂O₅ 2.82(30), Ta₂O₅ 78.39(22), MnO 0.12(2), F 0.12(12) and H₂O 1.30 (from the crystal structure data), (O = F) −0.30, total = 99.31 (32). Sodium was analysed before any of the other elements for each spot analysis to prevent volatilization.

The resultant chemical formula, calculated on the basis of 2 cations per formula unit at the *B* site is (Ca_{1.48}Na_{0.06}Mn_{0.01}□_{0.45})_{Σ2.00}(Ta_{1.88}Nb_{0.11}Sn_{0.01})_{Σ2}O₆[(OH)_{0.76}F_{0.20}O_{0.04}], which can be simplified to the charge-balanced end-member Ca_{1.5}Ta₂O₆(OH). This ideal formula corresponds to the following oxide weight percentages: CaO = 15.72, Ta₂O₅ = 82.60, H₂O = 1.68, total 100.00.

The Raman spectrum of hydroxycalciumicrolite was collected from a randomly oriented crystal on a Thermo-Almega microRaman system, using a 532 nm solid-state laser with a thermoelectric cooled CCD detector. The laser is partially polarized with 4 cm^{−1} resolution and a spot size of 1 μm.

The infrared (IR) absorption spectrum of hydroxycalciumicrolite was obtained from a powdered

sample (mixed with KBr and pelletized) using a Bruker Alpha FTIR spectrometer, with resolution 4 cm^{−1}.

X-ray and neutron crystallography

The powder X-ray diffraction data of hydroxycalciumicrolite were obtained using a Bruker D8 Advance DaVinci diffractometer with CuKα ($\lambda = 1.54058$ Å) radiation. Unit-cell parameters refined from the powder data are $a = 10.4280(8)$ Å and $V = 1134.0(2)$ Å³. Powder X-ray diffraction data for hydroxycalciumicrolite and fluorcalciumicrolite are compared in Table 1. Some forbidden lines for *Fd3m* are observed in hydroxycalciumicrolite: (110), (210) and (211).

A single crystal of hydroxycalciumicrolite with dimensions 0.05 mm × 0.04 mm × 0.02 mm was used for the structural investigation. X-ray diffraction measurements were made on a Bruker X8 APEX2 CCD diffractometer with graphite monochromatized MoKα radiation with frame widths of 0.5° in ω and 30 s counting time per frame. The

HYDROXYCALCIOMICROLITE, A NEW MEMBER OF THE MICROLITE GROUP

TABLE 2. Summary of crystallographic data and refinement results for hydroxycalciumicrolite.

Chemical formula	(Ca _{1.46} Na _{0.15}) _{Σ1.61} (Ta _{1.72} Nb _{0.28}) _{Σ2.00} O ₆ [(OH) _{0.65} F _{0.35}]
Space group	<i>P</i> 4 ₃ 32 (#212)
<i>a</i> (Å)	10.4205(1)
<i>V</i> (Å ³)	1131.53(2)
<i>Z</i>	8
ρ _{cal} (g/cm ³)	6.020
λ (Å)	0.71073
μ (mm ⁻¹)	35.10
2θ max. for data collection(°)	≤69
No. of reflections collected	6086
No. of independent reflections	749
No. of reflections with <i>I</i> > 2σ(<i>I</i>)	497
No. of parameters refined	35
<i>R</i> (int)	0.021
Final <i>R</i> factors [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.030, <i>wR</i> ₂ = 0.051
Final <i>R</i> factors (all data)	<i>R</i> ₁ = 0.050, <i>wR</i> ₂ = 0.044
Goodness-of-fit	1.11

SAINT program (Bruker, 2007) was used for data collection and reduction. The intensity data were corrected for X-ray absorption by the multi-scan

method using the Bruker program *SADABS* (Bruker, 2007). Observed systematic absence of reflections indicate the unique space-group

TABLE 3. Coordinates and displacements parameters of atoms for hydroxycalciumicrolite.

Atom	Wyckoff	<i>X</i>	<i>y</i>	<i>z</i>	occupancy	<i>U</i> _{eq}
Ta2	12 <i>d</i>	0.375	0.37388(2)	0.12388(2)	0.86(2)	0.0042(2)
Nb2	12 <i>d</i>	0.375	0.37388(2)	0.12388(2)	0.14(2)	0.0042(2)
Ta1	4 <i>a</i>	0.125	0.125	0.125	0.89(2)	0.0044(2)
Nb1	4 <i>a</i>	0.125	0.125	0.125	0.07(3)	0.0044(2)
Ca1	12 <i>d</i>	0.6217(2)	0.3717(2)	0.375	0.972(19)	0.0155(7)
Na1	4 <i>b</i>	0.625	0.625	0.625	0.31(3)	0.008(2)
O3	24 <i>e</i>	0.2517(5)	0.0592(5)	0.2482(6)	1	0.0124(11)
O2	24 <i>e</i>	0.4447(5)	0.2507(5)	0.2506(5)	1	0.0103(10)
F1	8 <i>c</i>	0.481(3)	0.481(3)	0.481(3)	0.35(9)	0.016(8)
O1	8 <i>c</i>	0.5046(14)	0.5046(14)	0.5046(14)	0.65(9)	0.001(4)
H1	8 <i>c</i>	0.5538(18)	0.5538(18)	0.5538(18)	0.65(37)	0.03
Atom	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ²³	<i>U</i> ¹³	<i>U</i> ¹²
Ta2	0.0042(2)	0.00422(17)	0.00422(17)	0.00172(12)	0.00020(11)	−0.00020(11)
Nb2	0.0042(2)	0.00422(17)	0.00422(17)	0.00172(12)	0.00020(11)	−0.00020(11)
Ta1	0.0044(2)	0.0044(2)	0.0044(2)	−0.00014(19)	−0.00014(19)	−0.00014(19)
Nb1	0.0044(2)	0.0044(2)	0.0044(2)	−0.00014(19)	−0.00014(19)	−0.00014(19)
Ca1	0.0159(8)	0.0159(8)	0.0146(11)	−0.0050(7)	0.0050(7)	0.0045(12)
Na1						
O3						
O2						
F1						
O1						
H1						

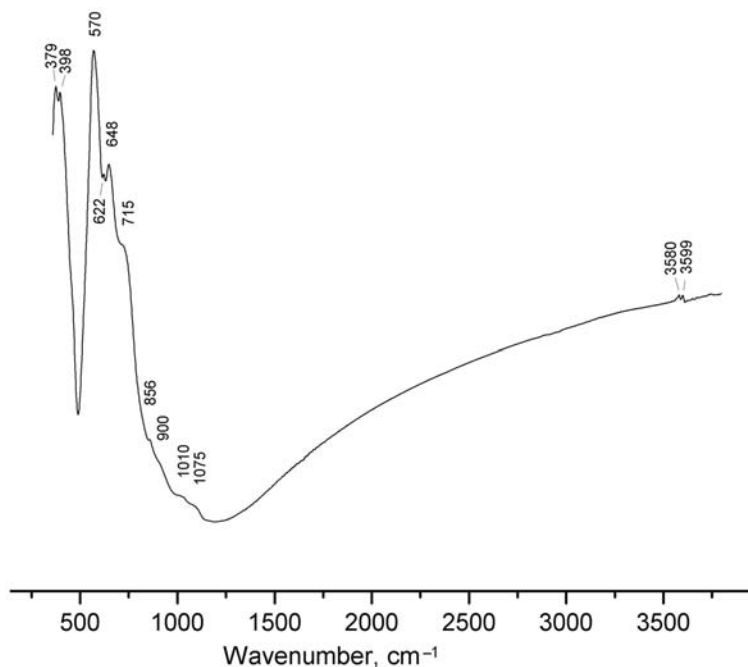


FIG. 3. Infrared spectrum of hydroxycalcimicrolite.

$P4_332$ (#212). The structure was solved and refined with *SHELX97* (Sheldrick, 2008). The details for data collection and structural refinements are summarized in Table 2. Atomic coordinates and displacement parameters are listed in Table 3. A table of structure factors and a crystallographic information file have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from http://www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Single-crystal neutron diffraction was carried-out to locate the H atom position with a Very Intense Vertical Axis Laue Diffractometer (VIVALDI) on a polychromatic thermal neutron beam (0.8–5.2 Å) coupled with a large solid-angle (eight steradians) cylindrical image plate detector, at the High Flux reactor of the Institut Laue-Langevin in Grenoble, France (Wilkinson *et al.*, 2002; McIntyre *et al.*, 2006).

Discussion

Infrared and Raman data

The IR spectrum of hydroxycalcimicrolite (Fig. 3) shows two weak bands at 3580 and 3599 cm^{-1} that are attributable to O–H stretching vibrations,

indicative of very weak or almost no hydrogen bonding (Libowitzky, 1999). Weak bands at 856, 900, 1010 and 1075 cm^{-1} correspond to overtones and combination modes. In general, H–O–H angle bending is associated with absorption peaks in the range 1500–1700 cm^{-1} ; their absence is consistent with all the hydrogen in hydroxycalcimicrolite present in OH groups. Recently, Andrade *et al.* (2013b) performed IR analysis and detected the bands at similar positions within experimental error, 3600 and 3581 cm^{-1} for fluorcalcimicrolite ($Fd\bar{3}m$).

The Raman bands related to O–H stretching vibrations are located at 3586 and 3614 cm^{-1} for hydroxycalcimicrolite (<http://rruff.info/R130269>) and at 3582 cm^{-1} for fluorcalcimicrolite (<http://rruff.info/R120127>) (Fig. 4).

Crystal structure

Hydroxycalcimicrolite is the first pyrochlore-supergroup ($A_2B_2X_6Y$) mineral exhibiting $P4_332$ symmetry (Fig. 5), instead of $Fd\bar{3}m$. The presence of weak reflections violating the F -lattice was observed from both X-ray (4850 reflections, average $I/\sigma(I) = 2.82$) and neutron diffraction

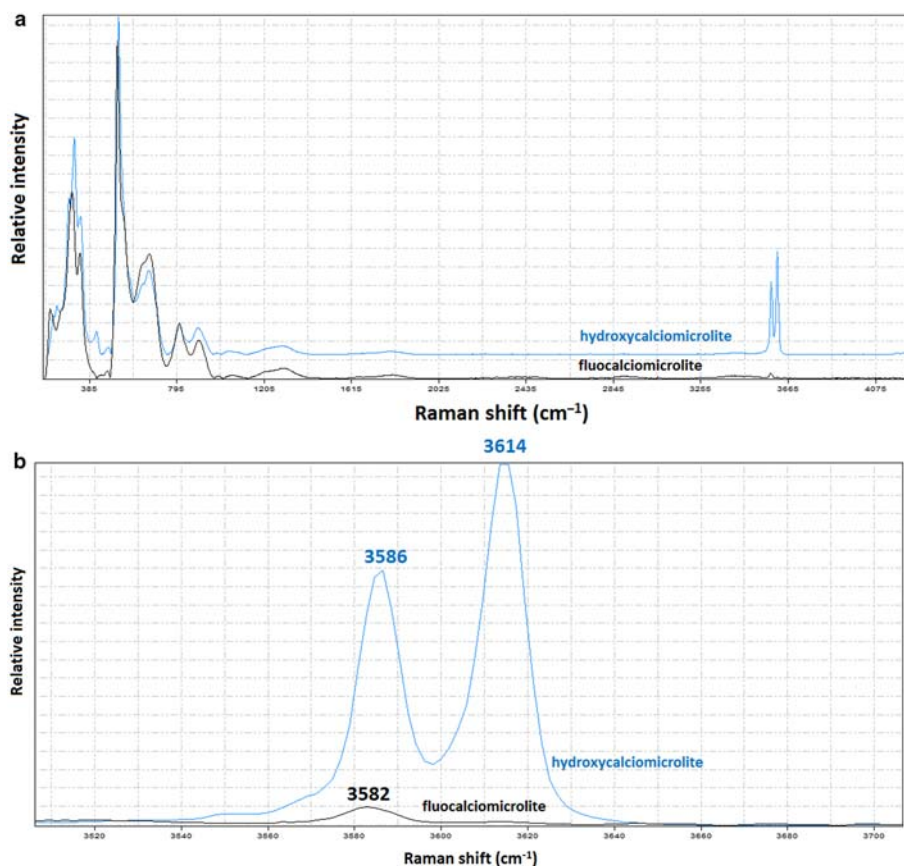


FIG. 4. (a) Raman spectra of hydroxycalciummicrolite (R130269), along with that of fluorcalciummicrolite (R120127) for comparison. (b) Detailed view of the OH region.

(4136 reflections, average $I/\sigma(I) = 1.16$), about 70% and 80% of the total, respectively. The lowering of symmetry from the F - to P -lattice is associated with the ordering of Ca cations and vacancies at the A site. Such symmetry change has also been observed in the synthetic compounds $\text{Ca}_{1.5}\text{Ta}_2\text{O}_6\text{F}$ and $\text{Ca}_{1.5}\text{Nb}_2\text{O}_6\text{F}$ (Le Berre *et al.*, 2007). In contrast, fluorcalciummicrolite has the space group $Fd\bar{3}m$ (Andrade *et al.*, 2013b) and does not show the same number of weak reflections violating the F -lattice symmetry. The lack of ordering in the type fluorcalciummicrolite is probably due to the low vacancy concentration in the A site: the empirical formula is $(\text{Ca}_{1.07}\text{Na}_{0.81}\square_{0.12})_{\Sigma 2.00}(\text{Ta}_{1.84}\text{Nb}_{0.14}\text{Sn}_{0.02})_{\Sigma 2.00}[\text{O}_{5.93}(\text{OH})_{0.07}]_{\Sigma 6.00}[\text{F}_{0.79}(\text{OH})_{0.21}]$ (Andrade *et al.*, 2013b). However, other occurrences may have lower Na content and more vacancies, so species with $P4_332$ or other lower-

symmetry space group may yet be discovered. Space group itself is not a reason to separate a mineral species. There are many minerals having different symmetries within the same mineral species (e.g. analcime, lazurite, vesuvianite etc.).

Additionally, the band splitting for the OH stretching vibrations, 3580 and 3599 cm^{-1} for IR (Fig. 3) and 3586 and 3614 cm^{-1} for Raman (Fig. 4), is related to the two distinct local environments for OH (e.g. vacancy vs. Na), and hence short-range order.

The structural model was refined in space group $P4_332$. The atoms Ta1, Nb1, Ca1, Ta2 and Nb2, were refined anisotropically. The preliminary refinement showed that Ca and Na are ordered into the Ca1 and Na1 sites, respectively. The final refinement converged with the Na content greater than that determined by the electron microprobe

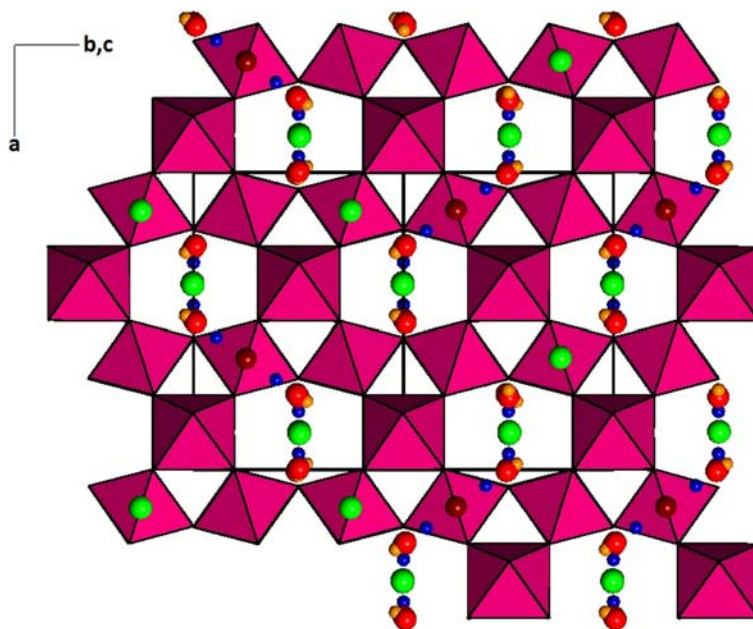


FIG. 5. Crystal structure of hydroxycalciummicrolite. Pink octahedra: TaO_6 groups, green spheres: Ca1 cations, brown spheres: Na1 cations, red spheres: O1 anions, orange spheres: F1 anions and dark blue spheres: H1 atoms.

analysis. This difference may be due to volatilization of sodium during the chemical analysis. Final atomic positions are given in Table 3 and selected bond lengths, bond angles and bond-valence sums in Table 4. Using the parameters published by Brese and O'Keeffe (1991), the empirical bond valences of the refined model have been calculated using the cation-site occupancies of Table 3. The bond-valence sums for O1 (0.80 valence units without H1) confirm that this oxygen atom is OH^- . The atoms Na1, (F1,O1), O2 and O3 were refined only isotropically due to the weak intensity of the reflections responsible for space group $P4_332$. In the refinement, the pyrochlore ($A_2B_2X_6Y$), Y site was split into two mutually exclusive nonequivalent sites, F1 and O1, separated by 0.43 Å. Also, the bond angles can be used to differentiate F1 from O1. The bond angle Ca1–F1–Ca1 is $115.84(92)^\circ$ (Table 4), so F1(Ca1)₃ is nearly planar triangular, while Ca1–O1–Ca1 is $106.30(64)^\circ$ and the O1(Ca1)₃ is a trigonal pyramidal, as expected for OH. Overall, each (O1,F1) is surrounded by a tetrahedron of three Ca1 and one (□,Na1). The very short $\text{Na}\cdots\text{H}$ distance of 1.28 Å implies that there is a short-range ordering such that if the Na1 site is occupied, the nearest two Y sites must be F, not OH, while if Y is OH, then the nearest Na1 site

must be vacant. Moreover, during the structural refinement, it was found that the crystal was twinned by inversion (twin law: $[\bar{1}00/0\bar{1}0/00\bar{1}]$) with a ratio of 0.70:0.30 for the two twin components. The morphological and optical indications for twinning were absent, so it is micro-twinning with the sizes of non-twinned blocks below the wavelength of visible light. The twinning by inversion is relatively common in the space group $P4_332$.

As heavy atoms are present within the structure, we investigated the position of hydrogen atoms present in the hydroxycalciummicrolite by means of single-crystal neutron diffraction. The VIVALDI diffractometer, that operates in Laue symmetry, was selected because of its high-intensity white-beam radiation that allows for faster data collection and use of smaller sample volume ($< 1 \text{ mm}^3$). The unit-cell parameters with $P4_332$ space group and non-hydrogen atom coordinates were based on single-crystal X-ray diffraction data. The reflections allowed in P but forbidden in the F -lattice centre were extremely weak. However, after some cycles of refinement with neutron data it was possible to locate the hydrogen atom at the Wyckoff position $8c$ (0.5519, 0.5519, 0.5519), ~ 1 Å from the O1 atom in the difference-Fourier map of nuclear

TABLE 4. Selected bond distances, bond angles and calculated bond-valence (BV) sums (in valence units) for hydroxycalciummicrolite.

Bond	Bond length (Å)	BV	Σ
Ca1–F1	2.160(11)	0.144(×2)	0.288
Ca1–O1	2.287(10)	0.266(×2)	0.532
Ca1–O2	2.583(5)	0.184(×2)	0.368
Ca1–O2	2.638(5)	0.158(×2)	0.316
Ca1–O3	2.683(6)	0.140(×2)	0.280
		Σ	1.784
Na1–F1	2.60(5)	0.009(×2)	0.018
Na1–O3	2.678(6)	0.029(×6)	0.174
		Σ	0.192
(Ta1,Nb1)–O3	1.965(6)	0.882(×6)	5.292
		Σ	5.292
(Ta2,Nb2)–O2	1.979(5)	0.849(×2)	1.698
(Ta2,Nb2)–O2	1.993(5)	0.818(×2)	1.636
(Ta2,Nb2)–O3	1.955(5)	0.907(×2)	1.814
		Σ	5.148
O1–Ca1	2.287(10)	0.266(×3)	0.798
O1–H1	0.89(2)	0.302	0.302
		Σ	1.100
F1–Ca1	2.160(11)	0.144(×3)	0.432
F1–Na1	2.60(5)	0.009	0.009
		Σ	0.441
O2–(Ta2,Nb2)	1.979(5)	0.849	0.849
O2–(Ta2,Nb2)	1.993(5)	0.818	0.818
O2–Ca1	2.583(5)	0.184	0.184
O2–Ca1	2.638(5)	0.158	0.158
		Σ	2.009
O3–(Ta2,Nb2)	1.955(5)	0.907	0.907
O3–(Ta1,Nb1)	1.965(6)	0.882	0.882
O3–Ca1	2.683(6)	0.140	0.140
O3–Na1	2.678(6)	0.029	0.029
		Σ	1.958
Bond-angles (°)			
Ca1–F1–Ca1	115.84(92)		
Ca1–O1–Ca1	106.30(64)		

density. Unfortunately, a complete refinement based on neutron data was not possible due to the weak intensity of the forbidden *F*-lattice reflections. The H-atom position found with neutrons was incorporated in the model based on X-ray diffraction.

The refinement of this model converged to $R_1 = 0.030$, $wR_2 = 0.051$, and the charge-balanced chemical formula obtained was $(\text{Ca}_{1.46}\text{Na}_{0.15})_{\Sigma 1.61}(\text{Ta}_{1.72}\text{Nb}_{0.28})_{\Sigma 2.00}\text{O}_6[(\text{OH})_{0.65}\text{F}_{0.35}]$. For simplicity, the structure was refined with the scattering factors of Ca, Na, Ta, Nb, O, F and trace elements such as Mn and Sn were ignored because of their negligible effects on the refinement. Apart from the

site splitting noted previously, there is no long-range order of F and OH. The O1–H1 vector is located along the threefold axis defined by O1–F1. The short O1–H1 distance (0.89 Å) and very long next-nearest O3···H1 (2.78 Å) imply that there is no significant hydrogen bonding.

Acknowledgements

We acknowledge FAPESP (processes 2011/22407-0 and 2013/03487-8), CNPq from the Brazilian government and Science Foundation Arizona for financial support. We also thank Dr. Kenneth Domanik (University of Arizona) for his advice about microprobe analysis and Dr. Garry McIntyre (Australian Nuclear Science and Technology Organization) for his suggestions about neutron diffraction data.

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