

Hydrokenopyrochlore, $(\square, \#)_2\text{Nb}_2\text{O}_6 \cdot \text{H}_2\text{O}$, a new species of the pyrochlore supergroup from the Sahatany Pegmatite Field, Antananarivo Province, Madagascar

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Abstract: The new mineral species hydrokenopyrochlore, ideally ${}^A(\square, \#)_2\text{Nb}_2\text{O}_6 \cdot {}^Y\text{H}_2\text{O}$, has been discovered in the Antandrokomby pegmatite, Sahatany Pegmatite Field, Antananarivo Province, Madagascar. It occurs as tan to beige subhedral crystals, up to 1 mm in size, with a resinous luster, associated with quartz, tourmaline, orthoclase, Li-bearing mica, hübnerite, stibiotantalite, and an undetermined heftetjernite-like mineral. Electron-microprobe analysis of hydrokenopyrochlore yielded (in wt%): WO_3 8.14, $\text{Sb}_2\text{O}_5(\text{tot})$ 14.33, Nb_2O_5 44.09, Ta_2O_5 13.97, SiO_2 0.51, SnO_2 0.21, CaO 0.86, MnO 0.04, Na_2O 1.79, Cs_2O 14.47, $\text{H}_2\text{O}_{\text{calc}}$ 2.23, total 100.64. On the basis of 2 *B*-site cations per formula unit and by recalculating the $\text{Sb}_2\text{O}_3\text{:Sb}_2\text{O}_5$ ratio in agreement with structural data, the chemical formula of hydrokenopyrochlore is $(\square_{1.32}\text{Sb}^{3+}_{0.35}\text{Na}_{0.26}\text{Ca}_{0.07})_{\Sigma 2}(\text{Nb}_{1.47}\text{Ta}_{0.28}\text{W}_{0.16}\text{Sb}^{5+}_{0.05}\text{Si}_{0.04})_{\Sigma 2.00}\text{O}_6[(\text{H}_2\text{O})_{0.55}\text{Cs}_{0.45}]$. The main diffraction lines, corresponding to multiple *hkl* indices, are [*d* in Å (visually estimated relative intensity) *hkl*]: 3.136 (s) 311, 3.006 (s) 222, 2.010 (ms) 333/511, 1.846 (s) 440, and 1.588 (ms) 622. The crystal structure study returned a cubic unit cell, space group $Fd\bar{3}m$, with $a = 10.4887(8)$ Å, $V = 1153.9(3)$ Å³, $Z = 8$. The crystal structure has been solved and refined to $R_1 = 0.056$ on the basis of 105 unique reflections with $F_o > 4\sigma(F_o)$ and 14 refined parameters. The crystal structure is formed by a framework of BO_6 octahedra, as is typical of the members of the pyrochlore supergroup. The *B* site has a mixed (Nb, Ta, W) occupancy. The *A* site is mainly vacant, whereas the *Y* site is occupied by both H_2O groups and Cs. The high Cs content of hydrokenopyrochlore seems to be indicative of the central miarolitic and most evolved portions of the pegmatitic dikes in the Sahatany Pegmatite Field.

Key-words: hydrokenopyrochlore; new mineral species; pyrochlore supergroup; cesium; niobium; crystal structure; Sahatany Pegmatite Field; Madagascar.

1. Introduction

The pyrochlore supergroup, whose members can be described by the general formula $A_{2-m}B_2X_{6-w} \cdot Y_1 - n$ (Atencio *et al.*, 2010), represents an interesting field of research for mineral systematics, owing to the large number of possible mineral species related to the complex crystal chemistry. According to the nomenclature scheme proposed by Atencio *et al.* (2010), five groups have been defined on the basis of the dominant *B*-site atoms, *i.e.* elsmoreite ($B = \text{W}^{6+}$), pyrochlore (Nb^{5+}), roméite (Sb^{5+}), microlite (Ta^{5+}), and betafite (Ti^{4+}). All these groups have

$X = \text{O}^{2-}$. Recently, two new groups have been formally added to the pyrochlore supergroup, having $B = \text{Al}^{3+}$ (ralstonite) and Mg^{2+} (coulsellite), and $X = \text{F}^-$ (Atencio *et al.*, 2017).

During a preliminary scanning electron microscope investigation of pyrochlore samples from granitic pegmatites of Madagascar, crystals showing a very high Cs content were identified. This finding suggested that a more detailed crystal-chemical investigation of these samples should be performed. Indeed, owing to stereochemical constraints, the occurrence of Cs is related to the “inverse” nature of pyrochlore, *i.e.* cations occur at the *Y* site, instead

of anions as is the case in “normal” pyrochlore (*e.g.*, [Ercit *et al.*, 1993](#)). This type of species is very rare in nature and it is only during the course of our own investigation that the very first natural “inverse” pyrochlore, cesiokenopyrochlore, has been described ([Agakhanov *et al.*, 2017](#)). The quantitative chemical analysis of the crystals described here, coupled with crystal-structure refinement, indicated that the amount of Cs was not sufficient to be dominant at the *Y* site. However, the occurrence of vacancies at *A* and the slight H₂O-dominance at *Y* allowed for the description of this mineral as a new member of the pyrochlore group, hydrokenopyrochlore, ideally having $A = \square$, $B = \text{Nb}$, $Y = \text{H}_2\text{O}$.

The mineral and its name have been approved by the IMA CNMNC (proposal # 2017-005). The name is in agreement with the nomenclature of the pyrochlore supergroup proposed by [Atencio *et al.* \(2010\)](#). Fragmented type material is deposited in the Mineralogical Collection of the Musée cantonal de géologie, University of Lausanne, Anthropole-Dorigny, CH-1015 Lausanne, Switzerland, under catalogue numbers MGL 080141 and 080142, and in the mineralogical collection of the Museo di Storia Naturale, Università di Pisa, Via Roma 79, Calci, Pisa, Italy, under catalogue number 19905.

This paper reports the description of the new mineral species hydrokenopyrochlore and discusses its relationships with other minerals of the pyrochlore supergroup.

2. Occurrence and mineral description

2.1. Occurrence and physical properties

Hydrokenopyrochlore was found in the Antandrokomby pegmatite (latitude 20°11'45" S; longitude 47°0'19" E; elevation 1300 m above sea level), near Mt. Ibity, in the southern part of the Sahatany Pegmatite Field, Manandona Valley, Vakinankaratra region, Antananarivo Province, Madagascar. The Antandrokomby pegmatite belongs to a tectonic unit known as the Itremo Group ([Fernandez *et al.*, 2003](#); [Tucker *et al.*, 2007](#)). Like all the most important pegmatites in the region, the Antandrokomby pegmatite is intruded into dolomitic marbles ([Pezzotta, 2005](#)). The pegmatites are characterized by boron enrichment and belong to the “Danburite Subtype” with lithium–cesium–tantalum geochemical signature ([Pezzotta, 2005](#)). Their Cs and Rb contents are correlated with the geochemical evolution, the highest contents being reported in the most evolved pegmatites, like the Antandrokomby pegmatite ([Simmons *et al.*, 2001](#)). Antandrokomby is a thin (1.2 m), steeply dipping dike. It is the type locality for manandonite ([Lacroix, 1912](#)) and londonite ([Simmons *et al.*, 2001](#)).

What would become the type material was submitted for identification to one of us at a mineral show by a French dealer. The circumstances of the find are unfortunately unknown. On the specimen, hydrokenopyrochlore occurs as tan to beige subhedral octahedral crystals, up to ~1 mm across. Streak is white, fracture is irregular, and luster is resinous. Scanning electron microscopy revealed that the crystals are porous, with hydrokenopyrochlore occurring

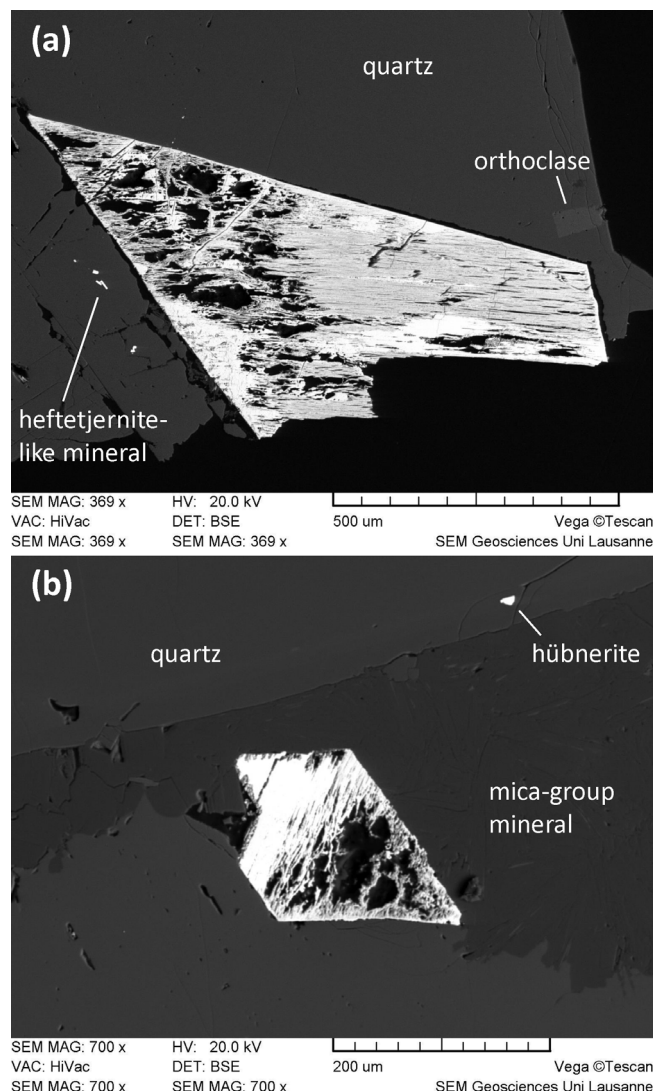


Fig. 1. Backscattered-electron images of subhedral crystals of hydrokenopyrochlore. In (a), associated minerals are quartz, orthoclase, and tiny euhedral inclusions of an undetermined heftetjernite-like mineral. In (b), hydrokenopyrochlore is associated with quartz, a mica-group mineral, and a tiny xenomorphic inclusion of hübnerite. Type material MGL 080141 (a) and MGL 080142 (b).

as relict domains, closely associated with quartz, orthoclase, minerals of the mica group, hübnerite, and a still-undetermined heftetjernite-like mineral (Fig. 1). Red tourmaline is also present; according to [Webber *et al.* \(2002\)](#) tourmalines from the miarolitic cavities from Antandrokomby are elbaite to schorl in composition.

Owing to this intimate association with other phases and its porous nature, micro-hardness and density of hydrokenopyrochlore could not be measured. On the basis of its empirical formula, the calculated density is 5.08 g/cm³. Optical properties were not measured, owing to the very small amount of available material and its chemical heterogeneity. The mean refractive index, obtained from the Gladstone–Dale relationship ([Mandarino, 1979, 1981](#)) and the calculated density, is 2.074 (on the basis of the empirical formula).

Table 1. Chemical data of hydrokenopyrochlore (average of 12 spot analyses).

Oxide	wt%	Range	e.s.d.
WO ₃	8.14	6.89–9.83	0.85
Sb ₂ O ₅ ^{tot}	14.33	12.13–16.58	1.38
Sb ₂ O ₅ [*]	1.71	—	—
Sb ₂ O ₃ [*]	11.37	—	—
Nb ₂ O ₅	44.09	39.28–47.02	1.95
Ta ₂ O ₅	13.97	11.01–17.15	1.67
SiO ₂	0.51	0.24–0.89	0.19
SnO ₂	0.21	0.11–0.30	0.06
CaO	0.86	0.24–1.64	0.40
MnO	0.04	0.00–0.10	0.03
Na ₂ O	1.79	1.31–2.21	0.29
Cs ₂ O	14.47	13.71–15.75	0.76
H ₂ O _{calc}	2.23		
Total	99.39		

Note: * calculated on the basis of structural data.

The exact position of hydrokenopyrochlore within the Antandrokomby pegmatite is unknown. Its hydrated and Cs-rich nature could be due to one of the following two processes: (i) primary crystallization within the centralmiarolitic and most evolved portions of pegmatitic dikes, rich in red tourmaline and Cs-bearing minerals, including pollucite, londonite, and Cs-rich beryl (e.g., [Simmons et al., 2001](#); [Gatta et al., 2010](#)), or (ii) secondary alteration of a Na-rich pyrochlore, under high Cs⁺ activity related to the hydrothermal or supergene alteration of a Cs-bearing mineral assemblage. The textural features point to the latter mechanism, whereby interaction between hypogene pyrochlore and Cs-rich fluids resulted in A-cation leaching (e.g., [Lumpkin & Ewing, 1995](#)).

2.2. Chemical data

Quantitative chemical analyses were carried out using a JEOL 8200 electron microprobe in wavelength-dispersive mode. The operating conditions were: accelerating voltage 15 kV, beam current 10 nA, focussed beam. Standards (element, emission line, analyser crystal) were: jadeite (NaK α , TAP), SnO₂ (SnL α , PETH), wollastonite (CaK α , PETH), Nb₂O₅ (NbL α , PETH), almandine (SiK α , TAP), Ta₂O₅ (TaL α , LIFH), pollucite (CsL α , PETH), W (WL α , LIFH), stibnite (SbL α , PETH), and MnTiO₃ (MnK α , LIFH). Fluorine, Cl, Bi, and Sc were sought but found to be below the detection limit, i.e. <0.27, 0.40, 0.07, and 0.09 wt%, respectively. Counting times were 30 s on the peak and 15 s on the backgrounds for all elements but Na (20 s on the peak and 10 s on the backgrounds). Direct H₂O determination could not be performed owing to the scarcity of available material and its inhomogeneity. Chemical data are given in [Table 1](#). The Sb₂O₃:Sb₂O₅ ratio was calculated in order to achieve a Sb³⁺:Sb⁵⁺ atomic ratio that is consistent with the structural data, considering Sb³⁺ and Sb⁵⁺ as A and B cations, respectively. The empirical formula of hydrokenopyrochlore, based on two B cations per formula unit (pfu) and following the

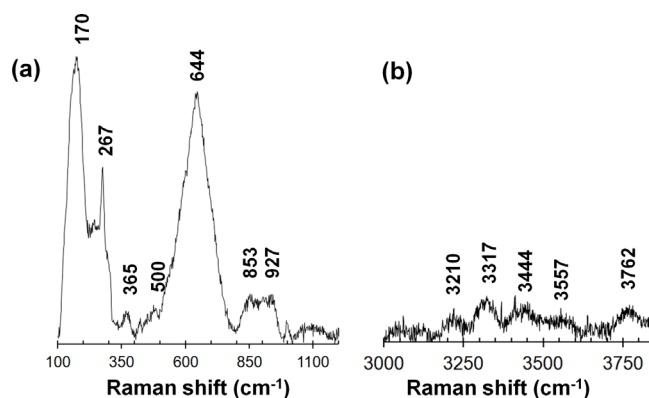


Fig. 2. Raman spectrum of hydrokenopyrochlore in the spectral regions (a) between 100 and 1200 cm⁻¹, and (b) between 3000 and 3850 cm⁻¹.

recommendations of [Atencio et al. \(2010\)](#), is $(\square_{1.32}\text{Sb}^{3+}_{0.35}\text{Na}_{0.26}\text{Ca}_{0.07})_{\Sigma 2}(\text{Nb}_{1.47}\text{Ta}_{0.28}\text{W}_{0.16}\text{Sb}^{5+}_{0.05}\text{Si}_{0.04})_{\Sigma 2}\text{O}_6[(\text{H}_2\text{O})_{0.55}\text{Cs}_{0.45}]$. This formula corresponds to a composition characterized by $A = \square$, $B = \text{Nb}$, and $Y = \text{H}_2\text{O}$. Consequently, the ideal end-member formula of hydrokenopyrochlore can be written as $\square_2\text{Nb}_2\text{O}_4(\text{OH})_2(\text{H}_2\text{O})$, with the O:OH ratio calculated in order to achieve electrostatic neutrality. It corresponds to (in wt%): Nb₂O₅ 88.06, H₂O 11.94, sum 100.00.

2.3. Micro-Raman spectroscopy

Unpolarised micro-Raman spectra were obtained on an unpolished sample of hydrokenopyrochlore in nearly-backscattered geometry with a Jobin-Yvon Horiba XploRA Plus apparatus, equipped with a motorized x-y stage and an Olympus BX41 microscope with a 10 $\times$ objective. The 532 nm line of a solid-state laser was used attenuated to 50%. The minimum lateral and depth resolution was set to a few μm . The system was calibrated using the 520.6 cm⁻¹ Raman band of silicon before each experimental session. Spectra were collected through multiple acquisitions with single counting times of 180 s. Backscattered radiation was analysed with a 1800 mm⁻¹ grating monochromator.

[Fig. 2](#) shows the observed Raman spectrum of hydrokenopyrochlore. The region between 100 and 1200 cm⁻¹ ([Fig. 2a](#)) has a strong band at 644 cm⁻¹, which is related to the symmetrical stretching mode of (Nb,Ta,W) O₆ octahedra. The weak shoulder at 500 cm⁻¹ could be interpreted as due to a slightly different (Nb,Ta,W)–O bond distance and could also be assigned to the symmetric stretching mode (e.g., [Jehng & Wachs, 1991](#)). The band at 170 cm⁻¹ is likely related to lattice vibrations, whereas bands at 267 and 365 cm⁻¹ could be assigned to (Nb,Ta,W) O₆ bending modes (e.g., [Debnath et al., 2009](#)). Finally, a broad and weak band formed by the superposition of two bands at 853 and 927 cm⁻¹ was observed in the spectrum of hydrokenopyrochlore but they were not assigned.

The region between 3000 and 3850 cm⁻¹ ([Fig. 2b](#)) is characterized by several weak bands, likely related to the O–H stretching modes of H₂O groups; the occurrence of

Table 2. Observed and calculated X-ray powder diffraction data for hydrokenopyrochlore. Intensity and d_{hkl} were calculated using the PowderCell 2.3 software (Kraus & Nolze, 1996) on the basis of the structural model given in Table 4. The five strongest reflections are given in bold. Intensities were visually estimated: s = strong; ms = medium-strong; m = medium; w = weak.

I_{obs}	d_{obs}	I_{calc}	d_{calc}	hkl
w	6.00	1	6.06	111
w	3.677	2	3.708	220
s	3.136	6	3.162	311
s	3.006	100	3.028	222
w	2.598	21	2.622	400
—	—	1	2.406	331
—	—	1	2.141	422
ms	2.010	7	2.019	333
s	1.846	34	1.854	440
w	1.771	1	1.773	531
—	—	1	1.748	442
w	1.657	3	1.658	620
ms	1.588	19	1.581	622
m	1.509	3	1.514	444
w	1.467	3	1.469	551

several bands could be related to different local environments. The presence of H₂O groups is also confirmed by the occurrence of two broad and weak bands centered at 1550–1600 cm^{−1} (not shown), likely related to O–H bending modes.

2.4. Crystallography

X-ray powder diffraction data were collected with a 114.6 mm Gandolfi camera and Ni-filtered CuK α radiation. Data are given in Table 2. The unit-cell parameters in the cubic symmetry, refined from the X-ray powder diffraction data on the basis of 11 unequivocally indexed reflections, using the method of Holland & Redfern (1997), are $a = 10.466(1)$ Å, $V = 1146.6(2)$ Å³.

X-ray single-crystal intensity data collection on hydrokenopyrochlore was performed using a Bruker Smart Breeze diffractometer equipped with an air-cooled CCD detector and graphite-monochromatized MoK α radiation. The detector-to-crystal working distance was 50 mm. Data were collected using ω and ϕ scan modes, in 0.5° slices, with an exposure time of 25 s per frame. The data were corrected for Lorentz and polarization factors, background effects, and absorption using the Apex2 software package (Bruker AXS Inc., 2004).

The statistical tests on the distribution of $|E|$ values ($|E^2 - 1| = 0.593$) suggested a possible acentric space group, e.g., $F43m$ or $F23$, in agreement with Rouse *et al.* (1998). Indeed, no reflections that violate the systematic absences expected for the conventional space-group symmetry $Fd\bar{3}m$ were observed. The refined unit-cell parameters are $a = 10.4887(8)$, $V = 1153.9(3)$ Å³, $Z = 8$. The crystal structure was refined using *Shelxl*-2014 (Sheldrick, 2015), starting from the atomic fractional coordinates of oxycalcioroméite (Biagioni *et al.*, 2013),

Table 3. Single-crystal X-ray diffraction details for hydrokenopyrochlore.

Crystal data	
X-ray formula	(□ _{1.27} Na _{0.39} Sb _{0.34}) _{Σ2} (Nb _{1.51} Ta _{0.49}) _{Σ2} O ₆ (H ₂ O _{0.53} Cs _{0.47})
Crystal size (mm)	0.090 × 0.070 × 0.050
Cell setting, space group	Cubic, $Fd\bar{3}m$
a (Å)	10.4887(8)
V (Å ³)	1153.9(3)
Z	8
Data collection and refinement	
Radiation, wavelength (Å)	MoK α , 0.71073
Temperature (K)	293
$2\theta_{\text{max}}$ (°)	61.54
Measured reflections	2137
Unique reflections	114
Reflections with $F_o > 4\sigma(F_o)$	105
R_{int}	0.0794
$R\sigma$	0.0303
Range of h, k, l	$-13 \leq h \leq 14, -15 \leq k \leq 9, -14 \leq l \leq 13$
$R [F_o > 4\sigma(F_o)]$	0.0555
R (all data)	0.0604
wR (on F_o^2)	0.1372
Goof	1.279
No. of least-squares parameters	14
Maximum and minimum residual peak (e Å ^{−3})	3.28 (at 1.99 Å from O) −2.45 (at 0.00 Å from A)

excluding the A' position. Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). Taking into account the results of the electron microprobe analysis, the following curves were used: Na vs. □ at the A site, Nb vs. Ta at the B site, and O vs. □ at both the O and Y sites. The refinement indicated the occurrence of an atom heavier than O at the Y site, in agreement with the occurrence of Cs which, for stereochemical reasons, should be hosted at this position (e.g., Ercit *et al.*, 1993). Moreover, the A site showed a very high isotropic displacement parameter, likely indicating a positional disorder related to the possible presence of the stereoactive Sb³⁺ cation. According to the chemical data, the B site hosts Nb and Ta, with minor W and Sb⁵⁺. The small amounts of Si have been assigned to B , in agreement with Atencio *et al.* (2010). The Sb³⁺:Sb⁵⁺ atomic ratio was adjusted in order to obtain the best fit between refined and calculated site scattering at this site. In this way, the occurrence of significant Sb³⁺ was supported and the A site was replaced by two split positions, *i.e.* A and A' , at the Wyckoff positions 16*d* and 96*g*, respectively. Their site-occupancy factors were fixed taking into account the chemical data. After several cycles of refinement, the anisotropic structural model converged to 0.0555 for 105 reflections with $F_o > 4\sigma(F_o)$ and 14 refined parameters.

Details of the data collection and refinement are given in Table 3. Fractional atom coordinates, site populations, and equivalent isotropic displacement parameters are reported in Table 4. Table 5 shows selected bond distances, whereas

Table 4. Atomic coordinates, Wyckoff site multiplicity, site population, and equivalent isotropic displacement parameters (in Å²) for hydrokenopyrochlore.

Site	Wyckoff site	Population	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
<i>A</i>	16 <i>d</i>	Na _{0.39}	½	½	½	0.025(9)
<i>A'</i>	96 <i>g</i>	Sb _{0.34}	0.483(3)	0.483(3)	0.551(3)	0.025(9)
<i>B</i>	16 <i>c</i>	Nb _{1.51(1)} Ta _{0.49(1)}	0	0	0	0.0163(7)
O	48 <i>f</i>	O _{6.00}	0.3145(12)	1/8	1/8	0.018(4)
<i>Y</i>	8 <i>b</i>	O _{0.53(1)} Cs _{0.47(1)}	3/8	3/8	3/8	0.040(3)

Table 5. Selected bond distances (in Å) in hydrokenopyrochlore.

<i>A</i>	– <i>Y</i>	2.2709(2) × 2	<i>A'</i>	–O	2.13(3)	<i>B</i>	–O	1.974(4) × 6	<i>Y</i>	–O	3.256(12) × 6
	–O	2.687(9) × 6		– <i>Y</i>	2.25(5)						
				–O	2.436(13) × 2						
				– <i>Y</i>	2.45(5)						
Mean		2.583	Mean		2.34	Mean		1.974	Mean		3.256

Table 6. Refined site scattering vs. calculated site scattering (in electrons) and proposed site occupancy for hydrokenopyrochlore.

Site	Refined site scattering	Proposed site occupancy	Calculated site scattering
<i>A</i>	2.1	□ _{0.83} Na _{0.13} Ca _{0.04}	2.2
<i>A'</i>	8.7	□ _{0.83} Sb _{0.17}	8.7
<i>B</i>	48.8	Nb _{0.74} Ta _{0.14} W _{0.08} Sb _{0.02} Si _{0.02}	47.8
O	8.0	O _{1.00}	8.00
<i>Y</i>	30.1	(H ₂ O) _{0.55} Cs _{0.45}	29.6

Table 7. Weighted bond-valence balance (in v.u.) in hydrokenopyrochlore.

	<i>A</i>	<i>A'</i>	<i>B</i>	<i>Y</i> (Cs)	Σanions
O	2×→0.02 ^{×64}	0.11 0.06 ^{×24}	2×→0.85 ^{×64}	0.05 ^{×64}	1.96
<i>Y</i> (H ₂ O)	2×→0.06 ^{×24}	0.08 0.05			0.25
Σcations	0.24	0.36	5.10	0.30	
Expected	0.21	0.51	5.06	0.45	

Note: left and right superscripts indicate the number of equivalent bonds involving anions and cations, respectively. For sites with mixed occupancy, the bond valences have been weighted.

refined site scatterings and those calculated on the basis of the proposed site occupancies are compared in Table 6. Finally, Table 7 gives the bond-valence sums (BVS) obtained using the bond-valence parameters of Brese & O'Keeffe (1991) and, for the pairs Sb³⁺–O and Sb⁵⁺–O, those given by Mills *et al.* (2009).

3. Crystal structure description

The crystal structure of hydrokenopyrochlore (Fig. 3) is characterized by BO₆ octahedra, polymerized to form the typical topology of the pyrochlore supergroup.

The *B* site has a mixed population, with major Nb and Ta, and minor W and Sb⁵⁺. Minor Si (0.04 *apfu*) can be hosted at this site or, more likely, could be related to the occurrence of dispersed crystalline or amorphous silicate phases, in agreement with the alteration suffered by the studied crystals. The average bond distance at the *B* site, 1.974 Å, has to be compared with a value of 1.99 and 2.01 Å, calculated using the ionic radii of Shannon (1976) and assuming a three-fold (if *A/A'* vacant and *Y* occupied by Cs) or four-fold (if *Y* occupied by H₂O and *A/A'* occupied by Na, Ca, or Sb) coordination of the oxygen atoms, respectively. The BVS at this position is 5.10

valence units (v.u.), close to the expected value of 5.06 v.u. calculated on the basis of the proposed site occupancy. The refined site scattering, 48.8 *epfu*, is in good agreement with the value calculated on the basis of the proposed site occupancy, *i.e.* 47.8 *epfu*.

The *A* site has an eight-fold coordination. It is mostly vacant, hosting only minor amounts of Na and Ca. When *A* is filled by these metals, *Y* is occupied by an H₂O group. The split position *A'*, mainly vacant, hosts minor Sb³⁺, in agreement with previous structural refinements (*e.g.*, Rouse *et al.*, 1998; Biagioni *et al.*, 2013). Also in this case, the occupancy of *A'* by Sb³⁺ is coupled with the occupancy of *Y* by H₂O, giving a five-fold coordination for *A'*.

The *Y* site can be occupied by Cs, as in inverse pyrochlores (*e.g.*, Ercit *et al.*, 1993), and H₂O. The refined site scattering suggested a mixed (O,Cs) site population, consistent with the requirement of electrostatic balance. The refined site scattering, 30.1 *epfu*, is in good agreement with the site scattering calculated according to the site population proposed on the basis of the electron microprobe data, 29.6 *epfu*.

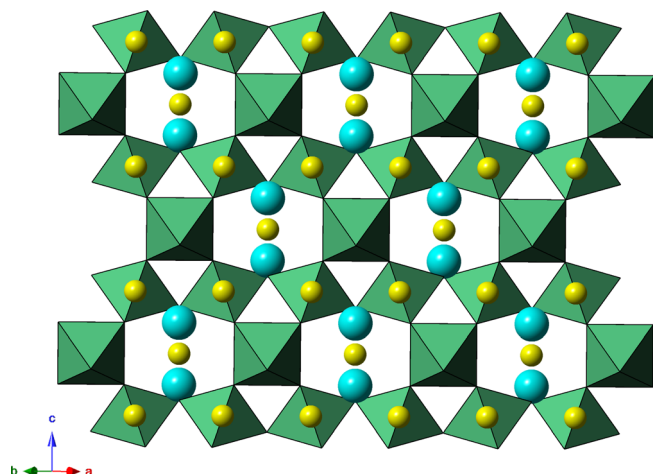


Fig. 3. Crystal structure of hydrokenopyrochlore. Circles represent the *A* (yellow) and *Y* (light blue) sites; Nb-centered octahedra are represented in green. For the sake of simplicity, the positions of the *A'* site are not shown.

4. Discussion

4.1. Crystal-chemistry of hydrokenopyrochlore

Hydrokenopyrochlore belongs to the pyrochlore group within the pyrochlore supergroup (Atencio *et al.*, 2010). It represents the member that is vacancy-dominant at the *A* site and H₂O-dominant at the *Y* site. It is the Nb-analogue of hydrokenomicrolite, ideally $\square_2\text{Ta}_2\text{O}_4(\text{OH})_2(\text{H}_2\text{O})$ (Andrade *et al.*, 2013). It is worth noting that the ideal end-member formula of hydrokenopyrochlore should be written as $\square_2\text{Nb}_2\text{O}_4(\text{OH})_2(\text{H}_2\text{O})$. Actually, the comparison between the empirical and the ideal formula represents an interesting predicament, since no (OH) groups occur in the studied material. Indeed, according to the empirical formula ${}^A(\square_{1.32}\text{Sb}^{3+}_{0.35}\text{Na}_{0.26}\text{Ca}_{0.07})^{\Sigma 1.45+} {}^B(\text{Nb}_{1.47}\text{Ta}_{0.28}\text{W}_{0.16}\text{Sb}^{5+}_{0.05}\text{Si}_{0.04})^{\Sigma 10.12+} {}^X(\text{O}_6)^{\Sigma 12.00-} {}^Y[(\text{H}_2\text{O})_{0.55}\text{Cs}_{0.45}]^{\Sigma 0.45+}$, the root-charge arrangement of the studied sample could be approximated as $(A_2)^{2+}(B_2)^{10+}(X_6)^{12-}(Y)^0$. In fact, the sample shows no (OH) groups at the *X* site (total charge 12−), a total charge at the *A* site (1.45+) closer to 2+ than zero, and a total charge at *Y* (0.45+) closer to zero than 1+. Therefore, in accord with Hawthorne (2002), the end-member composition of the studied sample should be ${}^A(\square_{4/3}\text{Sb}^{3+}_{2/3}){}^B\text{Nb}_2\text{XO}_6(\text{H}_2\text{O})$. In agreement with other authors (e.g., Bosi *et al.*, 2017), the ideal formula of hydrokenopyrochlore could be better written as $(\square, \#)_2\text{Nb}_2\text{O}_6 \cdot \text{H}_2\text{O}$, where “#” indicates an unspecified minor substituent needed for charge balance.

Hydrokenopyrochlore is a defect pyrochlore. Owing to its high Cs content, the studied material has an intermediate character between normal and inverse pyrochlore (e.g., Ercit *et al.*, 1993, 1994). In particular, the studied specimen is intermediate between ideal hydrokenopyrochlore and cesiokenopyrochlore, ideally $\square_2\text{Nb}_2(\text{O},\text{OH})_6\text{Cs}_{1-x}$ ($x \sim 0.20$), the first inverse natural pyrochlore which was described only recently (Agakhanov *et al.*, 2017) from the

Tetezantsio pegmatites, in the Betafo District (Antananarivo Province, Madagascar).

Hydropyrochlore, formerly described as kalipyrochlore by Ercit *et al.* (1994), and the recently approved hydroxykenopyrochlore (Miyawaki *et al.*, 2017), belong to the same pyrochlore group. Indeed, hydropyrochlore has $A = \text{H}_2\text{O}$, $B = \text{Nb}^{5+}$, and $Y = \text{H}_2\text{O}$, and hydroxykenopyrochlore has $A = \square$, $B = \text{Nb}^{5+}$, and $Y = (\text{OH})^-$. These two species can be compared with hydrokenopyrochlore, which has $A = \square$, $B = \text{Nb}^{5+}$, and $Y = \text{H}_2\text{O}$.

4.2. Looking for an ordered cation arrangement around *Y* site

As stated above, the studied specimen has an intermediate character between ideal hydrokenopyrochlore and cesiokenopyrochlore. Indeed, the site population at the *Y* site is $[(\text{H}_2\text{O})_{0.55}\text{Cs}_{0.45}]$. The weighted BVS given in Table 7 are the result of the average nature of the refined structure. Owing to the partial and mixed occupancies at the *A*, *B*, and *Y* sites, different local ordered configurations could occur. It may be interesting to discuss the possible local configuration around the *Y* site, the main factor responsible for the intermediate normal–inverse character of the studied sample.

When present, Cs has a regular six-fold octahedral coordination, with a Cs–O distance of 3.26 Å, to be compared with an ideal Cs–O distance of 3.05 Å, calculated using the ionic radii given by Shannon (1976) for ${}^{\text{VI}}\text{Cs}^+$ and ${}^{\text{IV}}\text{O}^{2-}$. The larger distance is likely the result of the partial occupancy of this site and the average nature of the refined structure. In order to avoid too short cation–cation distances, when Cs occupies the *Y* site, the *A* and *A'* positions should be empty. This results in 0.90 vacancies pfu related to the occurrence of Cs (0.45 apfu). On the contrary, when Cs is absent, the *Y* site can be occupied by H₂O groups (0.55 apfu), and the site population at the (*A* + *A'*) sites is $(\square_{0.42}\text{Sb}_{0.34}\text{Na}_{0.26}\text{Ca}_{0.08})^{\Sigma 1.10}$. Taking into account the site multiplicity, for every H₂O group, the surrounding (*A* + *A'*) site would have a total site occupancy of $\square_{0.76}\text{Sb}_{0.62}\text{Na}_{0.47}\text{Ca}_{0.15}$. Neglecting minor Ca, this occupancy could be approximated as $\square_{1.00}\text{Sb}_{0.5}\text{Na}_{0.5}$. Consequently, every H₂O group would be at bond distance from only two atoms, i.e. one Sb at *A'* and one Na at *A*. An idealized local arrangement is shown in Fig. 4. In such an ordered atomic arrangement, Sb^{3+} is characterized by a five-fold coordination, being coordinated by two H₂O groups and three O atoms. The Sb–O distances range between 2.13 and 2.45 Å. The actual bond distances are larger than the expected one, owing to the average nature of the refined structure. As a consequence, the corresponding BVS, calculated assuming full occupancy of the Sb position, is 2.09 v.u., lower than the ideal BVS of 3.00 v.u.. The *A* site, hosting Na and minor Ca, has an eight-fold coordination. Assuming full-Na occupancy, a BVS of 1.11 v.u. is achieved, in good agreement with the expected value. In such a configuration, the oxygen atom of the H₂O group at the *Y* site would have a BVS in the range 0.6–0.8 v.u., and this H₂O group would be likely involved in hydrogen

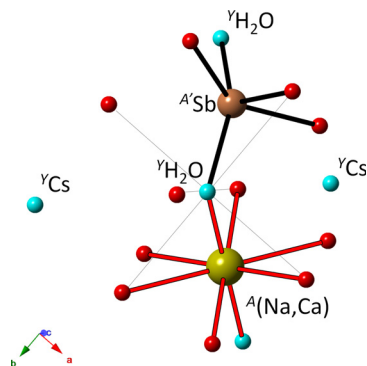


Fig. 4. Hypothetical local organization around Y_2O groups. Among four symmetry-related (A/A') positions, only two are occupied.

bonds with surrounding O atoms hosted at the O site. Moreover, it is likely that the actual position of H_2O groups could be displaced away from the $8b$ site, and the relatively high U_{eq} value shown by the atoms hosted at the Y site could be related to this positional disorder. As a matter of fact, Ercit *et al.* (1994) and Filippo *et al.* (1995) found that H_2O groups occupy higher-multiplicity positions near the $8b$ Y site. Taking into account the weighted BVS for Y, a BVS of 0.26 v.u. is achieved.

Finally, different configurations occur for the O site, tetrahedrally coordinated by two B sites and two (A/A') sites. The weighted BVS of the O site is 1.96 v.u. Actually, as different configurations are possible, a lower BVS could be achieved. For instance when only the B site is occupied, a total BVS of 1.70 v.u. can be calculated for the O site. Ercit *et al.* (1994) interpreted a similarly low BVS at the O site (1.63 v.u.) in hydroxyrochlore as resulting from the mixed (O,OH) occupancy at this position. In fact, a shortening of the B–O distance or the occurrence of W^{6+} could help to approach the ideal value of 2 v.u. for the O site in hydrokenopyrochlore, without requiring the occurrence of significant amounts of $(OH)^-$ groups. For this reason, the proposed ideal formula of hydrokenopyrochlore could be preferably written as $(\square, \#)_2Nb_2O_6 \cdot H_2O$, since the occurrence of (OH) groups is not supported by the present crystal-chemical investigation.

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