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HENRYMEYERITE, A NEW HOLLANDITE-TYPE Ba–Fe TITANATE FROM THE KOVDOR COMPLEX, RUSSIA

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ABSTRACT

A new hollandite-type titanate, henrymeyerite, occurs in a vein of tetra-ferriphlogopite – calcite – dolomite carbonatite of the Kovdor alkaline ultramafic complex, Kola Peninsula, in Russia. The mineral was found in a single mineralized vug as acicular crystals less than 0.2 mm in length. The crystals represent a combination of two tetragonal prisms and a bipyramid. Henrymeyerite is opaque, black, and has an adamantine luster. In reflected light, the mineral is greyish brown and has a strong bireflectance. Reflectance values R_ε and R_ω are given for λ over the interval 420–720 nm. Henrymeyerite is associated with dolomite, fluorapatite, tetra-ferriphlogopite, rimkorolgite, catapleiite, collinsite, and pyrite. The composition of henrymeyerite, as determined by electron microprobe, is (wt.%): BaO 18.25, TiO_2 67.78, FeO 9.20, Nb_2O_5 1.00, Ce_2O_3 0.56, La_2O_3 0.50, Na_2O 0.40, SiO_2 0.37, K_2O 0.05, CaO 0.02, sum 98.13. Stoichiometrically, this composition closely corresponds to the Ba–Fe end-member of the cryptomelane group, $BaFe^{2+}Ti_7O_{16}$. Henrymeyerite is tetragonal, space group $I4/m$, $Z = 1$, a 10.219(3), c 2.963(1) Å, V 309.4(3) Å^3. The crystal structure of the mineral was refined to $R_1 = 0.027$ for 173 unique reflections with $|F_o| \geq 4\sigma_F$ using single-crystal X-ray-diffraction data. The structure of henrymeyerite corresponds to the undistorted hollandite archetype; no indication of splitting of the Ba site along [001] was observed. The available single-crystal data also indicate the absence of long-range order of the Ba^{2+} cations within the structural tunnels. The mineral is named for Prof. Henry O.A. Meyer (1937–1995) in honor of his contributions to the petrology and mineralogy of mantle-derived xenoliths and kimberlitic rocks.

Keywords: henrymeyerite, hollandite, cryptomelane group, carbonatite, Kovdor complex, Russia.

SOMMAIRE

Nous décrivons ici la henrymeyerite, titanate apparenté à la hollandite, découvert dans un filon de carbonatite à tétra-ferriphlogopite – calcite – dolomite dans le complexe alcalin et ultramafique de Kovdor, péninsule de Kola, en Russie. Le minéral se trouve dans une seule cavité tapissée de cristaux aciculaires n'atteignant même pas 0.2 mm en longueur. La morphologie des cristaux est une combinaison de deux prismes tétragonaux et d'une bipyramide. La henrymeyerite est opaque et noire, avec éclat adamantin. En lumière réfléchie, le minéral est brun grisâtre, et possède une forte biréflectance. Les valeurs de réflectivité R_ε et R_ω sont fournies pour des longueurs d'onde λ sur l'intervalle 420–720 nm. La henrymeyerite est associée à dolomite, fluorapatite, tétra-ferriphlogopite, rimkorolgite, catapléiite, collinsite, et pyrite. Sa composition, déterminée par microsonde électronique (% pondéraux), est: BaO 18.25, TiO_2 67.78, FeO 9.20, Nb_2O_5 1.00, Ce_2O_3 0.56, La_2O_3 0.50, Na_2O 0.40, SiO_2 0.37, K_2O 0.05,

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CaO 0.02, pour un total de 98.13. Selon sa stoechiométrie, la composition correspond au pôle Ba–Fe du groupe de la cryptomelane, $BaFe^{2+}Ti_7O_{16}$. La henrymeyerite est tétragonale, groupe spatial $I4/m$, $Z = 1$, a 10.219(3), c 2.963(1) Å, V 309.4(3) Å^3. La structure cristalline de ce minéral a été affinée jusqu'à un résidu $R_1 = 0.027$ en utilisant 173 réflexions uniques avec $|F_o| \geq 4\sigma_F$, les données de diffraction X étant prélevées sur cristal unique. La structure de la henrymeyerite correspond à celle de l'archetype non déformé de la hollandite. Il n'y a aucune indication d'un dédoublement du site Ba le long de [001]. Les données disponibles indiquent aussi l'absence d'une mise en ordre à longue échelle des ions Ba^{2+} dans les canaux de la structure. Nous honorons, par le nom choisi, le professeur Henry O.A. Meyer (1937–1995), pour ses contributions à la pétrologie et la minéralogie des xénolithes dérivés du manteau et des roches kimberlitiques.

(Traduit par la Rédaction)

Mots-clés: henrymeyerite, hollandite, groupe de la cryptomelane, carbonatite, complexe de Kovdor, Russie.

INTRODUCTION

Members of the hollandite structural family have been intensively studied over the last two decades as potential repositories for industrial fission products (Ringwood *et al.* 1979) and hosts of large-ion lithophile elements in crustal and mantle rocks (*e.g.*, Zhang *et al.* 1993, Foley *et al.* 1994). Crystal structures of most naturally occurring hollandite-type oxides, collectively known as the cryptomelane mineral group, have been characterized in great detail. Exceptions are Ba–Fe titanates of the general formula $Ba_x(Fe^{2+},Fe^{3+},Ti)_{\Sigma 8.0}O_{16}$ ($x \approx 1.1$). These phases are relatively common in rock types such as lamproites and agpaitic pegmatites (*e.g.*, Mitchell 1995, Chakhmouradian & Mitchell 1999), where they typically occur in minor amounts or form intimate intergrowths with other minerals. Consequently, it had not been previously possible to determine their crystal structures. In this work, we describe a new hollandite-type mineral corresponding closely in composition to the end-member $BaFe^{2+}Ti_7O_{16}$, and give a detailed characterization of its structure. We have named this mineral *henrymeyerite* to honor Prof. Henry O.A. Meyer (1937–1995) for his contribution to the petrology and mineralogy of mantle-derived xenoliths and kimberlitic rocks, and for his services to the mineralogical community with the Mineralogical Society of America and the International Mineralogical Association. The mineral and the name henrymeyerite have been approved by the Commission on New Minerals and Mineral Names (CNMMN) of IMA (vote 99–016). Type material is deposited at the Geological Museum of the Kola Science Center in Apatity, Russia.

BACKGROUND INFORMATION

With the exception of akaganéite [β-FeO(OH,Cl)], all naturally occurring cryptomelane-group minerals can be divided into two chemically distinct subgroups, manganates and titanates. The manganates have the general formula $AMn_8(O,OH)_{16}$, and include several mineral species that differ in the population of the eight-coordinated *A*-site (Na, K, Sr, Ba or Pb). The subgroup of titanates consists of priderite [$(K_{1.2}Ba_{0.4})(Fe_{1.1}Mg_{0.2}Ti_{6.7})_{\Sigma 8.0}O_{16}$] (Norrish 1954, Sinclair & McLaughlin 1982) and four Ba-dominant phases with either V^{3+} or Cr^{3+} replacing Ti in the octahedrally coordinated *B*-site (Scott & Peatfield 1986, Szymański 1986, Xiong *et al.* 1989, Dmitriyeva *et al.* 1992). All members of this subgroup crystallize with tetragonal symmetry, but typically show slight deviations from the archetypal hollandite structure [α-MnO_2 or TiO_2 (*H*)] (Zhang & Burnham 1994). These deviations are largely due to splitting of the cation sites into two independent positions (mannardite: Szymański 1986) or incommensurate ordering of the *A*-site cations (ankangite: Wu *et al.* 1990, Shi *et al.* 1991). However, most of the titanates maintain the $I4/m$ symmetry characteristic of the undistorted structure.

On the basis of results of chemical analyses and synthesis experiments, Norrish (1954) inferred the existence of a solid solution between K–Fe and Ba–Fe hollandite-type titanates. He showed that the then newly discovered mineral priderite is a K-dominant member of this series. For the hypothetical Ba end-member, he used the provisional name "Ba-priderite". Subsequently, a mineral of approximate composition $(Ba_{0.7}K_{0.1})(Fe_{1.1}Ti_{6.9})_{\Sigma 8.0}O_{16}$ was described from the Kovdor carbonatite complex (Russia) as "barian priderite" by Zhuravleva *et al.* (1978). It is noteworthy that the mineral from Kovdor has an unusually low cation total in the *A* site, possibly resulting from poor analytical data. The term "barian priderite" and its derivatives (*e.g.*, "Ba–Fe-priderite") have been extensively used by Russian mineralogists to characterize hollandite-type phases with a preponderance of Ba at the *A* site and Fe as a major substituting element at the *B* site (Men'shikov *et al.* 1979, Lazebnik *et al.* 1985, Chakhmouradian & Evdokimov 1997). In the Western mineralogical literature, these phases have been typically referred to as Ba–Fe hollandite-type titanates (Mitchell & Bergman 1991) or "Ba–Fe hollandite" (Platt 1994, Chakhmouradian & Mitchell 1999). Regardless of some terminological differences, the authors of previously published studies (Men'shikov *et al.* 1979, Lazebnik *et al.* 1985, Mitchell & Meyer 1989, Mitchell & Vladykin 1993, Gaspar *et al.* 1994) have demonstrated that naturally occurring priderite shows a wide range of compositions, differing in K/Ba and Fe/Ti values. Mitchell & Meyer (1989) and Mitchell (1995) suggested that the nomenclature of naturally occurring hollandite-type titanates should be redefined taking into account the existence of two barium end-member compositions, $BaFe^{2+}Ti_7O_{16}$ and $BaFe^{3+}{}_2Ti_6O_{16}$. The hexatitanate end-member $BaFe^{3+}{}_2Ti_6O_{16}$ has been synthetically prepared in several studies (*e.g.*, Cheary *et al.* 1996, Loezos *et al.* 1999). Prior to this work, the compound $BaFe^{2+}Ti_7O_{16}$ had not been synthesized, but compositionally similar Ba–Mg titanates are well known (Dubeau & Edgar 1985, Fanchon *et al.* 1987, Cheary & Squadrito 1989). Prior to our study, neither $BaFe^{2+}Ti_7O_{16}$ nor $BaFe^{3+}{}_2Ti_6O_{16}$ had been approved as valid mineral species by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association.

OCCURRENCE AND PROPERTIES

Henrymeyerite occurs in a late-stage mineral assemblage associated with carbonatitic rocks of the Kovdor alkaline ultramafic complex, Russia (~67°3'N, ~30°3'E). This complex belongs to a group of alkaline intrusions of Devonian age situated along the ancient Kovdor – Khibina – Ivanovka fault zone developed in Precambrian basement of the Fennoscandian Shield (Orlova 1993). The Kovdor intrusion is composed of diverse plutonic ultramafic, melilitic, alkaline and carbonatitic rocks emplaced in Archean gneisses of the Belomorskaya suite (Kukharenko *et al.* 1965). At Kovdor, carbonatites and associated phoscorites are among the latest of the petrographic series, and cross-cut all other rock types with the exception of nepheline and cancrinite syenites. The phoscorites and carbonatites comprise a small intrusion and a system of veins in the southwestern part of the complex, at the contact between the earlier-formed clinopyroxenites, melteigite–ijolites and fenites. The phoscorite–carbonatite unit is now well exposed owing to extensive mining operations in the Kovdor iron-ore pit.

Henrymeyerite was found in a vein of tetra-ferriphlogopite – calcite – dolomite carbonatite exposed at the +10 m horizon of so-called "anomalous ores". These rocks contain abundant clinohumite and are believed to metasomatically replace primary phoscorites. The metasomatism also resulted in crystallization of uranoan pyrochlore, and hence, generally high ("anomalous") radioactivity of these rocks. The henrymeyerite-bearing carbonatite cross-cuts a metasomatized phoscoritic rock composed of forsterite, clinohumite, fluorapatite, magnetite, phlogopite and calcite. The carbonatite vein has a nearly vertical dip and a thickness of 20–30 cm; its outcropping portion is approximately 6 m long. Henrymeyerite was discovered in one of several mineralized vugs within the carbonatite body. The mineral is associated with dolomite, fluorapatite, niobian anatase (?), tetra-ferriphlogopite, rimkorolgite [$Mg_5Ba(PO_4)_4 \bullet 8H_2O$], catapleiite ($Na_2ZrSi_3O_9 \bullet 2H_2O$), collinsite [$Ca_2Mg(PO_4)_2 \bullet 2H_2O$], and pyrite. Other vugs were carefully examined for the presence of henrymeyerite, but this search proved unsuccessful. Hence, the amount of material available for our study was limited to a few crystals.

Henrymeyerite forms well-developed acicular crystals up to 0.2 mm in length and several tens of μm in thickness. The crystals represent a combination of two tetragonal prisms terminated by an obtuse tetragonal bipyramid (Fig. 1). The most probable combination of forms is {100}, {110} and {101}. Macroscopically, the crystals are black and show a distinct adamantine luster. Henrymeyerite is opaque, and has a reddish brown streak. The density of the mineral, as determined by comparison with heavy liquids of known density (Clerici solution), is 4.0(1) g/cm^3. This value is in reasonable agreement with a calculated density of 4.20(1) g/cm^3. Attempts to determine the micro-indentation hardness were largely unsuccessful because the mineral is very brittle and breaks into fine splinters even when minimum loads are applied. Rough estimates of the Mohs hardness range from 5 to 6. In reflected light, henrymeyerite is greyish brown, and in samples oriented lengthwise, it shows a weak bireflectance in shades of brown. Reflectance measurements in the range 420–720 nm were made relative to a SiC standard using a MSF 10 spectrophotometer. The reflectance values for henrymeyerite measured in air are given in Table 1.

COMPOSITION

The composition of henrymeyerite, determined using the same crystal as that characterized structurally, was obtained using energy-dispersion spectrometry (EDS) on a Hitachi 570 scanning electron microscope equipped with a LINK ISIS analytical system incorporating a Super ATW Light Element Detector (133 eV FwHm Mn*K*α). EDS spectra were acquired for 180 seconds (live time) with an accelerating voltage of 20 kV and a beam current of 0.86 nA. Full ZAF corrections were applied to the raw X-ray data. The following mineral standards were used for the chemical analysis of henrymeyerite: benitoite (Ba), ilmenite (Fe, Ti), jadeite (Na), wollastonite (Ca, Si), orthoclase (K), and loparite-(Ce) (La, Ce, Nb). The accuracy of the method was confirmed by wavelength-dispersion electron-microprobe analysis of K–Ba hollandite-type minerals, and *REE*-bearing perovskite-type titanates using an automated CAMECA SX–50 instrument located at the University

TABLE 1. REFLECTANCE VALUES (%) FOR HENRYMEYERITE

λ, nm	R_ω	R_ε	λ, nm	R_ω	R_ε	λ, nm	R_ω	R_ε
420	13.0	14.2	540	11.6	12.6	660	11.3	13.8
440	12.2	13.4	560	11.5	12.6	680	11.3	14.1
460	12.0	13.0	580	11.4	12.7	700	11.2	14.4
480	11.9	12.8	600	11.4	12.9	720	11.2	14.5
500	11.8	12.7	620	11.4	13.2			
520	11.8	12.6	640	11.4	13.5			

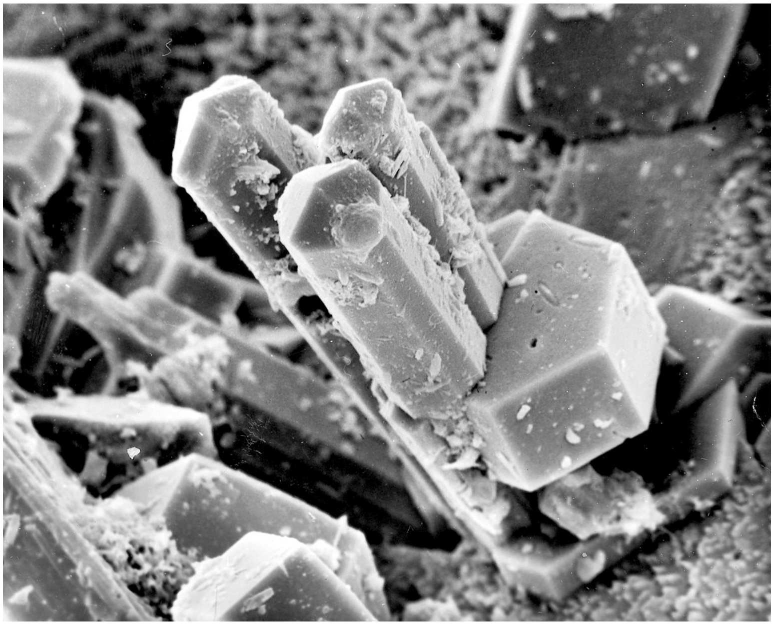

FIG. 1. Slender prismatic crystals of henrymeyerite intergrown with stubby hexagonal prisms of fluorapatite and dolomite rhombohedra. Width of field of view is *ca.* 0.2 mm.

of Manitoba (Mitchell & Vladykin 1993, Chakhmouradian & Mitchell 1998). Other elements present in some hollandite-group titanates (Cr, V, Sr, Mn, Mg, Al, Zr and Th) were sought but were not detected.

From Table 2, it is evident that henrymeyerite is a Ba–Fe titanate with negligible amounts of other cations. The Fe content in this mineral ranges from 9.0 to 9.5 wt.% FeO (total iron expressed as FeO), clearly indicating that henrymeyerite corresponds to the barium–iron heptatitanate $BaFe^{2+}Ti_7O_{16}$ rather than to the hexatitanate $BaFe^{3+}{}_2Ti_6O_{16}$. When recalculated with all Fe expressed as Fe^{2+}, the formula of henrymeyerite is $(Ba_{0.96}Na_{0.10}K_{0.01}REE_{0.05})_{\Sigma 1.12}(Fe^{2+}{}_{1.03}Ti_{6.82}Nb_{0.06}Si_{0.04})_{\Sigma 7.95}O_{16}$ and, thus, it closely approaches that of the heptatitanate end-member. Unfortunately, the amount of material available to us was insufficient to confirm the divalent state of Fe in henrymeyerite by Mössbauer spectroscopy. Note that a small deficiency of cations in the *B* site is probably an artifact resulting from the presence of minor Ti^{3+} in the mineral (*cf.* X-ray photoelectron-spectroscopy data of Myhra *et al.* 1988).

CRYSTAL STRUCTURE

Single-crystal diffraction studies of henrymeyerite were done using a Bruker PLATFORM three-circle diffractometer equipped with a SMART charge-coupled device (CCD) detector with a crystal-to-detector distance of 5 cm. The CCD area detector allows simultaneous detection of X-ray intensities over slices of reciprocal space, facilitating examination of superstructures, twinning, exsolution and defects in crystal structures (Burns 1998). In comparison with conventional scintillation detectors, the CCD detector offers improved sensitivity to weak reflections, higher resolution and reduced data-collection times. The X-ray-diffraction data were collected on a crystal 0.06 × 0.2 mm in size, using Mo$K\alpha$ X-radiation and ω scans, with framewidths of 0.03° and 60 s spent counting for each frame. More than a hemisphere of three-dimensional data was collected for $0 \leq 2\theta \leq 56.44°$ in approximately 24 hours. The data were integrated using the Bruker program SAINT, and corrections for Lorentz, polarization, and background effects were applied. An empirical correction for absorption was performed using intensities of equivalent reflections with the crystal modeled as an ellipse. The unit-cell dimensions refined by least-squares techniques are *a* 10.219(3), *c* 2.963(1) Å and *V* = 309.4(3) $Å^3$. A total of 1982 reflections were collected, of which 219 reflections were unique, with 173 classed as observed ($|F_o| \geq 4\sigma_F$).

Scattering curves for neutral atoms, as well as anomalous dispersion corrections, were taken from the *International Tables for X-ray Crystallography* (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure. Systematic absences and reflection statistics indicated the space group *I*4/*m*,

TABLE 2. COMPOSITION OF HENRYMEYERITE, ITS SYNTHETIC ANALOGUE, AND THEORETICAL COMPOSITIONS OF END-MEMBER Ba-Fe HOLLANDITE-GROUP TITANATES

	HENRYMEYERITE			$BaFe^{2+}Ti_7O_{16}$	$BaFe^{3+}{}_2Ti_6O_{16}$	SYNTHETIC SAMPLE**
Oxide	Mean* (wt.%)	Range (wt.%)	Standard deviation			
Na_2O	0.40	0.28-0.55	0.07	-	-	-
K_2O	0.05	0.01-0.08	0.02	-	-	-
CaO	0.02	0.00-0.06	0.02	-	-	-
BaO	18.25	17.47-19.20	0.61	19.54	19.35	20.66
La_2O_3	0.50	0.15-0.87	0.32	-	-	-
Ce_2O_3	0.56	0.21-0.88	0.22	-	-	-
Fe_2O_3	-	-	-	-	20.15	-
FeO	9.20†	8.97-9.46†	0.16	9.16	-	10.34†
TiO_2	67.78	66.94-69.04	0.66	71.30	60.50	69.00
SiO_2	0.37	0.27-0.58	0.09	-	-	-
Nb_2O_5	1.00	0.64-1.39	0.21	-	-	-
Total	98.13			100.00	100.00	100.00
Structural formulae calculated on the basis of 16 atoms of oxygen						
Na	0.10			-	-	-
K	0.01			-	-	-
Ca	-			-	-	-
Ba	0.96			1.00	1.00	1.07
La	0.02			-	-	-
Ce	0.03			-	-	-
Σ*A*	1.12			1.00	1.00	1.07
Fe	1.03			1.00	2.00	1.14
Ti	6.82			7.00	6.00	6.86
Si	0.04			-	-	-
Nb	0.06			-	-	-
Σ*B*	7.95			8.00	8.00	8.00

* Average of 8 microprobe analyses.
** Synthetic analogue of henrymeyerite, average of 11 microprobe analyses (normalized).
† Total Fe expressed as FeO.

corresponding to the archetypal hollandite structure. A model that included refined positional parameters and anisotropic displacement parameters gave a final R_1 value of 0.027 for 173 reflections with $|F_o| \geq 4\sigma_F$. In the final cycle of refinement, the peaks in the difference-Fourier maps were below 0.64 e/Å^3. Importantly, the difference-Fourier map showed no indication of splitting of the Ba site (00½) along [001]. Relatively high displacement-parameters for Ba [U_{eq} = 0.0296(5) Å^2] signify positional disorder at the 2*b* site.

The final atomic coordinates, anisotropic displacement parameters and selected interatomic distances for henrymeyerite are given in Table 3. The mean (*B*–O) distance observed is close to that expected from the chemical composition of the mineral (1.982 and 1.979 Å, respectively). Observed and calculated structure-factors for henrymeyerite (Table 4) may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada. The refined structural parameters were used to generate a calculated powder-pattern for the mineral (Table 5), as the amount of material available to us was insufficient to measure the actual pattern.

The structure of henrymeyerite shown in Figure 2, consists of edge-sharing $(Ti,Fe)O_6$ octahedra forming double chains along [001]. These chains form tunnels approximately 4.8 Å across by sharing corners available for bonding. In common with other hollandite-type compounds (*e.g.*, Zhang *et al.* 1993), the six-coordinated polyhedra are distorted, having the four shared edges [2 × O(1)–O(1') and 2 × O(1)–O(2)] significantly shorter than those unshared (Table 3). The tunnels accommodate Ba and minor amounts of other large cations. Note that in henrymeyerite, Ba enters only the 2*b* site, whereas the 4*e* positions remain vacant. In common with redledgeite [$Ba(Cr,Fe^{3+},V)_2Ti_6O_{16}$], the small distance between the adjacent 2*b* sites along [001] (~ 2.97 Å) prohibits more than approximately half of these positions to be occupied by Ba (Szymański 1986, Foley *et al.* 1997). In tetragonal hollandite-type phases with a significant excess of large cations over one atom per formula unit (*apfu*), this excess is accommodated in the "off-center" 4*e* site displaced along [001] relative to 2*b* (*e.g.*, priderite: Post *et al.* 1982, Sinclair & McLaughlin 1982).

TABLE 3. FINAL POSITIONAL AND DISPLACEMENT PARAMETERS (Å^2) AND SELECTED INTERATOMIC DISTANCES FOR HENRYMEYERITE

Atom	Wyckoff position	s.o.f.	x	y	z	U_{eq}*	U_{11}	U_{22}	U_{33}	U_{12}
Ba	2*b*	0.54	0	0	1/2	0.0296(5)	0.0290(6)	0.0290(6)	0.0310(9)	0
Ti+Fe	8*h*	1.00	0.34985(8)	0.16604(8)	0	0.0090(3)	0.0090(5)	0.0121(5)	0.0060(4)	0.0021(4)
O(1)	8*h*	1.00	0.1558(3)	0.2037(3)	0	0.0112(7)	0.010(2)	0.015(2)	0.009(2)	0.000(1)
O(2)	8*h*	1.00	0.5390(3)	0.1672(3)	0	0.0115(8)	0.010(2)	0.013(2)	0.012(2)	0.000(1)

Ba-O(1) (×8)	3.010(3) Å	O(1)-O(1)	2.963(2) Å
Ti-O(1) (×2)	1.992(2) Å	O(2)-O(2)	2.963(2) Å
Ti-O(1')	2.019(3) Å	O(1)-O(2') (×2)	2.810(3) Å
Ti-O(2) (×2)	1.977(2) Å	O(2)-O(2') (×2)	2.890(3) Å
Ti-O(2')	1.933(3) Å	O(2)-O(1') (×2)	2.881(3) Å
(Ti-O)$_{mean}$	1.982(2) Å	O(1)-O(1') (×2)	2.607(3) Å
		O(1)-O(2) (×2)	2.632(2) Å

*$U_{eq} = 1/3(\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j a_i a_j)$; U_{13} and U_{23} = 0 for all atoms.

The absence of superstructure reflections suggests that the structure of henrymeyerite is devoid of long-range ordering of the Ba^{2+} cations within the tunnels. As only about one half of the *A* sites can be occupied in Ba-dominant hollandites, some of these structures develop a commensurate long-range ordering along [001]. Among titanates, an ordered arrangement of Ba cations and vacancies in the tunnels has been described in a "Ba–Ti hollandite" from the Tian Shan Mountains (Dmitriyeva *et al.* 1992) and the synthetic compound $Ba_{1.2}Mg_{1.2}Ti_{6.8}O_{16}$ (Fanchon *et al.* 1987). In both these cases, the ordering represents the regular sequence ...Ba–Ba–☐–Ba–☐..., and results in a quintupled supercell along the corresponding axis (*ca.* 14.8–14.9 Å). It is noteworthy that this sequence yields the maximum occupancy of *A* sites by Ba, *i.e.*, approximately 1.33 *apfu* (Foley *et al.* 1997).

SYNTHETIC $BaFe^{2+}Ti_7O_{16}$

A synthetic analogue of henrymeyerite was prepared using the ceramic technique from stoichiometric quantities of $BaCO_3$, $FeTiO_3$ and TiO_2 (high-purity grade). The reagents were dried at 150°C for 24 h, and then mixed and ground in an agate mortar. The mixture was calcined at 1000°C and, after regrinding, heated at 1300°C in air for 48 hours. The composition of the ceramic powder sample was determined using the same methods, operating conditions and standards as those described above for henrymeyerite. The synthetic sample consists of relatively large (≤40 μm) crystals of Ba–Fe titanate intergrown with smaller grains of rutile. Compositionally, the Ba–Fe titanate approximates the ideal formula $BaFe^{2+}Ti_7O_{16}$ (Table 2, anal. 4). Recalculation of the average electron-microprobe data for this

TABLE 5. X-RAY POWDER DIFFRACTION DATA FOR HENRYMEYERITE AND ITS SYNTHETIC ANALOGUE

HENRYMEYERITE*		SYNTHETIC SAMPLE			HENRYMEYERITE*		SYNTHETIC SAMPLE		
I_{calc}	d (Å)	I_{obs}	d (Å)	h k l	I_{calc}	d (Å)	I_{obs}	d (Å)	h k l
3	7.226			1 1 0	<1	1.682	3	1.671	5 0 1
9	5.109			2 0 0	1	1.682			4 3 1
15	3.613	20	3.57	2 2 0	1	1.616	4	1.598	620 + 260
100	3.232	100	3.19	310 + 130	33	1.598	31	1.587	521 + 251
10	2.846	8	2.850	1 0 1	10	1.481	10	1.485	0 0 2
4	2.555	3	2.526	4 0 0	6	1.461	10	1.450	611 + 161
34	2.486	20	2.483	211 + 121	<1	1.445	2	1.430	5 5 0
18	2.285	13	2.259	420 + 240	1	1.445	<1	1.430	1 7 0
40	2.236	40	2.227	3 0 1	<1	1.417	1	1.402	4 6 0
11	2.048	5	2.039	321 + 231	26	1.405	20	1.394	541 + 451
6	2.004	7	1.982	510 + 150	1	1.371	<1	1.372	2 2 2
31	1.901	29	1.891	411 + 141	4	1.355			631 + 361
6	1.806	8	1.787	4 4 0	12	1.347	9	1.347	312 + 132
4	1.753	2	1.734	530 + 350	8	1.342			730 + 370
22	1.703	17	1.684	6 0 0	2	1.310			7 0 1

* Pattern was calculated on the basis of single-crystal refinement data and chemical composition of henrymeyerite using the program FULLPROF.

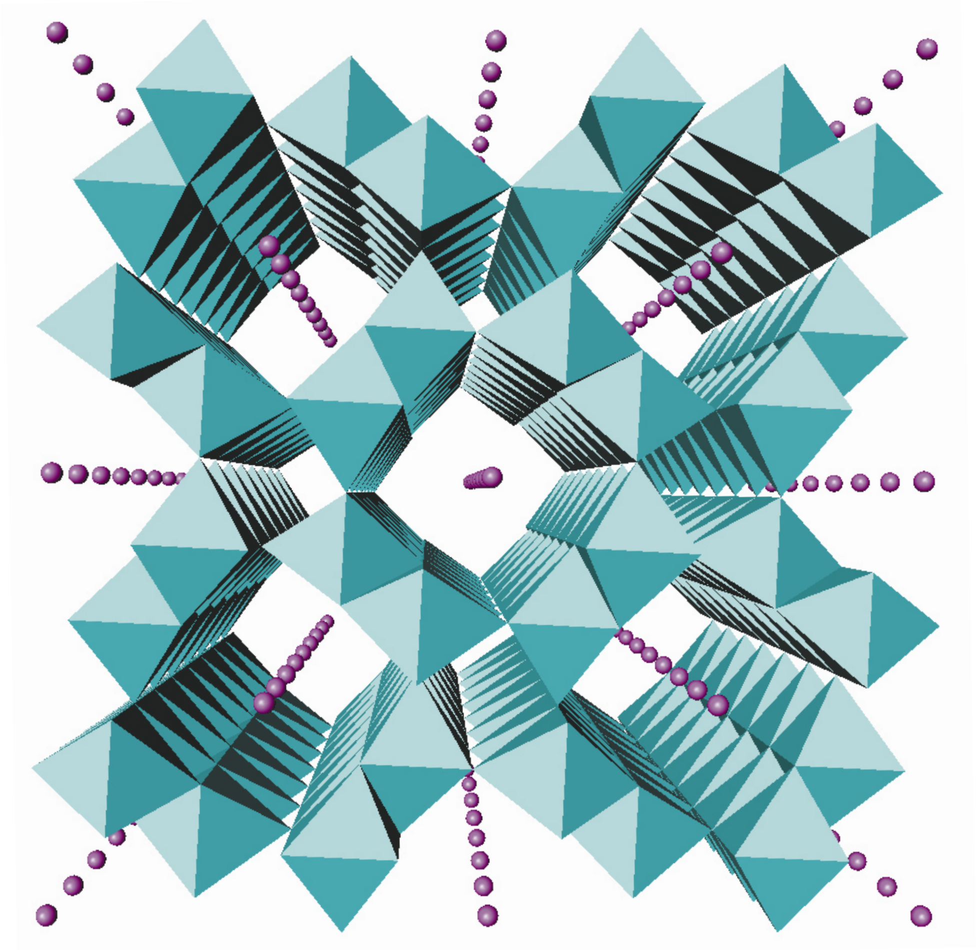

FIG. 2. Polyhedral representation of the structure of henrymeyerite, perspective view approximately along [001]. Note double-chain walls of $(Ti,Fe)O_6$ octahedra (green) forming large and small square tunnels along [001]. Within the large tunnels, 2*b* positions partially occupied by Ba are denoted by purple circles.

compound on the basis of 16 atoms of oxygen and assuming complete occupancy at the *B* site shows that iron was partially oxidized to Fe^{3+} during the synthesis. However, the proportion of the hexatitanate component $BaFe^{3+}_2Ti_6O_{16}$ is relatively small (~ 7 mol.%), and can be disregarded.

The XRD powder pattern of synthetic $BaFe^{2+}Ti_7O_{16}$ (Table 5) was obtained on a Philips 3710 diffractometer using Cu*K*α radiation. The diffractometer was operated at 40 kV and 30 mA in a step-scan mode. The pattern does not show splitting of (*hk*0) reflections, indicating that the symmetry of synthetic $BaFe^{2+}Ti_7O_{16}$ is tetragonal. The unit-cell parameters calculated by least-squares techniques [*a* 10.099(2), *c* 2.9684(6) Å] are in reasonable agreement with the parameters obtained for the single crystal of henrymeyerite. Note that the parameter *a* is sensitive to axial elongation of the BO_6 octahedra; hence, some discrepancy in *a* between henrymeyerite and its analogue probably arises from differences in degree of polyhedron distortion. A detailed structural study of synthetic $BaFe^{2+}Ti_7O_{16}$ is currently under way.

DISCUSSION

To illustrate relationships among henrymeyerite and other known cryptomelane-group Ba titanates, we used the diagram based on four major elements substituting for Ti in the *B* sites: Fe, V, Cr and Nb (Fig. 3). No distinction was made between Fe^{2+} and Fe^{3+}, as the overwhelming majority of studies do not provide any spectroscopic data. Data plotted in Figure 3 indicate that Ba–Fe, Ba–Cr and Ba–V end-members of the cryptomelane group probably form extensive solid-solutions, with the general formula $Ba_{x+1/2y}[Fe^{2+}_x(Fe^{3+},V^{3+},Cr^{3+})_y Ti_{8-x-y}]O_{16}$, where $0 \le x \le 1$ and $0 \le y \le 2$. The corresponding end-member compositions are redledgeite

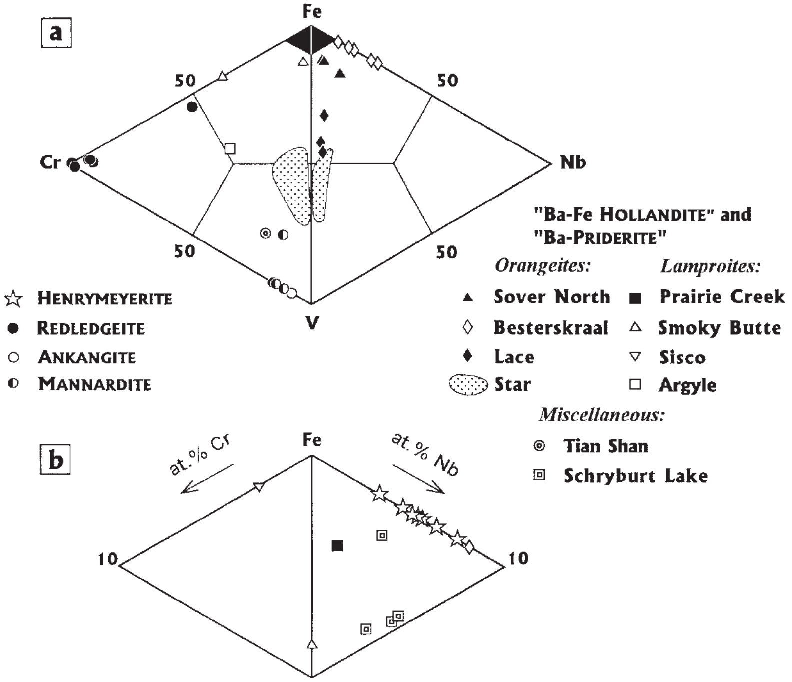

FIG. 3. Compositions (at.%) of cryptomelane-group titanate minerals in terms of different *B*-site cations (excluding Ti). (a) Quaternary plot in terms of Cr–Fe–Nb–V; (b) detailed view of the shaded area. This diagram incorporates only Ba-dominant compositions; priderite and structurally unassigned phases with K/Ba > 1.0 are not shown. Data corresponding to henrymeyerite are from this study; other data were taken from Gatehouse *et al.* (1986), Scott & Peatfield (1986), Mitchell & Meyer (1989), Xiong *et al.* (1989), Mitchell & Bergman (1991), Dmitriyeva *et al.* (1992), Platt (1994), Mitchell (1995), and Foley *et al.* (1997). Note that hollandite-type minerals from some localities, *e.g.*, Murun and Pegmatite Peak (Mitchell & Vladykin 1993, Chakhmouradian & Mitchell 1999) lack detectable Cr, V and Nb; their compositions plot at the Fe apex of the diagram.

($BaCr_2Ti_6O_{16}$), mannardite [($(Ba \bullet H_2O)V_2Ti_6O_{16}$], henrymeyerite ($BaFe^{2+}Ti_7O_{16}$), and Ba–Fe hexatitanate $BaFe^{3+}_2Ti_6O_{16}$. These end-members, with a possible exception of $BaFe^{3+}_2Ti_6O_{16}$, crystallize with tetragonal symmetry (Scott & Peatfield 1986, Foley *et al.* 1997, this work). Synthetic hollandites approaching $BaFe^{3+}_2Ti_6O_{16}$ in composition may be tetragonal (*I*4/*m*: Mitchell & Chakhmouradian, unpubl. data) or monoclinic (*I*2/*m*: Loezos *et al.* 1999). Note that mannardite, which plots near the V apex of the diagram (Fig. 3), contains significant amounts of molecular H_2O, and has the $I4_1/a$ symmetry (Scott & Peatfield 1986, Szymański 1986). An unnamed "Ba–Ti hollandite" described by Dmitriyeva *et al.* (1992) contains high levels of Cr, Fe and Mg, and has a reduced tetragonal symmetry (*I*4) owing to commensurate ordering of Ba cations in tunnels. Hence, the "quaternary" hollandites $Ba_{x+1/2y}[Fe^{2+}_x(Fe^{3+},V^{3+},Cr^{3+})_yTi_{8-x-y}]O_{16}$ probably crystallize with tetragonal symmetry, but may deviate slightly from the archetypal structure depending on the presence or absence of H_2O molecules and Ba ordering in tunnels.

In common with cryptomelane-group minerals from other carbonatite occurrences (Gaspar *et al.* 1994, Platt 1994), henrymeyerite contains appreciable Nb (up to 1.4 wt.% Nb_2O_5). Other evolved silica-undersaturated rocks such as agpaitic nepheline syenites and Group-II kimberlites (orangeites) may also contain Nb-rich priderite or related phases (Men'shikov *et al.* 1978, Mitchell 1995). The highest Nb contents (up to 6.8 wt.% Nb_2O_5 or 0.40 *apfu* Nb) have been observed for hollandite-group titanates in orangeites from the Star mine and Besterskraal, South Africa (Mitchell & Meyer 1989, Mitchell 1995). Hollandite-type minerals do not easily incorporate pentavalent cations, as these cations increase the total positive charge of the structural framework and prohibit accommodation of K and Ba in tunnels. It is noteworthy that several hollandites with pentavalent Sb have been synthetically prepared (*e.g.*, $K_2Fe_5Sb_3O_{16}$: Zhang & Burnham 1994), and the existence of similar Nb compounds in nature cannot be ruled out. However, Figure 3 demonstrates that coupled substitutions such as $2Ti^{4+} \Leftrightarrow Nb^{5+} + Fe^{3+}$ and $2Ti^{4+} \Leftrightarrow Nb^{5+} + Cr^{3+}$ probably have a limited significance for naturally occurring hollandite-type phases crystallizing at low to moderate pressures.

The conditions of crystallization of henrymeyerite are difficult to assess. Mineralized vugs and fractures are common in the central and eastern parts of the Kovdor phoscorite–carbonatite unit, where the rocks underwent extensive cataclasis and hydrothermal alteration (Liferovich *et al.* 1998). Circulation of hydrothermal fluids was tectonically controlled by a system of northeast- and north-trending faults. In the zone of cataclasis and alteration, cavernous dolomite carbonatites host the greatest diversity of minerals, some of which (rimkorolgite, krasnovite, girvasite, kovdorskite and juonniite) have been thus far described only at Kovdor. The composition of henrymeyerite and other late-stage phases from the mineralized vugs clearly indicates that the parental hydrothermal fluid was enriched in Ba, Nb, Sr, Sc and Zr. Liferovich *et al.* (1998, 1999) suggested that these incompatible elements were mobilized from the wallrock phoscorites and carbonatites by the fluid. The abundance of phosphates in the mineralized vugs attests to a high activity of $(PO_4)^{3-}$ ions in the fluid, which decreased progressively with increasing alkalinity in the system (Kukharenko *et al.* 1965). According to Liferovich *et al.* (1998), the hydrothermal alteration of dolomite carbonatites probably took place in the temperature range 160–230°C.

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