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Ankangite from the Monte Arsiccio mine (Apuan Alps, Tuscany, Italy): occurrence, crystal structure, and classification problems in cryptomelane group minerals

Cristian Biagioni*, Paolo Orlandi and Marco Pasero

Dipartimento di Scienze della Terra - Università di Pisa - Via S. Maria 53, 56126 Pisa, Italy

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Abstract. — A new occurrence of ankangite, a rare member of the hollandite structural family, is described. Ankangite was found in small fractures in dolomitic marble at the Monte Arsiccio mine, a small deposit of baryte, pyrite and Fe oxides in the Apuan Alps, Tuscany, Italy. The mineral occurs as prismatic black crystals, up to 5 mm in length, associated with "apatite", anatase, arsenopyrite, Ba-rich K-feldspar, baryte, dolomite, pyrite, quartz, sphalerite, stibnite, valentinite, and zinkenite. The crystal structure of ankangite from the Monte Arsiccio mine was refined to $R_1 = 0.016$. Ankangite is a member of the titanate subgroup in the cryptomelane group. The classification and nomenclature of the hollandite-group minerals are discussed.

Riassunto. — Viene descritto un nuovo ritrovamento di ankangite, un raro membro della famiglia strutturale dell'hollandite. L'ankangite è stata trovata in piccole fratture del marmo dolomitico della miniera di Monte Arsiccio, un piccolo deposito di barite, pirite e ossidi di Fe delle Alpi Apuane (Toscana, Italia). Questo minerale si presenta in cristalli prismatici neri, lunghi fino a 5 mm, associati a "apatite", anatasio, arsenopirite, barite, dolomite, K-feldspato ricco in Ba, pirite, quarzo, sfalerite, stibnite, valentinite e zinkenite. La struttura dell'ankangite della miniera di Monte Arsiccio è stata raffinata fino a $R_1 = 0.016$. L'ankangite è un membro del sottogruppo dei titanati, all'interno del gruppo del criptomelano. Viene discussa la classificazione e la nomenclatura dei minerali del gruppo dell'hollandite.

Key words: *ankangite, crystal structure, classification, Monte Arsiccio mine, Apuan Alps, Tuscany.*

Introduction

During the last three decades, the members of the hollandite structural family have been intensively studied as potential repositories for radioactive wastes (Ringwood *et al*., 1979) and as hypothetical minor silicate phases in the Earth's mantle, because feldspars at very high pressures transform into a hollandite-type structure (Ringwood *et al*., 1967; Zhang *et al*., 1993; Foley *et al*., 1994). Most naturally occurring hollandite-type oxides, belonging to the cryptomelane mineral group, have been structurally characterized in great detail; they present a common structural framework of octahedrally coordinated cations, interlinked by edge-sharing to form double columns delimiting a central tunnel (2x2 tunnel structure; Pasero,

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* Corresponding author, E-mail:biagioni@dst.unipi.it

2005). All these phases, with the exception of akaganéite, can be divided into two chemically distinct subgroups, manganates and titanates. The latter consists of priderite and four Ba-dominant phases with V^{3+}, Cr^{3+} and Fe^{2+} replacing Ti in octahedra: ankangite (Xiong *et al*., 1989), mannardite (Scott and Peatfield, 1986), redledgeite (Strunz, 1961; Strunz, 1963; Scott and Peatfield, 1986), and henrymeyerite (Mitchell *et al*., 2000). These species have a tetragonal symmetry, but typically show slight deviations from the archetypal hollandite structure, mainly due to the splitting of the cation sites in two independent positions, as in mannardite (Szymański, 1986), or due to incommensurate ordering within the tunnel site, as in ankangite (Shi *et al*., 1991). However, usually the titanates maintain the *I*4/*m* symmetry corresponding to the undistorted structure.

Ankangite is a rare member of the titanate subgroup. It was first described from the Shiti baryte deposit (Ankang County, Shaanxi Province, China) in a quartz vein associated with baryte, barytocalcite, roscoelite, and diopside. Its crystal structure was determined in space group *I*4/*m*, with cell parameters $a = 10.118(1)$, $c = 2.956(3)$ Å. Oscillation photographs, taken along [001], showed weak diffractions at about 1/2.27 **c***, assigned to a one-dimensional incommensurate modulation (Xiong *et al*., 1989; Xiang *et al*., 1990; Wu *et al*., 1990). According to the latter authors, the formation of an incommensurately modulated structure in ankangite is due to the existence of vacancies and to the displacement of Ba ions within the tunnels. Shi *et al*. (1991) proposed for ankangite a supercell 14 times longer than the basic 3 Å subcell [$a = 10.126(4)$, $c = 41.41(2)$ Å], and space group *P*4/*m*.

Ankangite was also reported as an accessory mineral in corundum-bearing hornfels from the Khibiny alkaline pluton, Kola Peninsula, Russia (Mikhailova *et al*., 2007), and in quartz layers from metamorphosed Cr-V-bearing carbonate-siliceous sediments of the Sludyanka complex, Southern Lake Baikal, Siberia, Russia (Reznitskii *et al*., 2007; Armbruster *et al*., 2008).

In this work, we describe the first Italian occurrence of ankangite in the baryte-pyrite-Fe oxides deposit of Monte Arsiccio mine, Apuan Alps, Tuscany. This new find allowed us to collect high-quality single-crystal X-ray diffraction data and to refine the crystal structure of ankangite.

OCCURRENCE AND GEOLOGICAL SETTING

Ankangite was found at the Sant'Olga level of the Monte Arsiccio mine, a small Ba-Fe deposit in the Apuan Alps (Tuscany, Italy) which was operated prior to 1989. The main ore body is an almost conformable lens characterized by a distinct zoning, with pyrite + baryte at the bottom, and iron oxides (magnetite and hematite) + baryte at the top, with various accessory sulfides and sulphosalts. The mineralization is hosted at the contact between phyllites of the Scisti di Fornovolasco Formation, probably related to the Palaeozoic basement of Apuan Alps, and Triassic dolomitic limestones of the Grezzoni Formation. The mineralization shows evidence of metamorphic deformation and/or recrystallization at macro- and microscopic levels.

Carmignani *et al*. (1972, 1976) considered this ore deposit as the product of metasomatic replacement of carbonate rocks, genetically linked to a hypothetical synkinematic intrusive body. Alternatively, according to Costagliola *et al*. (1990), the deposit was formed as primary sedimentary-diagenetic mineralization, which was subsequently metamorphosed and partly remobilized during the Tertiary Apenninic orogeny.

Ankangite occurs in small sub-horizontal veins (N90E 20S) embedded in the dolomitic marble or in a fine-grained mixture of baryte, pyrite, and arsenopyrite. In these veins, ankangite is associated with "apatite", anatase, arsenopyrite, Ba-rich K-feldspar, baryte, dolomite, pyrite, quartz, sphalerite, stibnite, valentinite, and zinkenite. Ankangite occurs as black prismatic crystals up to 5 mm in length, with a sub-metallic luster (Fig. 1).

MINERALOGICAL CHARACTERIZATION

X-ray data

The X-ray powder pattern of ankangite (Table 1) was obtained with a 114.6 mm Gandolfi camera, with Ni-filtered Cu$K\alpha$ radiation. The calculated intensities were obtained using the POWDERCELL program (Kraus and Nolze, 2000) on the basis of the refined crystal structure. All the expected strong lines were observed.

A single-crystal X-ray diffraction study was carried out using a cleavage fragment of ankangite, mounted with *c* as the rotation axis on a Weissenberg camera. It did not show any evidence of additional reflections in long-exposed oscillation photographs, indicating a basic *c* periodicity of about 2.95 Å. In contrast to the Shiti material studied by Xiong *et al*. (1989), we did not observe any evidence of incommensurate superlattice ordering in the Monte Arsiccio samples.

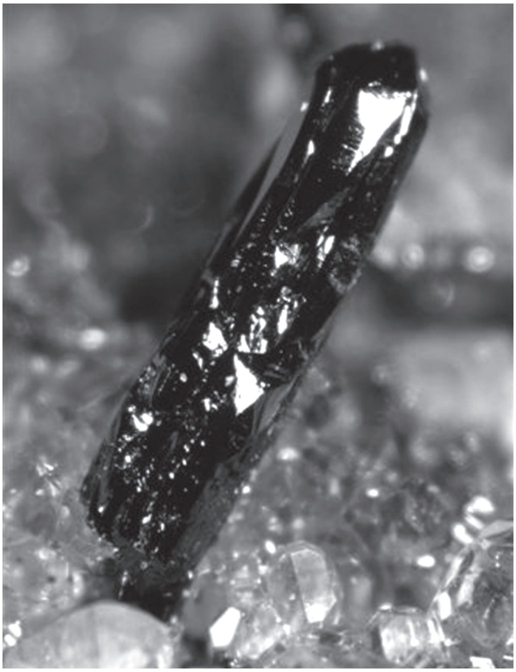

Fig. 1 – 2 mm long prismatic crystal of ankangite on baryte. Monte Arsiccio mine, Stazzema, Apuan Alps, Tuscany.

TABLE 1
X-ray powder diffraction data for ankangite

I_{obs}	d_{obs}	d_{calc}	I_{calc}	*hkl*
-	-	7.171	1.21	110
w	5.069	5.071	10.34	200
m	3.581	3.586	29.85	220
vs	3.206	3.207	100.00 51.98	130 310
w	2.885	-	-	-
w	2.850	2.836	12.42	101
vw	2.540	2.536	5.04	400
s	2.476	2.475	11.76 54.74	211 121
m	2.275	2.268	18.03 7.62	240 420
s	2.227	2.224	54.32	301
w	2.045	2.037	1.02 10.01	231 321
w	1.994	1.989	8.31	510
s	1.892	1.890	6.91 32.56	141 411
w	1.795	1.793	5.47	440
w	1.745	1.739	1.19 3.98	530 350
m	1.694	1.690	30.27	600
s	1.592	1.588	7.20 35.23	521 251

Note: visually estimated intensities from 114.6 mm Gandolfi camera, with Cu*Ka* radiation; vs = very strong; s = strong; m = medium; w = weak; vw = very weak. Calculated intensities from the refined crystal-structure parameters.

Chemical analysis

A crystal of ankangite in polished section was analyzed using an ARL-SEMQ microprobe under the following analytical conditions: accelerating voltage 15 kV, specimen current 20 nA, beam diameter 3 μm. The following standards were used: baryte (Ba*L*α), synthetic TiO_2 (Ti*K*α), metallic vanadium (V*K*α), synthetic Cr_2O_3 (Cr*K*α), and ilmenite (Fe*K*α). The average composition and range are reported in Table 2.

The empirical formula for ankangite from Monte Arsiccio, based on 16 oxygen atoms, is $Ba_{0.93}(Ti_{5.93}V_{1.79}Cr_{0.32}Fe^{2+}_{0.05})_{\Sigma=8.08}O_{16}$. Iron is assumed to occur in this mineral as Fe^{2+} on the basis of its parageneses with Fe^{2+} sulfides. With respect to the ideal formula AM_8O_{16}, there is a small deficit of A cations and a small excess of M cations in the empirical formula of Monte Arsiccio material, and it might seem appropriate to include Fe^{2+} together with Ba^{2+}. However, Fe^{2+} was grouped together with octahedrally coordinated cations because of its small ionic radius and its structural behaviour in other naturally occurring titanates of cryptomelane group, such as in henrymeyerite, $BaTi_7Fe^{2+}O_{16}$ (Mitchell *et al*., 2000).

TABLE 2
Electron microprobe data of ankangite (average of 22 analyses)

	wt.%	range	e.s.d.
BaO	18.24	17.19 – 19.31	0.62
TiO_2	60.66	58.21 – 62.97	1.31
V_2O_3	17.15	14.63 – 18.80	1.22
Cr_2O_3	3.08	1.12 – 5.00	1.17
FeO	0.42	0.16 – 0.75	0.20
Total	99.54	98.30 –101.15	0.92

CRYSTAL STRUCTURE AND CRYSTAL CHEMISTRY

A cleavage fragment of ankangite, measuring approximately 0.4 x 0.16 x 0.12 mm^3, was mounted on a SIEMENS P-4 four-circle diffractometer equipped with a graphite-monochromated Mo*K*α X-ray source. The unit-cell parameters were refined in space group $I4/m$ to $a = 10.142(1)$ and $c = 2.9533(3)$ Å by least square fitting of 28 reflections in the range $30° < 2\Theta < 50°$. Intensity data were collected up to 70° in 2Θ, with a scan speed of 2°/min and scan range ± 0.52 in Θ. A total of 1088 reflections were collected, which were reduced to a set of 386 unique reflections ($R_{int} = 0.0288$) after Lorentz-polarization and absorption corrections (y-scan measures).

Refinement was performed using the SHELX-97 package of programs (Sheldrick, 1997) to a conventional R factor of 0.016 ($wR_2 = 0.0427$, GooF = 1.242). The structure was refined using the atomic fractional coordinates of hollandite (Post *et al*., 1982) as a starting model and neutral atom scattering factors according to the chemical composition. A difference Fourier synthesis revealed the presence of a satellite Ba site (Ba2) slightly displaced along the *c* axis with respect to the Ba1 site, located at the inversion center (0, 0, 0). After the refinement of the occupancy of both Ba sites, we adjusted the Ti/V ratio at the M site so as to guarantee the electrostatic neutrality of the structure. The resulting structural formula of ankangite from Monte Arsiccio is $Ba_{1.16}(Ti_{5.68}V_{2.32})O_{16}$.

Table 3 reports the positional and equivalent isotropic displacement parameters, and Table 4 gives selected interatomic bond distances. Ankangite is structurally related to hollandite: it consists of a framework of octahedra linked together by edge-sharing to form double columns, which in turn share corners to give rise to a three-dimensional framework containing 2x2 tunnels (Fig. 2).

The octahedra are occupied predominantly by

Table 3

Positional parameters and equivalent isotropic U_{eq} displacement parameters in ankangite

Site	*x*	*y*	*z*	U_{eq}	*Refined occupancy*
Ba1	0	0	0	0.0230(2)	$Ba_{0.72}$
Ba2	0	0	0.12883(1)	0.0257(9)	$Ba_{0.44}$
Ti	0.16562(3)	0.65083(2)	½	0.0068(1)	$Ti_{0.71}V_{0.29}$
O1	0.1671(1)	0.4607(1)	½	0.0076(2)	O
O2	0.2034(1)	0.8445(1)	½	0.0062(2)	O

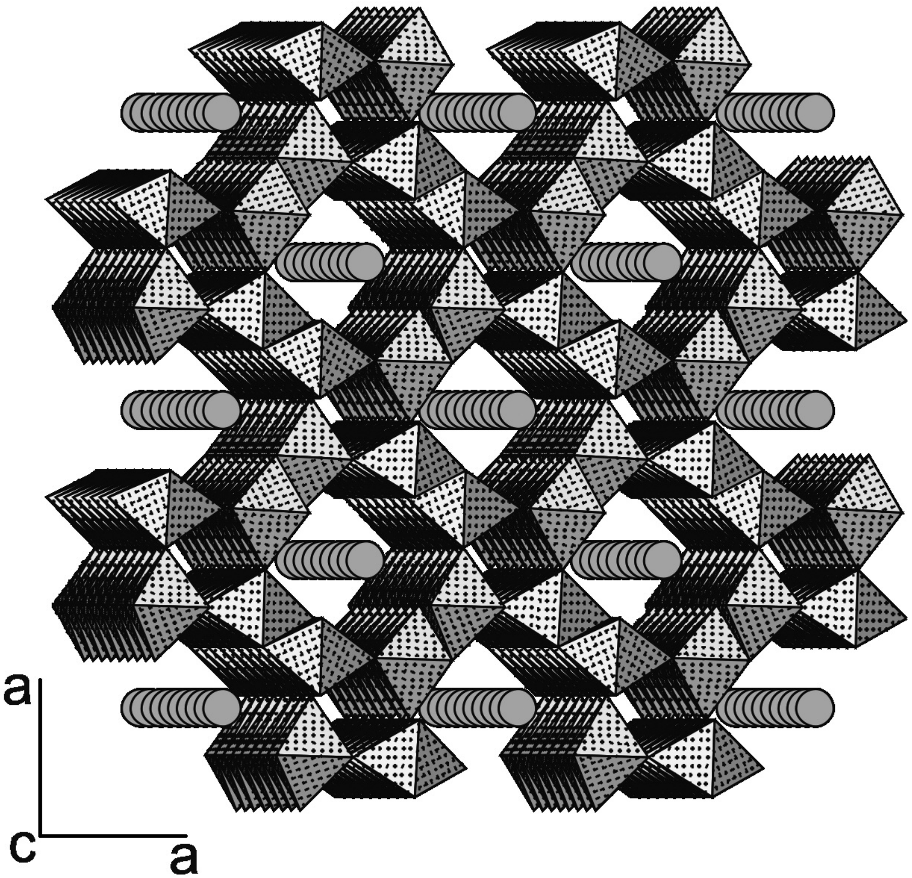

Fig. 2 – Crystal structure of ankangite. Within the tunnels, only the Ba1 site at (0,0,0) is shown.

Table 4
Selected interatomic distances (Å) in ankangite

Ba1	- O2 x 8	2.987(1)	Ti	- O1	1.929(1)
				- O1' x 2	1.962(1)
Ba2	- O2 x 4	2.82(1)		- O2 x 2	1.987(1)
	- O2 x 4	3.19(1)		- O2'	2.001(1)

tetravalent metal transition ions (Mn^{4+} or Ti^{4+}), which can be substituted by trivalent or divalent cations. The charge balance is accomplished by the introduction of large cations (K^+, Na^+, Ba^{2+}, Pb^{2+} or Sr^{2+}) within the tunnels. Ankangite belongs to the chemical subgroup of titanates; in the octahedra Ti^{4+} is substituted by V^{3+} and, in minor amounts, by Cr^{3+} and Fe. The tunnel sites are occupied by Ba^{2+}. Ankangite differs from redledgeite (Gatehouse *et al.*, 1986; Foley *et al.*, 1997) in having V^{3+} instead of Cr^{3+} as the main cation substituting for Ti^{4+}. It is chemically very similar to mannardite; the latter mineral, however, has a doubled periodicity along the *c* axis and it contains H_2O.

The unit-cell translation along the tunnel (c = 3 Å) is shorter than the minimum Ba-Ba distance acceptable from the standpoint of electrostatic repulsion; therefore, partial occupancy at these cation sites is required. The structural refinement points to the presence of two independent Ba sites. The Ba1 site at (0,0,0) lies at the center of the cell whereas Ba2 site is shifted by 0.38 Å from Ba1 along the *c* axis. We suggest two possible sequences of filling the Ba sites: in the first case (left side of Fig. 3), every second Ba1 site is empty, and the total occupancy along the tunnel is 50%, *i.e.* 1 atom per formula unit. The other possibility (right side of Fig. 3) is the sequence |Ba2b-Ba2a-□|, with a total occupancy along the tunnel of 66%, *i.e.* 1.33 *apfu*. The total barium occupancy resulting from the structural refinement (1.16 *apfu*) may be interpreted to indicate a statistical distribution of these two sequences.

Nomenclature of Cryptomelane Group Minerals

Ankangite, ideally $BaTi_6V_2O_{16}$, is a member of titanate subgroup of the hollandite structural family. The introduction of mono- and divalent cations in the tunnels requires the substitution of the tetravalent octahedrally-coordinated cation by a lower-valence cation. This substitution mechanism can be classified as a coupled heterovalent substitution at two sites (*i.e.*, [vacancy] + $2M^{4+} \rightarrow A^{2+} + 2M^{3+}$) leading to a valence-imposed double-site occupancy (Hatert and Burke, 2008).

In addition, the M^{3+} cation (rarely, as in henrymeyerite, M^{2+}) can be one of several different species, giving rise to a number of homovalent substitutions. Therefore, the nomenclature of these minerals needs to reflect both the dominant occupant of the tunnel site(s) and the dominant charge-compensating cation in the octahedrally-coordinated M site(s).

At present, the titanate subgroup of the cryptomelane group includes four different minerals with Ba in the tunnel site(s): redledgeite, mannardite, ankangite, and henrymeyerite. Whereas mannardite differs from the other three minerals chemically (*i.e.* it contains H_2O and, thus, it is a hydrated analogue of ankangite) and structurally (it has a different unit cell and space group), the three remaining titanates differ only in the main substituent of Ti in the octahedrally-coordinated site: Cr^{3+} in redledgeite, V^{3+} in ankangite, and Fe^{2+} in henrymeyerite.

This classification approach is apparently not followed for the manganate subgroup. The latter subgroup includes five different minerals: coronadite, cryptomelane, hollandite, manjiroite, and strontiomelane, which contain Pb, K, Ba,

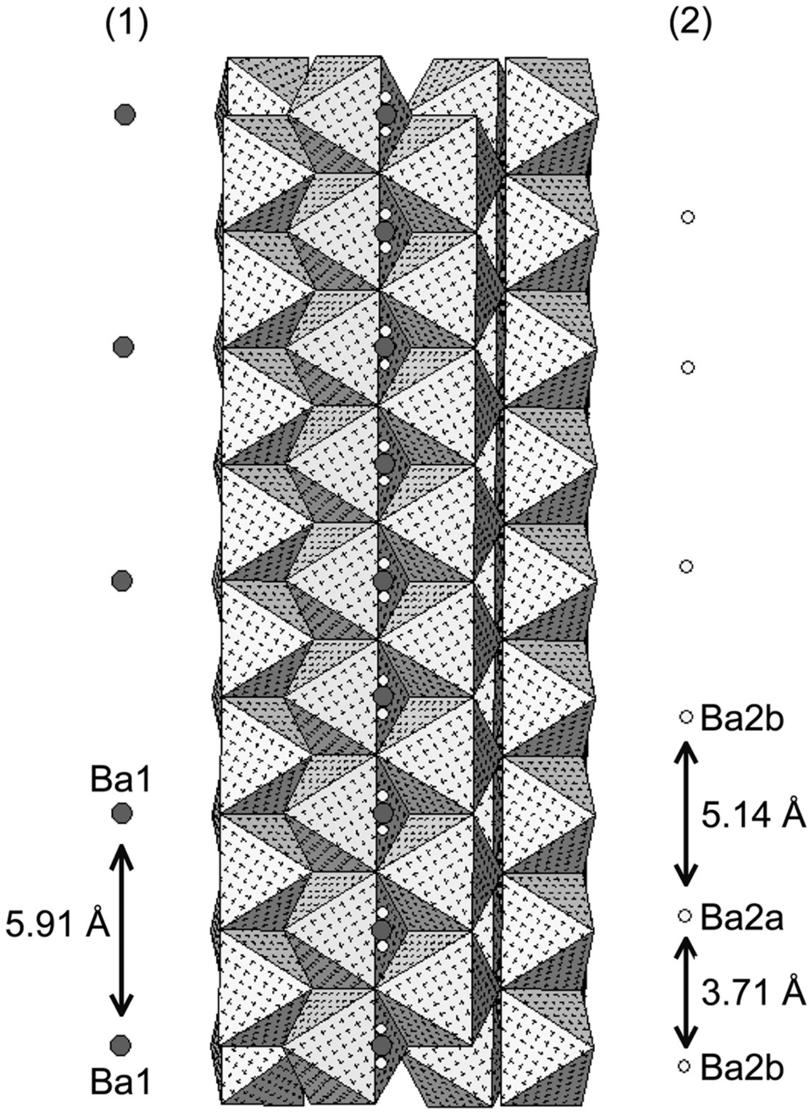

Fig. 3 – The two possible idealized distribution of Ba cations in the tunnel sites: 1) |Ba1-□|, and 2) |Ba2b-Ba2a-□|. The labels Ba2a and Ba2b refer to the two equivalent Ba2 positions above and below the mirror plane, respectively.

Na, and Sr, respectively, as the dominant tunnel cation. Let us have a closer look at hollandite, whose ideal formula can be written as $BaMn^{4+}{}_6Mn^{3+}{}_2O_{16}$. The chemical analyses reported in the literature show variable amount of Fe in this mineral. The first problem that needs to be addressed is the difficulty to assessing the true valence state of Mn and Fe. According to Post *et al*. (1982), the reduced form of Mn is, for steric reasons, Mn^{3+}, and not Mn^{2+}, as it was suggested in the earlier studies. Routinary analyses performed with EPMA do not permit the assessment of the real valence of the elements and typically Mn and Fe are reported as total Mn and total Fe. Notwithstanding this shortcoming, it is possible to distinguish two types of hollandite, a low-Fe type (*e.g*. samples from Langenberg, Germany, and Gowari Wadhona, India, containing 0.11 wt.% and 1.71 wt.% Fe_2O_3 respectively; Frondel *et al*., 1960; Miura, 1986), and a Fe-rich type (as exemplified by hollandite with 12.63 wt.% Fe_2O_3 from Stuor, Sweden; Post *et al*., 1982). The latter authors calculated the following chemical formula for hollandite from Stuor, using a Mn^{3+}:Mn^{4+} ratio of 0.08 to maintain electrostatic balance:

$(Ba_{0.75}Pb_{0.16}Na_{0.10}K_{0.04})_{\Sigma=1.05}(Mn^{4+}{}_{6.08}Fe^{3+}{}_{1.32}Mn^{3+}{}_{0.50}Al_{0.23}Si_{0.08})O_{16}$.

According to this formula, the introduction of mono- and divalent cations in the tunnels is balanced by the substitution of Mn^{4+} by trivalent cations; the main substituent is Fe^{3+}, suggesting the existence of the hypotethical end-member $BaMn^{4+}{}_6Fe^{3+}{}_2O_{16}$. This is a potentially new species of the cryptomelane group. It is interesting to note that, although the ideal chemical formula of hollandite is given in the IMA List of Minerals as $BaMn^{4+}{}_6Mn^{3+}{}_2O_{16}$, the hollandite from the type locality (Kajlidongri, India), described by Fermor (1909; *cf*. Frondel and Heinrich, 1942), is Fe-rich and very close to the Fe^{3+} end-member.

From the above discussion, it appears that the crystal-chemistry of hollandite-type minerals needs to be critically re-examined and the overall nomenclature of this group revised. This calls for a careful review of the published data, with special attention to the extent of atomic substitutions in the octahedral site(s) and dominant charge-compensating octahedral cation in the other members of the manganate subgroup.

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