

Nomenclature tunings in the hollandite supergroup

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Abstract: The hollandite supergroup includes a number of manganese (IV) and titanium oxides, often referred to as tunnel oxides due to their structural features, *i.e.* octahedral walls, 2×2 octahedra wide, cross-linked to each other to build up a tunnel structure. Tunnels host mono- and divalent cations, and water molecules. Based on the nature of the tunnel cation, the generic formula of these minerals may be written as either $A^{2+}[M^{4+}_6M^{3+}_2]O_{16}$ (more rarely, $A^{2+}[M^{4+}_7M^{2+}]O_{16}$) or $A^+[M^{4+}_7M^{3+}]O_{16}$ (more rarely, $A^+[M^{4+}_7.5M^{2+}_{0.5}]O_{16}$), where $A^{2+} = \text{Pb, Ba, Sr}$; $A^+ = \text{K, Na}$; $M^{4+} = \text{Mn, Ti}$; $M^{3+} = \text{Mn, Fe, Cr, V}$; $M^{2+} = \text{Fe}$. The hollandite supergroup is divided into two groups depending on the dominant tetravalent cation in the octahedral walls: the coronadite group ($M^{4+} = \text{Mn}$), and the priderite group ($M^{4+} = \text{Ti}$). Two main considerations led to the preparation of this report: (i) M^{3+} (or M^{2+}) cations, even if they share the same site as M^{4+} , are essential for charge-balance, therefore each combination of dominant A^{2+} (or A^+), M^{4+} , and M^{3+} (or M^{2+}) cations corresponds to a distinct species; (ii) the presence/absence of “zeolitic” water in the tunnels should not represent the discriminant between two species. Based on these guidelines, our main actions have been the following: hollandite is redefined as the Ba-Mn³⁺ end-member of the coronadite group; concurrently, type hollandite is redefined as ferrihollandite, a new name to denote the Ba-Fe³⁺ end-member; ankangite is discredited, as a H₂O-free variety of mannardite; the ideal end-member formulae of all known minerals of the hollandite supergroup are defined; six potentially new mineral species in the hollandite supergroup are envisaged. This report has been approved by the IMA CNMNC.

Key-words: hollandite supergroup, coronadite group, priderite group, nomenclature.

1. Introduction

Minerals of the hollandite supergroup are structurally characterized by octahedral walls (2×2 octahedra wide) cross-linked to each other to build up a tunnel structure. Hence these compounds are generally referred to as tunnel oxides (Pasero, 2005).

On chemical grounds, the hollandite supergroup can be divided into two groups, based on the dominant tetravalent sixfold-coordinated cation: the coronadite group ($^{\text{VI}}M^{4+} = \text{Mn}$), and the priderite group ($^{\text{VI}}M^{4+} = \text{Ti}$).¹ The nomenclature of these minerals depends on both the dominant tunnel cation (A^+ or A^{2+}) and the dominant charge-compensating octahedral cation (M^{3+} , more rarely M^{2+}).

The rule that each combination of dominant tunnel cation and dominant charge-compensating cation (hereafter DCCC) corresponds to a distinct mineral species has been adopted as the reason for the approval by the IMA CNMNC of some recent new minerals of the supergroup. This has been recently formalized with the introduction of the concept of “valence-imposed double site occupancy” (Hatert & Burke, 2008). However, for some of the grandfathered minerals of the supergroup (*e.g.*, hollandite,

cryptomelane, priderite), a clear definition of the end-member formula is lacking. As a consequence, minerals with different compositions are mentioned in the literature with the same name. For the sake of consistency within the whole hollandite supergroup and in agreement with the general guidelines on mineral nomenclature, those minerals should be regarded as distinct species.

Therefore, a re-definition of the end-member formulae, based on the original description of type material, is desirable. In fact, the chemical formulae so far accepted for hollandite, cryptomelane, and priderite may represent a source of confusion, as they do not provide a clear identification of the dominant tunnel cation and the dominant charge-compensating cation.

The purpose of this report is to provide a consistent nomenclature of the hollandite supergroup and to list a number of potentially new (not approved at the moment) mineral species that can be identified on the basis of the general crystal-chemical rules.

The report has been submitted to the CNMNC and received its complete approval.

2. Basic structural features

The ideal topological symmetry of 2×2 tunnel oxides is tetragonal, space group $I4/m$ ($a \approx 10.0$, $c \approx 2.9 \text{ \AA}$), which is

¹The names of the groups are after the oldest mineral among manganese and titanium oxides, which are coronadite and priderite, respectively. The name of the supergroup is after the most widespread mineral, which is hollandite.

Table 1. Different unit-cell parameters given for the minerals of the hollandite supergroup.

	Name	Space group	Unit-cell parameters	Ref.
Coronadite group (M ⁴⁺ = Mn)	Coronadite	<i>I2/m</i>	$a = 9.938, b = 2.868, c = 9.834 \text{ \AA}, \beta = 90.39^\circ$	Post & Bish (1989)
	Hollandite	<i>I4/m</i>	$a = 9.96, c = 2.86 \text{ \AA}$	Byström & Byström (1950)
		<i>P2₁/n</i>	$a = 10.02, b = 5.76, c = 9.89 \text{ \AA}, \beta = 90.60^\circ$	Mukherjee (1960)
		<i>I2/m</i>	$a = 10.026, b = 2.878, c = 9.729 \text{ \AA}, \beta = 91.03^\circ$	Post <i>et al.</i> (1982)
	Cryptomelane	<i>I4/m</i>	$a = 9.82, c = 2.83 \text{ \AA}$	Richmond & Fleisher (1942)
		<i>I2/m</i>	$a = 9.79, b = 2.88, c = 9.94 \text{ \AA}, \beta = 90.62^\circ$	Mathieson & Wadsley (1950)
	Manjiroite	<i>I4/m</i>	$a = 9.916, c = 2.864 \text{ \AA}$	Nambu & Tanida (1967)
Strontiomelane	<i>P2₁/n</i>	$a = 10.00, b = 5.758, c = 9.88 \text{ \AA}, \beta = 90.64^\circ$	Meisser <i>et al.</i> (1999)	
Priderite group (M ⁴⁺ = Ti)	Priderite	<i>I4/m</i>	$a = 10.139, c = 2.966 \text{ \AA}$	Post <i>et al.</i> (1982)
	Redledgeite	<i>I2/m</i>	$a = 10.135, b = 2.95, c = 10.129 \text{ \AA}, \beta = 91.03^\circ$	Gatehouse <i>et al.</i> (1986)
		<i>I4/m</i>	$a = 10.150, c = 2.952 \text{ \AA}$	Foley <i>et al.</i> (1997)
	Mannardite	<i>I4₁/a</i>	$a = 14.357, c = 5.908 \text{ \AA}$	Szymański (1986)
		<i>I4/m</i>	$a = 10.071, c = 14.810 \text{ \AA}$	Bolotina <i>et al.</i> (1992)
	Ankangite	<i>P4/m</i>	$a = 10.126, c = 41.41 \text{ \AA}$	Shi <i>et al.</i> (1991)
	Henrymeyerite	<i>I4/m</i>	$a = 10.142, c = 2.953 \text{ \AA}$	Biagioni <i>et al.</i> (2009)
<i>I4/m</i>		$a = 10.219, c = 2.963 \text{ \AA}$	Mitchell <i>et al.</i> (2000)	

displayed, for instance, in priderite. In some cases, structural refinements have been carried out in monoclinic (pseudo-tetragonal) space groups, with $a \approx c \approx 10.0 \text{ \AA}$, and $\beta \approx 90^\circ$, such as *I2/m* (e.g., cryptomelane) or *P2₁/n* (e.g., strontiomelane). The lowering of symmetry may be related to minor framework distortions and/or to the ordering of cations and vacancies within the tunnels, which may give rise to structures with multiple periodicities and incommensurate structures as well (Table 1).

Nickel & Grice (1998) state that:

The polymorphic forms of a mineral are regarded as different species if their structures are topologically different. However, if the crystal structure of the polymorphs have essentially the same topology, differing only in terms of a structural distortion or in the order – disorder relationship of some of the atoms comprising the structure, such polymorphs are not regarded as separate species.

Therefore, structural varieties in the hollandite supergroup should not be considered as distinct mineralogical species.

3. Chemical composition and calculation of the ideal formulae

For the recalculation of the ideal chemical formulae from electron-microprobe analyses, in the lack of any direct indication of the valence state of manganese or iron by spectroscopic methods, we suggest to formalize the method that has been adopted for several minerals of the supergroup, *i.e.* to recalculate the analytical data on the basis of 8 total octahedral cations and 16 oxygen atoms per formula unit (*pfu*). In general, when all Mn is given as MnO₂ and all Fe as Fe₂O₃, 8 octahedral cations should provide more than 32 positive charges, and the charge-balance could be achieved by partitioning total Mn content between Mn⁴⁺ and Mn³⁺. In some cases within the priderite group, where there is no Mn, the charge-balance can be obtained by partitioning total Fe between Fe³⁺ and Fe²⁺.

In some of the older chemical analyses, total manganese is already split between MnO₂ and MnO. However, it is accepted today that the reduced state of Mn in all minerals of the hollandite supergroup is Mn³⁺ and not Mn²⁺ (e.g., Post *et al.*, 1982). Therefore, those analyses should be recalculated accordingly. If the total positive charges are less than 32, all Mn and Fe will be given in their higher valence states. In those cases, charge-balance can be achieved by minor substitution of O²⁻ by (OH)⁻. However, due to the overall charge-balance requirements, the above substitution is not assumed to play an important role in any of the hollandite-supergroup minerals. Another possible mechanism for balancing the chemical formula could be represented by some excess tunnel cations. Since the periodicity along the tunnel is shorter than the ideal cation–cation distance, usually the tunnel sites are occupied approximately at the 50 % level, which gives one tunnel cation *pfu*, or a bit more; for example, Foley *et al.* (1997) suggest a maximum Ba occupancy of 1.33 atoms *pfu* in redledgeite.

The ideal crystal chemical formula of the minerals of the hollandite supergroup depends on the valence state of both the tunnel and charge-compensating cations, and should be written in one of the following ways:

- (1) if the dominant tunnel cation has charge 2+:
 $A^{2+}[M^{4+}_6M^{3+}_2]O_{16}$ (or, more rarely, $A^{2+}[M^{4+}_7M^{2+}]O_{16}$);
- (2) if the dominant tunnel cation has charge 1+:
 $A^+[M^{4+}_7M^{3+}]O_{16}$ (or, more rarely, $A^+[M^{4+}_{7.5}M^{2+}_{0.5}]O_{16}$).

In the above formulae, the species-forming cations so far known among minerals are: A²⁺ = Pb, Ba, Sr; A⁺ = K, Na; M⁴⁺ = Mn, Ti; M³⁺ = Mn, Fe, Cr, V; M²⁺ = Fe.

The water content of the minerals of the hollandite supergroup is a controversial issue. Formally, all but two minerals of the supergroup are anhydrous. The only minerals whose formulae include water molecules are manjiroite (Nambu & Tanida, 1967), and mannardite (Scott & Peatfield, 1986). However, some minor water has been

detected in selected analyses of other members of the hollandite supergroup, *e.g.* coronadite (Lindgren & Hillebrand, 1904; Post & Bish, 1989), cryptomelane (Richmond & Fleischer, 1942), and hollandite (Byström & Byström, 1950; Frondel *et al.*, 1960; Miura, 1986). In the light of the “zeolitic” character of water in tunnel oxides, H₂O molecules should not be regarded as an essential component. In other words, the presence/absence of water molecules should not discriminate between two distinct species. Among known minerals, the mannardite–ankangite pair is problematic in this respect.

4. Minerals of the hollandite supergroup

4.1. Coronadite group

4.1.1. Coronadite

The first description of coronadite is after the Clifton-Morenci copper district, Arizona, USA (Lindgren & Hillebrand, 1904). The chemical analysis on type material conforms with the ideal chemical formula $\text{Pb}(\text{Mn}^{4+}_6\text{Mn}^{3+}_2)\text{O}_{16}$. The crystal structure of coronadite has been refined in the space group *I2/m* by Post & Bish (1989).

4.1.2. Hollandite

According to the type description of hollandite from Kajlidongri (India) by Fermor (1906), the name hollandite should be applied to the member of the coronadite group having Ba as dominant tunnel cation and Fe³⁺ as DCCC. However, the name hollandite has been widely used by the mineralogical community to describe the more common phase having Mn³⁺ as DCCC. “Fe³⁺-hollandite” has been also reported from Stuur Njuoskes, Ultevis, Sweden (Post *et al.*, 1982), the Sanbagawa metamorphic belt, Japan (Enami & Banno, 2001), and few other localities. As stated above, “Mn³⁺-hollandite” is more widespread and known from several occurrences (*e.g.*, Miura, 1986; Miura *et al.*, 1987; Cabella *et al.*, 1992; Franceschelli *et al.*, 1996; Enami & Banno, 2001). The crystal structure of hollandite has been solved by Byström & Byström (1950) in the space group *I4/m* and refined by Post *et al.* (1982) in the space group *I2/m*. Although for priority reasons the name hollandite should be reserved to the Ba-Fe³⁺ end-member of the coronadite group, in recognition of the fact that the name “hollandite” typically refers to a manganese oxide mineral, we propose to adopt the name *hollandite* for the Ba-Mn³⁺ end-member, and to introduce the closely related name *ferrihollandite* for the Ba-Fe³⁺ end-member. The proposed neotype specimen of hollandite is the one from Gowani Wadhona, India (Miura, 1986).

4.1.3. Cryptomelane

The name cryptomelane was introduced in the mineralogical literature by Richmond & Fleischer (1942), who adequately characterized as a distinct mineral species material

previously denoted under the generic name of “psilomelane”, today obsolete. Richmond & Fleischer (1942) studied and analyzed samples from four different occurrences, all from the U.S. The samples are chemically distinct, but all have K⁺ as a dominant tunnel cation. Two samples (from Deming, New Mexico, and Philipsburg, Montana) have Mn³⁺ as DCCC, one sample (from Mena, Arkansas) has Fe³⁺ as DCCC, one sample (from Tombstone, Arizona) has Zn²⁺ as DCCC. At all other occurrences known since the original description, cryptomelane has Mn³⁺ as a DCCC; therefore it seems convenient to re-define cryptomelane as the K-Mn³⁺ end-member of the coronadite group with the ideal chemical formula $\text{K}(\text{Mn}^{4+}_7\text{Mn}^{3+})\text{O}_{16}$. The two samples from Mena, AR, and Tombstone, AZ, could be defined as potentially new mineral species, with the ideal formulae $\text{K}(\text{Mn}^{4+}_7\text{Fe}^{3+})\text{O}_{16}$ and $\text{K}(\text{Mn}^{4+}_{7.5}\text{Zn}^{2+}_{0.5})\text{O}_{16}$, respectively. Fe-rich cryptomelane (possibly with Fe³⁺ as DCCC) is also known from the Sausar Group, India (Miura *et al.*, 1987) and Montaldo di Mondovì, Piedmont, Italy (Cabella *et al.*, 1992). The crystal structure of cryptomelane has been refined by Post *et al.* (1982) in the space group *I2/m*.

4.1.4. Manjiroite

Manjiroite is a rare mineral first described by Nambu & Tanida (1967) from the Kohare mine, Iwate Prefecture, Japan. Its chemical composition, disregarding the water content (see above), points to the ideal end-member formula $\text{Na}(\text{Mn}^{4+}_7\text{Mn}^{3+})\text{O}_{16}$. No structural information is available for manjiroite; according to the original description, the mineral is tetragonal, space group *I4/m*.

4.1.5. Strontiomelane

Strontiomelane has been described as a strontium analogue of cryptomelane (Meisser *et al.*, 1999). Its ideal chemical formula is $\text{Sr}(\text{Mn}^{4+}_6\text{Mn}^{3+}_2)\text{O}_{16}$. The type locality is the Praborna mine, St. Marcel, Aosta Valley, Italy. No structural information is available; according to the original description, the mineral is monoclinic, space group *P2₁/n*. The length of the *b* axis is twice the typical value of ≈ 2.9 Å.

4.2. Priderite group

4.2.1. Priderite

The first description of priderite is from the Kimberley district, Western Australia (Norrish, 1951). According to the original chemical analysis, priderite is the K-Fe³⁺ end-member with the ideal chemical formula $\text{K}(\text{Ti}^{4+}_7\text{Fe}^{3+})\text{O}_{16}$. The crystal structure of priderite has been refined by Sinclair & McLaughlin (1982) and by Post *et al.* (1982) in the space group *I4/m*. The 3+ oxidation state of iron was confirmed by Mössbauer spectroscopy by Pring & Jefferson (1983) and by McCammon *et al.* (1999).

4.2.2. Redledgeite

Redledgeite was defined as a new mineral species by Strunz (1961). The type locality is the Red Ledge mine, California, USA. Actually, the mineral was discovered by Gordon & Shannon (1928), who misidentified it as a variety of rutile and named it “chromrutile”, a name which is obsolete today. Redledgeite is the Ba-Cr³⁺ end-member of the priderite group and its ideal chemical formula may be written as Ba(Ti⁴⁺₆Cr³⁺₂)O₁₆. The crystal structure of redledgeite has been refined by Gatehouse *et al.* (1986) in the space group *I2/m* and by Foley *et al.* (1997) in the space group *I4/m*.

4.2.3. Mannardite

Mannardite was first described by Scott & Peatfield (1986). The type locality is Rough Claims, British Columbia, Canada. Chemically, it represents the Ba-V³⁺ end-member of the priderite group. The ideal chemical formula is Ba(Ti⁴⁺₆V³⁺₂)O₁₆·H₂O. The crystal structure of mannardite has been refined in the space group *I4₁/a* by Szymański (1986) and in the space group *I4/m* by Bolotina *et al.* (1992). In the former case the short axis *c* is twice and, in the latter case, five times larger than the typical value of ≈2.9 Å. Since the presence or absence of H₂O molecules in the hollandite-supergroup minerals is not a discriminant factor, the formula of mannardite could be written as Ba(Ti⁴⁺₆V³⁺₂)O₁₆.

4.2.4. Ankanigite

Ankanigite, first described from the Shiti Ba deposit, Ankang County, Shaanxi Province, China (Xiong *et al.*, 1989) is very similar to mannardite in its chemical composition. The only difference between mannardite and ankanigite is in the absence of H₂O in the latter species. Ankanigite was approved as a mineral by the CNMNC based also on the difference in the length of the *c* unit-cell parameter (which is doubled in mannardite). The crystal structure of ankanigite has been refined in the space group *I4/m* by Shi *et al.* (1991) and by Biagioni *et al.* (2009), Shi *et al.* (1991) also proposed a possible superstructure with the space group *P4/m* and the *c* axis 14 times longer than the typical value of ≈2.9 Å. Since the presence or absence of H₂O molecules and the multiple character of the *c* axis length in the hollandite-supergroup minerals are not species-defining parameters, ankanigite is discredited as a variety of mannardite.

4.2.5. Henrymeyerite

Henrymeyerite is the most recent entry in the hollandite supergroup; it represents the Ba-Fe²⁺ end-member of the priderite group, Ba(Ti⁴⁺₇Fe²⁺)O₁₆. First described from the Kovdor mine, Kola Peninsula, Russia by Mitchell *et al.* (2000), it was likely found previously in other localities but described as a Ba-Fe priderite (*i.e.*, Mitchell & Lewis,

1983; Wagner & Velde, 1986; Platt, 1994). Its crystal structure has been refined in the space group *I4/m* (Mitchell *et al.*, 2000).

5. Potential new mineral species in the hollandite supergroup

Besides “K-Fe³⁺ cryptomelane” and “K-Zn²⁺ cryptomelane” mentioned above, a survey of literature data reveals that other minerals should deserve the status of distinct mineral species.

- (1) Zhuravleva *et al.* (1978) described the Ba-Fe³⁺ member of the priderite group from the Kovdor carbonatite complex (Russia). Later, other occurrences of the same phase were reported (*e.g.*, Reguir *et al.*, 2003). According to Mitchell *et al.* (2000), the existence of a wide range of compositions in priderites suggests the existence of two barium end-members, namely BaTi₇Fe²⁺O₁₆ (*i.e.*, henrymeyerite), and the separate species BaTi₆Fe³⁺₂O₁₆.
- (2) Mitchell & Lewis (1983) described the K-Fe²⁺ member of the priderite group, occurring in peridotite from Prairie Creek, Arkansas, USA. The same phase was also found at the Catalão I carbonatite complex, Goiás State, Brazil (Gaspar *et al.*, 1994).
- (3) Mitchell & Haggerty (1986) described the K-V³⁺ member of the priderite group, occurring in a kimberlite from New Elands, South Africa. The same phase was also found at the Star mine, Winburg district, South Africa (Mitchell & Meyer, 1989).
- (4) Jacques *et al.* (1989) described the K-Cr³⁺ member of the priderite group, occurring at the Argyle lamproite, Western Australia. The same phase was also described in the Mengying kimberlite, Shandong Province, China (Zhou & Lu, 1994).

6. Summary

The main outputs of this IMA-approved report are:

- (1) Redefinition of hollandite as the Ba-Mn³⁺ end-member of the coronadite group, and concurrent re-definition of type hollandite as ferrihollandite, a new name to denote the Ba-Fe³⁺ end-member.
- (2) Discreditation of the mineral ankanigite (=mannardite variety).
- (3) Definition of the ideal end-member formulae of all existing and potentially new mineral species of the hollandite supergroup, as summarized in Table 2.

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Table 2. Tunnel cation, dominant charge-compensating cation (DCCC), and ideal chemical formula in minerals of the hollandite supergroup.

	Name	Tunnel cation	DCCC	Ideal chemical formula	
Coronadite group ($M^{4+} = Mn$)	Coronadite	Pb ²⁺	Mn ³⁺	Pb(Mn ⁴⁺ ₆ Mn ³⁺ ₂)O ₁₆	
	Ferrihollandite	Ba ²⁺	Fe ³⁺	Ba(Mn ⁴⁺ ₆ Fe ³⁺ ₂)O ₁₆	
	Hollandite	Ba ²⁺	Mn ³⁺	Ba(Mn ⁴⁺ ₆ Mn ³⁺ ₂)O ₁₆	
	Cryptomelane	K ⁺	Mn ³⁺	K(Mn ⁴⁺ ₇ Mn ³⁺ ₂)O ₁₆	
	Manjiroite	Na ⁺	Mn ³⁺	Na(Mn ⁴⁺ ₇ Mn ³⁺ ₂)O ₁₆	
	Strontiomelane	Sr ²⁺	Mn ³⁺	Sr(Mn ⁴⁺ ₆ Mn ³⁺ ₂)O ₁₆	
	New root name	K ⁺	Fe ³⁺	K(Mn ⁴⁺ ₇ Fe ³⁺ ₂)O ₁₆	
	New root name	K ⁺	Zn ²⁺	K(Mn ⁴⁺ _{7.5} Zn ²⁺ _{0.5})O ₁₆	
	Priderite group ($M^{4+} = Ti$)	Priderite	K ⁺	Fe ³⁺	K(Ti ⁴⁺ ₇ Fe ³⁺ ₂)O ₁₆
		Redledgeite	Ba ²⁺	Cr ³⁺	Ba(Ti ⁴⁺ ₆ Cr ³⁺ ₂)O ₁₆
Mannardite		Ba ²⁺	V ³⁺	Ba(Ti ⁴⁺ ₆ V ³⁺ ₂)O ₁₆	
Ankangite (to be discredited)		Ba ²⁺	V ³⁺	(= mannardite)	
Henrymeyerite		Ba ²⁺	Fe ²⁺	Ba(Ti ⁴⁺ ₇ Fe ²⁺ ₂)O ₁₆	
New root name		Ba ²⁺	Fe ³⁺	Ba(Ti ⁴⁺ ₆ Fe ³⁺ ₂)O ₁₆	
New root name		K ⁺	Fe ²⁺	K(Ti ⁴⁺ _{7.5} Fe ²⁺ _{0.5})O ₁₆	
New root name		K ⁺	V ³⁺	K(Ti ⁴⁺ ₇ V ³⁺ ₂)O ₁₆	
New root name		K ⁺	Cr ³⁺	K(Ti ⁴⁺ ₇ Cr ³⁺ ₂)O ₁₆	

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