

**STRONTIOMELANE, $\text{SrMn}^{4+}_6\text{Mn}^{3+}_2\text{O}_{16}$,
A NEW MINERAL SPECIES OF THE CRYPTOMELANE GROUP
FROM ST. MARCEL – PRABORNA, AOSTA VALLEY, ITALY**

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ABSTRACT

Strontiomelane is a new mineral species from the Praborna mine near Saint-Marcel, Aosta Valley, Italian Alps. It occurs as small anhedral inclusions (about 100–200 μm) and veinlets associated with braunite, cryptomelane, hollandite, quartz, fluorapatite, titanite, jadeite and strontio Piemontite. The new species is opaque, black with a submetallic luster and a strong grey-white pleochroism; in plane-polarized light in oil immersion, it presents a medium anisotropy with grey-blue to white tints. Strontiomelane, whose ideal formula is $\text{SrMn}^{4+}_6\text{Mn}^{3+}_2\text{O}_{16}$, crystallizes in space group $P2_1/n$ (14) with a 10.00(1), b 5.758(7), c 9.88(1) Å, β 90.64(6)° and $Z = 2$. The strongest lines in the X-ray powder pattern [d in Å(I)(hkl)] are: 3.15(100)($\bar{1}03$), 3.13(80)(103), 2.409(80)(122), 2.170(60)(320) and 1.556(50)(225). The calculated density is 4.66(1) $\text{g}\cdot\text{cm}^{-3}$. Strontiomelane is the Sr end-member of the cryptomelane group. The proposed name is derived from the chemical element strontium and the color black, *melas,- anos* in Greek.

Keywords: strontiomelane, strontium, manganese oxide, cryptomelane group, Praborna, Alps, Italy.

SOMMAIRE

La strontiomélane est une nouvelle espèce minérale découverte à la mine de Praborna, près de Saint-Marcel, vallée d'Aoste dans les Alpes italiennes. Cette espèce se présente en petites inclusions xénomorphes de 100–200 μm ainsi qu'en veinules. Les minéraux associés à la strontiomélane sont: la braunite, la cryptomélane, la hollandite, la fluorapatite, la titanite, le quartz, la jadéite et la strontio Piémontite. La strontiomélane est noire, opaque, avec un éclat submétallique et un fort pléochroïsme gris blanc; en nicols croisés, elle présente une anisotropie d'intensité moyenne avec des teintes gris bleuâtre à blanc. La formule chimique idéale de la strontiomélane est $\text{SrMn}^{4+}_6\text{Mn}^{3+}_2\text{O}_{16}$. Cette espèce cristallise dans le groupe d'espace $P2_1/n$ (14) avec a 10.00(1), b 5.758(7), c 9.88(1) Å, β 90.64(6)° et $Z = 2$. Les raies principales du diagramme de poudre [d en Å(I)(hkl)] sont: 3.15(100)($\bar{1}03$), 3.13(80)(103), 2.409(80)(122), 2.170(60)(320) et 1.556(50)(225). La densité calculée est de 4.66(1). La strontiomélane est le terme strontifère du groupe de la cryptomélane. L'étymologie du nom dérive de l'élément strontium et du grec *melas,- anos*, signifiant noir.

Mots-clés: strontiomélane, strontium, oxyde de manganèse, groupe de la cryptomélane, Praborna, Alpes, Italie.

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INTRODUCTION

Cryptomelane – hollandite-type compounds are tetragonal or monoclinic (pseudotetragonal) complex oxides, of general formula $A_xB_8O_{16} \cdot nH_2O$ ($0 \leq x \leq 2$, $0 \leq n \leq 0.16$) (Burns & Burns 1979, Kudo *et al.* 1990, Waychunas 1991). Only members with $A = Ba, K, Na, Pb, Sr$ and $B = Cr^{3+}, Fe^{3+}, Mg, Mn^{4+}, Ti, V^{3+}, Zn, Zr$ (Perseil 1988, 1990, Fleischer & Mandarino 1995) are actually known as mineral species. In this paper, we describe the properties of a newly established member of the series, strontiomelane, discovered at the Praborna mine, in Aosta Valley, Italian Alps.

BACKGROUND INFORMATION

Natural examples of this solid-solution series are typically manganian (ideally with $B = Mn^{4+}$): cryptomelane ($A = K$), hollandite *sensu stricto* ($A = Ba$), manjiroite ($A = Na$) and coronadite ($A = Pb$). Small amounts of Ce, La, Nd, Y, P and Nb have also been observed by Fodor *et al.* (1994) and Mitchell & Meyer (1989) in natural hollandites. An ever wider variety of synthetic phases with the hollandite-type structure have been reported, with $A = Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Ag, Tl$ and Pb , and $B = Sc, Ti, Cr, Mn^{4+}, Fe, Co, Ni, Cu, Zn, Al, Ga, In, Si, Ge,$ and Sn , defining 30 end-member compositions (Pentlinghaus 1978, Zhang & Burnham 1994).

In the group of manganian phases, the crystal structure of pure synthetic hollandite, $BaMn_8O_{16}$, was first studied by Byström & Byström (1950): large cations, like Ba, occupy the A site within the tunnel formed by corner-sharing of columns of edge-sharing ($Mn^{4+}O_6$) octahedra along [001]. These authors showed that the ideal structure possesses a tetragonal symmetry, $I4/m$. Two monoclinic structures are recognized in this group: Mukherjee (1960) found evidence of a monoclinic symmetry, space group $P2_1/n$, for natural ferrian hollandite, $BaFeMn_7O_{16}$, and Miura (1987) investigated a natural potassium- and iron-rich hollandite from India and found a monoclinic structure, $I2/m$. In contrast with the observations of Byström & Byström (1950), Mukherjee (1960), Post *et al.* (1982) and Miura *et al.* (1987) reported that with increasing Ba^{2+} content, with respect to K^+ , the symmetry of cryptomelane changes from tetragonal to monoclinic.

For several years, significant amounts of Sr have been found in minerals of this group. Occurrences of Sr-bearing hollandite have been reported in several localities: 1) the Falotta and Parsettens mines, Oberhalbstein, Graubünden, Switzerland, as a supergene mineral (with 2–4 wt.% SrO) resulting from the oxidation of Sr-bearing sursassite and barite (Perseil 1990), 2) the Cerchiara mine, eastern Liguria, Italy (1.93–3.72 wt.% SrO; $250 < T < 300^\circ C$, $2 < P < 3$ kbar), (Cabella *et al.* 1994), and 3) the Upper Jurassic quartzitic meta-arenites of the Maritime Alps, Italy (SrO

content up to 1.54 wt.%; $T = 350^\circ C$, $P < 7$ kbar); Cabella *et al.* 1994).

Preliminary studies of the ore from the Praborna mine by electron microprobe has suggested the emergence of a new Sr end-member in the cryptomelane group, associated with strontioepimontite in the same sample (Perseil 1988). The mineral is named strontiomelane, from the element strontium and from the Greek *melas*, - *anos*, black. The new species was approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association prior to publication. The holotype material is deposited at the Geological Museum of Lausanne, Switzerland (#MGL 58770). Cotype material is also preserved at the Laboratoire et Galerie de Minéralogie, Muséum National d'Histoire Naturelle, Paris, France (#SM 7090.96).

OCCURRENCE

The Praborna manganese deposit is situated about 5 km south of the village of Saint-Marcel, in a lateral valley of Val d'Aosta, Italy. Manganese-enriched horizons are embedded in a 4- to 8-m thick quartzitic layer that represents the basal part of the sedimentary cover of an ophiolitic sequence, tectonically related to the Piemont Nappe. During the Alpine orogenesis, this ore concentration was metamorphosed in the eclogite facies in Cretaceous times and then retrograded to the greenschist facies in Tertiary times (Mottana 1986). During the late stages of the polyphase Alpine metamorphism, in the greenschist facies, the manganese-rich horizons were subsequently cross-cut by networks of veins and late fractures responsible for the mobilization of several elements like K, Ba, Sr, Sb, W and As (Martin-Vernizzi 1982, Mottana & Griffin 1986, Perseil 1985, 1988, 1991, Perseil & Smith 1995). Strontiomelane crystallized during this late stage of veining.

The mineralogical association of Praborna, with a long and complex metamorphic story, has already produced two new mineral species: piemontite, a manganese end-member of the epidote group (Kenngott 1853) and roméite, a calcium-antimony oxide, structurally related to pyrochlore (Damour 1841, Brugger *et al.* 1997).

HABIT AND PARAGENESIS

Strontiomelane occurs as thin (100–200 μm), sub-metallic, black, elongate xenomorphic inclusions commonly aggregated with braunite in quartz and, more rarely, in violet pyroxene (variety "violan" of diopside-aegirine-jadeite) and in strontioepimontite. Thin late-stage veinlets of the new species were also observed associated with braunite, hollandite, cryptomelane, jadeite, strontioepimontite, Sb-bearing titanite, As-bearing fluorapatite and quartz. On polished surfaces, strontiomelane differs slightly from braunite by a lower hardness and a poorer polish.

TABLE 1. REFLECTANCE VALUES OF STRONTIOMELANE

Reflectance maximum [R % max.]	Reflectance minimum [R % min.]	Wavelengths (COM) [λ , nm]
34.2	26.0	470
31.7	24.4	543
30.6	23.4	587
29.7	22.3	657

Objective: LEITZ 50/0.85; standard LEITZ WTIC, measured in air.

PHYSICAL PROPERTIES

In polished sections, microscopically, strontiomelane is an opaque mineral. Observed in oil immersion, in plane-polarized reflected light, the mineral is grey with a strong grey-white pleochroism similar to that

of hollandite; between crossed polars, its anisotropy is moderate, with a grey-blue to white tint. No internal reflections are noted, and the color of the streak is sepia.

Reflectance values of the new species are presented in Table 1. The observed values of reflectivity of strontiomelane lie in the range of hollandite and cryptomelane (Perseil & Pinet 1976, Picot & Johan 1982).

The Vickers hardness, measured by micro-indentation using a load of 100 g, gives a mean of 398 and a range of 309–450 (number of measurements: 16). Strontiomelane is brittle, with a rarely observed cleavage.

The size of the new mineral precluded a direct measurement of the density. It was calculated from the composition richest in Sr (Table 2, #6) and the refined unit-cell parameters: $4.66(1) \text{ g cm}^{-3}$.

X-ray-diffraction study

As all the available grains of the new mineral species are quite small, the crystallographic study was made with a Gandolfi camera. X-ray-diffraction data and analytical conditions are presented in Table 3.

Compared with the ionic radius of Ba^{2+} and K^+ , that of Sr^{2+} is smaller. Its presence as an occupant of the tunnel in the structure produces a collapse of distorted walls of octahedra, which reduces the symmetry to monoclinic (Zhang & Burnham 1994). The powder pattern of strontiomelane was successfully indexed with a cell of monoclinic symmetry. The refined unit-cell parameters, calculated by a least-squares method, are: a 10.00(1), b 5.758(7), c 9.88(1) Å, β 90.64(6)°, V 568.85 Å³, $a/b = 1.736$; $c/b = 1.715$ and $Z = 2$.

That some peaks are lacking in the powder diagram suggests space group $P2_1/n$ (14). Moreover, the unit cell calculated with space group $I2/m$ (12) does not agree

TABLE 2. CHEMICAL COMPOSITION OF STRONTIOMELANE, ST. MARCEL - PRABORNA, AOSTA VALLEY, ITALY

	1	2	3	4	5	6
MnO ₂ wt%	60.36	59.83	59.87	61.99	59.93	58.71
Mn ₂ O ₃	18.80	18.67	18.79	12.86	16.81	16.51
Fe ₂ O ₃	2.45	2.44	2.53	6.27	5.24	6.27
TiO ₂	0.46	0.49	0.45	2.07	0.53	0.70
CoO	0.01	0.08	0.02	0.14	0.00	0.00
CuO	0.00	0.00	0.00	0.00	0.00	0.00
NiO	0.00	0.01	0.00	0.00	0.00	0.00
SiO ₂	0.18	0.37	0.23	0.14	0.45	0.45
K ₂ O	1.42	1.44	1.50	0.59	0.89	0.83
Na ₂ O	0.17	0.11	0.20	0.27	0.08	0.17
PbO	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.14	0.14	0.14	0.00	0.00	0.00
BaO	3.95	3.70	3.27	2.82	1.73	1.39
SrO	9.15	9.44	9.56	9.64	12.15	12.77
Σ	97.09	96.72	96.56	96.79	97.81	97.80
	Structural formulae*					
Mn ⁴⁺ apfu	5.71	5.68	5.69	5.79	5.62	5.52
Mn ³⁺	1.96	1.95	1.97	1.32	1.73	1.71
Fe ³⁺	0.25	0.25	0.26	0.64	0.53	0.64
Ti	0.05	0.05	0.05	0.21	0.05	0.07
Cu	0.00	0.00	0.00	0.02	0.00	0.00
Co	0.00	0.01	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00
Si	0.03	0.06	0.03	0.02	0.07	0.06
Σ	8.00	8.00	8.00	8.00	8.00	8.00
K	0.25	0.25	0.26	0.10	0.15	0.14
Na	0.05	0.03	0.05	0.07	0.02	0.04
Pb	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.02	0.02	0.02	0.00	0.00	0.00
Ba	0.21	0.20	0.18	0.15	0.09	0.07
Sr	0.73	0.75	0.76	0.76	0.96	1.01
Σ	1.26	1.25	1.27	1.08	1.22	1.26

* The structural formulae are calculated on the basis of eight octahedrally coordinated cations, whose concentrations are quoted in apfu (atoms per formula unit). These data were acquired with a CAMEBAX electron microprobe at the Muséum National d'Histoire Naturelle, Paris. Operating conditions: 15 kV, 10 nA. Standards and X-ray lines used for analysis: strontianite (SrL α), barite (BaL α), orthoclase (KK α), albite (NaK α), rutile (TiK α), rhodonite (MnK α), hematite (FeK α), Co metal (CoK α), Cu metal (CuK α), Ni metal (NiK α), galena (PbM β) and wollastonite (SiK α , CaK α).

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR STRONTIOMELANE FROM PRABORNA, ITALY

I_{obs}	d_{obs}	d_{calc}	hkl	I_{rel}	d_{obs}	d_{calc}	hkl
10	7.02	7.02	1 0 1	10	1.997	1.994	3 2 2
30	4.96	4.95	0 0 2	5	1.982	1.993	3 2 2
30	3.52	3.52	2 1 1	5	1.937	1.940	1 0 5
30	3.50	3.51	2 0 2	30	1.855	1.852	5 1 1
100	3.15	3.13	1 0 3	30	1.843	1.844	1 2 4
80	3.13	3.13	1 0 3	>5	1.772	1.763	1 3 2
5	2.86	2.88	0 2 0	>5	1.749	1.755	4 0 4
30	2.75	2.767	0 2 1	5	1.702	1.707	5 0 3
5	2.504	2.496	2 2 0	20	1.668	1.663	6 0 0
>5	2.481	2.473	0 0 4	20	1.648	1.638	5 1 3
80	2.409	2.416	1 2 2	50	1.556	1.551	2 2 5
40	2.229	2.226	4 0 2	20	1.436	1.441	0 4 0
30	2.217	2.217	1 1 4	20	1.369	1.371	2 4 1
60	2.170	2.179	3 2 0	20	1.355	1.364	5 1 5
				20	1.303	1.301	3 0 7

Gandolfi camera, 114.6 mm in diameter. FeK α Mn-filtered radiation, 40 kV, 20 mA. Intensities estimated visually. Quartz added as an internal standard.

with the observed d values. Certain weak lines cannot be indexed in this space group.

CHEMICAL COMPOSITION AND DISCUSSION

Back-scattered electron images obtained by scanning electron microscopy show the distribution of Sr in the crystal (Figs. 1, 2). These images have been used to choose the areas most enriched in Sr, to be analyzed with the electron microprobe. The results of selected analyses are presented in Table 2. Considering all the microprobe results, the crystals also display zones of Ba-rich (hollandite) to (K+Na)-rich (cryptomelane) composition. According to Byström & Byström (1950), Fleischer (1964) and Burns & Burns (1979), the structural formulae of hollandite and cryptomelane are recalculated on the basis of 16 atoms of oxygen, implying some Mn as Mn^{3+} instead of Mn^{4+} in order to account for charge balance. In recalculating the data, we have assumed that Sr enters the channel site, as do Ba, K and Na, and we have estimated the ratio Mn^{3+}/Mn^{4+} on the basis of the relationship $Mn^{3+} + Mn^{4+} + Fe^{3+} + Ti^{4+} + Si^{4+} + Co^{2+} + Cu^{2+} + Ni^{2+} = 8$.

With this calculation, all the strontiomelane compositions are compatible with the formula $(Sr,K,Ba)_{1.25}(Mn,Fe,Ti)_8O_{16}$ and, ideally, $SrMn^{4+}_6Mn^{3+}_2O_{16}$. This

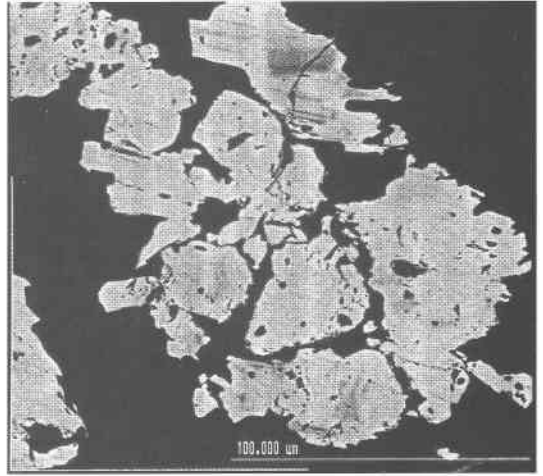


FIG. 1. Back-scattered SEM image of strontiomelane from Praborna. Scale bar: 100 μ m.

implies, among other substitutions, the following set starting from α - MnO_2 (or, more conveniently, $\square Mn^{4+}_8O_{16}$):

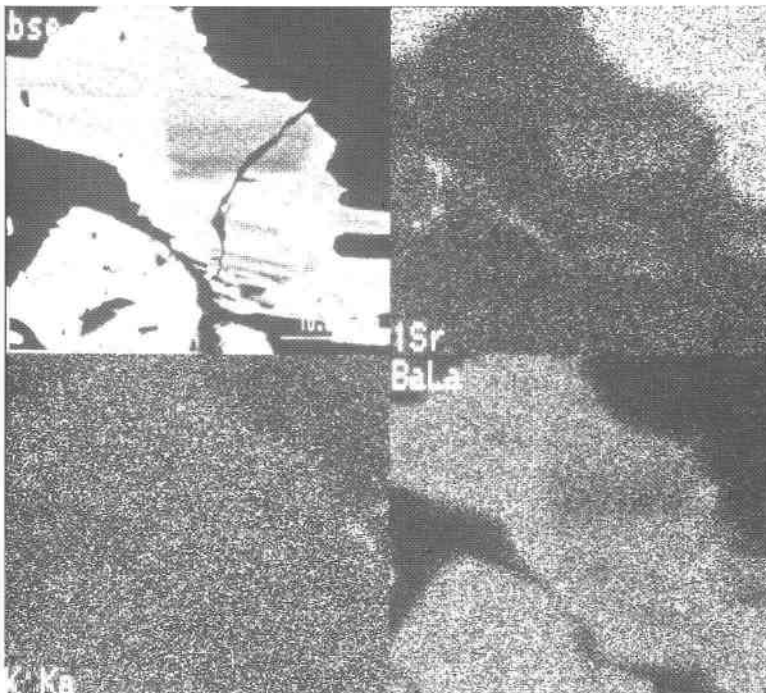
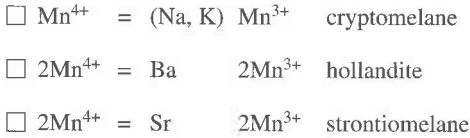


FIG. 2. Back-scattered SEM image and X-ray images of Sr ($L\alpha$), K ($K\alpha$) and Ba ($L\alpha$) in Ba- and K-rich strontiomelane from Praborna. Scale bar: 10 μ m.



hence the choice of a plot in terms of $2(\text{Na} + \text{K}) - \text{Sr} - \text{Ba}$ in Figure 3a. This diagram shows that there is a continuous solid-solution between hollandite and cryptomelane and between cryptomelane and strontiomelane in the analyzed crystal. It is less clear whether a complete solution also exist between strontiomelane and hollandite.

Considering the octahedrally coordinated sites, Mn is replaced by Fe^{3+} and Ti^{4+} , a feature already noticed in the late parageneses at Praborna (Perseil & Smith 1995). Byström & Byström (1950) and Fleischer (1964) have mentioned the substitution of Mn^{4+} by Al^{3+} and Fe^{3+} in the cryptomelane – hollandite solid-solution

series, and Post *et al.* (1982) have investigated the role of Ti^{4+} in the octahedral site. The $\text{Fe}^{3+} - (\text{Mn}^{4+} + \text{Mn}^{3+}) - \text{Ti}^{4+}$ diagram (Fig. 3b) shows a significant replacement of Mn by the other two cations. Moreover, intermediate Ba-rich members of the priderite series ($\text{Ba}, \text{K}, \text{Sr})_{1-2}(\text{Ti}, \text{Fe}, \text{Mn})_8\text{O}_{16}$ have been described by Perseil (1991), suggesting that a solution between priderite and hollandite – cryptomelane – strontiomelane exists at Praborna.

No H_2O has been detected by infrared (IR) spectroscopy (Nicolet 740 IR plan II microscope, scan between 4000 and 2000 cm^{-1}). However, once the $\text{Mn}^{3+}:\text{Mn}^{4+}$ ratio has been calculated using the above equation, sums of weight percent oxide are low. The sum of oxides has a mean value of 96.2 considering all the analyses done on the sample, and 96.7 for analyses of strontiomelane only. The standard deviation is 1.5 and, therefore, the sum of oxide can be considered to be significantly lower than 100. There are three hypotheses, all compatible with one another, to explain this feature: 1) there is some H_2O in the channel, but its amount is below the detection limit of the IR spectrometer apparatus used, 2) other large-size cations are present as trace elements in the structure and have not been detected by electron microprobe, and 3) microdefects at the surface of the polished thin sections preclude accurate analysis.

Despite this problem, we consider that at least at Praborna, strontiomelane is the Sr end-member of a solid solution involving cryptomelane and hollandite as the other two end-members. Either present as inclusions or as veinlets, strontiomelane is related to late metasomatism involving Sr, but also Ba, K and Sb. Strontiomelane in Praborna is not a product of alteration, but of hypogene origin, such as some hollandite-group phases described by Fleischer (1964). Other cations, *e.g.*, Ag^+ , Tl^+ , Li^+ , Cs^+ , Rb^+ , Mg^{2+} , Ca^{2+} , Ce^{3+} , La^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Eu^{3+} and Dy^{3+} , can enter the channels of the isostructural series cryptomelane – hollandite (Pentinghaus 1978, Fodor *et al.* 1994, Zhang & Burnham 1994) with corresponding new end-members. This structural characteristic provides an insight in the search of structural hosts in synroc (Ringwood *et al.* 1988) for the immobilization of radioelements (*e.g.*, ^{90}Sr and ^{137}Cs) rejected from nuclear fuel in the recovery process.

ACKNOWLEDGEMENTS

We are greatly obliged to the metallurgical laboratories of the Federal Polytechnic School of Lausanne for the use of their microhardness apparatus. K. Schenk (Institut de cristallographie, Université de Lausanne), Ph. Thélin (Institut de minéralogie, Université de Lausanne) and M. Guiraud (Laboratoire de minéralogie, MNHN Paris) provided valuable suggestions to improve the check-list for the new mineral proposal and helped in revising the manuscript. Valuable comments on the manuscript were received from A. Mottana and an anonymous referee.

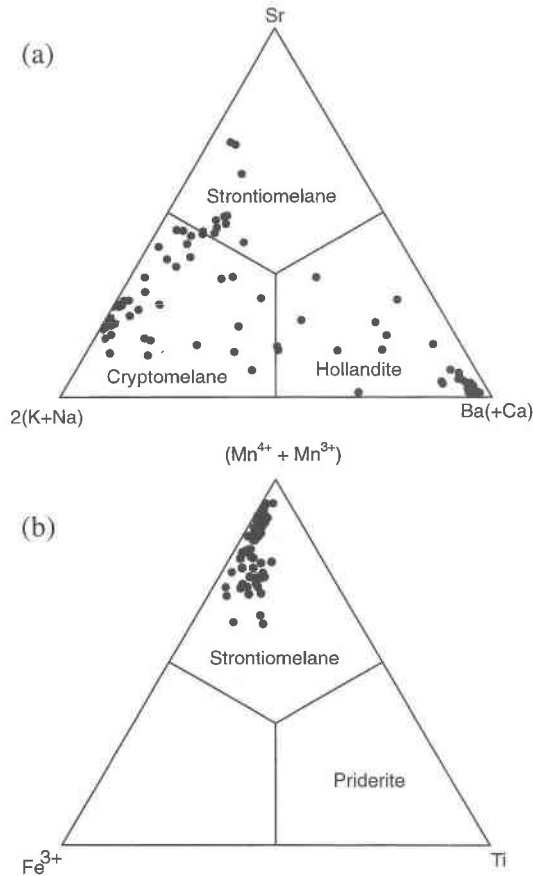


FIG. 3. The composition of cryptomelane-group minerals from Praborna (95 data-points) in terms of the A- and B-site occupancies (a and b, respectively).

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Received January 17, 1997, revised manuscript accepted January 27, 1999.