Strontian hollandite in a quartz schist from the Saruta-gawa area in the Sanbagawa metamorphic terrain, central Shikoku, Japan

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Abstract

Strontian hollandite (up to 3.45 wt.% SrO) is found to occur in a piemontite-bearing quartz schist of the Sanbagawa metamorphic terrain in central Shikoku, Japan. Hollandite occurs as an aggregate of fine crystals (up to 100 μ m long) associated with braunite. From the central part of the aggregate outward, its BaO, Fe₂O₃ and TiO₂ contents increase and its MnO₂, K₂O and SrO contents decrease. Chemical variation in the hollandite suggests K (Mn⁴⁺, Ti⁴⁺) $\leftrightarrow$ (Ba, Sr)Fe³⁺ substitution. Hollandite is tetragonal or pseudotetragonal, and lattice constants are $a=9.90(4)$ Å and $c=2.87(5)$ Å.

Introduction

Hollandite typically occurs in manganese deposits (e.g. Miura *et al.*, 1987). In the Sanbagawa and Nagasaki metamorphic terrains, the manganese ore bodies, which mainly consist of braunite, piemontite and quartz, occur in quartz schists. Hollandite-cryptomelane series minerals have been reported from this manganese deposit (e.g. Minakawa and Momoi, 1989; Minakawa, 1992).

Byström and Byström (1950) analysed the structure of hollandite from Swedish manganese ores on the basis of the tetragonal cell. Hollandite is sometimes slightly distorted from tetragonal symmetry to monoclinic. Many authors have reported the structure of monoclinic hollandite (e.g. Post *et al.*, 1982; Miura, 1986). Hollandite group minerals are characterized by tunnels in their structures. Their general formula is described as $A_xB_8O_{16} \cdot nH_2O$. The tunnels are partially filled with A cations such as Ba²⁺, Sr²⁺, Pb²⁺, K⁺, or Na⁺. Minerals with the hollandite structure have either Mn⁴⁺ or Ti⁴⁺ as the major B cation. The Mn phases include cryptomelane (A cation=K), hollandite (A=Ba), coronadite (A=Pb) and manjiroite (A=Na).

In the course of the petrological study of the Sanbagawa metamorphic rocks in central Shikoku, strontian hollandite (up to 3.45 wt.% SrO; Registration No. GSJ M31217) was found in a piemontite-bearing quartz schist from the Saruta-gawa area located in Iyomishima City, Ehime Prefecture. Strontian hollandite-cryptomelane

containing up to 3.72 wt.% SrO has been discovered in braunite-bearing manganese deposits from Italy and Switzerland (Perseil, 1988, 1990; Cabella *et al.*, 1994). In this paper, the mode of occurrence, chemistry and crystallographic data of the strontian hollandite in the Sanbagawa metamorphic rock are described.

Mode of occurrence and petrography

The Saruta-gawa area is located in the Sanbagawa metamorphic terrain in central Shikoku. The Sanbagawa terrain of the intermediate high-pressure type in central Shikoku is divided into the chlorite, garnet, albite-biotite and oligoclase-biotite zones with increasing metamorphic temperature (e.g., Higashino, 1975; S. Banno *et al.*, 1978; Enami, 1982, 1983; Higashino, 1990). The hollandite-bearing quartz schist (1.9 m in width) occurs between layers of basic schist in the albite-biotite zone (Fig. 1). In this zone, the common mineral assemblage of basic schist is hornblende + chlorite + mus-

FIG. 1. Metamorphic zone map of the Saruta-gawa area with the sample locality (Higashino *et al.*, 1984; Higashino, 1990).

FIG. 2. Back-scattered electron image of hollandite and braunite. Black part is quartz.

covite + epidote + albite + quartz. The quartz schist consists of piemontite-richer and -poorer parts. The piemontite-richer part, showing dark red color, occurs as a layer or lens (up to 17 cm in width) in the piemontite-poorer part (pink color). The piemontite-richer part is mainly composed of piemontite, quartz, hematite, dolomite and calcite with subordinate amounts of apatite, chlorite, muscovite, braunite and hollandite. Dolomite occurs as a porphyroblast up to 3 mm in size. Dolomite in the Sanbagawa metamorphic rocks was reported by Enami and Higashino (1988), and they pointed out that dolomite + quartz assemblage occurs in the oligoclase-biotite and albite-biotite zones of higher grade and was not observed in the garnet and chlorite zones of lower grade. It is consistent with their observation that the studied dolomite-bearing quartz schist occurs in the albite-biotite zone. The piemontite-poorer part consists of quartz, albite, piemontite, dolomite, calcite, muscovite and hematite with accessories of titanite and apatite. Hollandite occurs as a nodule 10 mm long and 5 mm wide. This nodule consists of a braunite core (2.5 mm long, 1 mm wide) and hollandite mantle. The mantle is composed of an aggregate of fine hollandite crystals (up to 100 μm long) with subordinate amounts of calcite, muscovite, quartz and piemontite (Fig. 2).

Hollandite mineralogy and discussion

X-ray diffraction of hollandite

The X-ray powder pattern obtained by the diffractometer method using Cu/Ni radiation is given in Table 1, where it is indexed by analogy with the pattern calculated from structural parameters of tetragonal $\text{Ba}_2\text{Mn}_8\text{O}_{16}$ (JCPDS 29-188). This mineral gives a powder pattern of tetragonal or pseudotetragonal hollandite, and the unit cell parameters, derived by the least-square method using all diffractions except for a broad peak, are: $a = 9.90(4) \text{ \AA}$ and $c = 2.87(5) \text{ \AA}$. Minakawa and Momoi (1989) and Minakawa

TABLE 1. X-ray powder patterns of hollandite and a pattern calculated from structural parameters of tetragonal $\text{Ba}_2\text{Mn}_8\text{O}_{16}$.

1		2		3		
d	l	d	l	d	l	hkl
6.997	10	6.98	50	6.944	24	110
4.946	14	4.93	30	4.910	2	200
3.506	20	3.47	80	3.472	30	220
3.132	100	3.13	100	3.105	100	310,130
2.761	6	2.68	10	2.746	19	101
2.457	5			2.455	1	400
2.411	29	2.40	90	2.397	47	211,121
				2.315	1	330
2.213	18	2.24	5	2.196	21	420,240
2.171	13	2.15	80	2.154	35	301
1.985	4	1.98	5	1.9723	15	321
				1.9259	5	510
1.842	9	1.83	60	1.8302	26	411
1.743	3b	1.74	2	1.7359	5	440
1.698	4			1.6841	6	530,350
1.656	7	1.65	20	1.6367	15	600
				1.6190	3	501,431
				1.5527	1	260
1.548	13	1.55	70	1.5376	16	521,251
1.438	4	1.43	20	1.4300	5	002
a=9.90(4) Å		a=9.90 Å		a=9.82 Å		
c=2.87(5) Å		c=2.86 Å		c=2.86 Å		

- 1 Hollandite. Saruta-gawa area, Iyomishima City, Ehime Prefecture, Japan. b=broad. Cu/Ni radiation. Diffractometer method. The present study.
- 2 Hollandite. Langenberg, Saxony, Germany. FeK α radiation. Camera method. JCPDS Card No. 13-115.
- 3 $\text{Ba}_2\text{Mn}_8\text{O}_{16}$. The powder pattern calculated from structural parameters. JCPDS Card No. 29-188.

(1992), however, reported hollandite of monoclinic type from the Sanbagawa and Nagasaki metamorphic terrains.

Nambu *et al.* (1964) and Nambu and Tanida (1980) divided hollandite into hydrous and anhydrous types. Hydrous hollandite (about 5 wt.% H_2O) belongs to the tetragonal system and occurs as a primary mineral from hydrothermal deposits or oxidation products of other manganese oxide minerals. Anhydrous hollandite (less than 1 wt.% H_2O) belongs to the monoclinic system and occurs in metamorphosed manganese deposits. The present hollandite should be anhydrous type because of its mode of

occurrence, whereas it belongs to the tetragonal or pseudotetragonal system. This fact implies that the conclusion of Nambu *et al.* (1964) and Nambu and Tanida (1980) is not always valid.

Chemistry of hollandite

Chemical analysis was performed using a JEOL JCXA-733 electron-probe microanalyser at Nagoya University. Accelerating voltage, specimen current and beam diameter were kept at 15 kV, 1.2×10^{-8} A and 3 μ m, respectively. Formula of hollandite was calculated based on O=16, assuming total Mn and Fe as MnO₂ and Fe₂O₃, respectively. Chemical compositions of hollandite are presented in Table 2. The total of analysis is only 96.2–98.5 wt.%. Some water is probably present in channels in the structure.

Hollandite was observed only in a piemontite-rich part of the quartz schist. It

TABLE 2. Chemical compositions of hollandite.

	central part -----marginal part									
SiO ₂	0.00	0.20	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00
TiO ₂	0.75	0.74	0.71	0.87	0.89	0.98	1.13	1.40	2.74	3.77
Al ₂ O ₃	1.41	1.38	1.24	1.25	1.25	1.14	1.19	1.16	1.04	1.04
Cr ₂ O ₃	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ₂ O ₃	6.31	6.41	7.00	7.54	8.01	8.66	8.60	8.80	10.1	10.6
MnO ₂	74.0	75.7	75.3	72.5	71.0	69.8	70.6	71.8	67.5	63.0
MgO	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01
NiO	0.01	0.02	0.02	0.00	0.02	0.00	0.00	0.00	0.03	0.02
CaO	0.16	0.08	0.04	0.07	0.09	0.03	0.02	0.04	0.01	0.10
Na ₂ O	0.23	0.21	0.15	0.10	0.07	0.06	0.12	0.06	0.03	0.01
K ₂ O	1.97	1.96	1.89	0.73	0.64	0.27	0.70	1.35	1.10	0.15
BaO	8.23	8.15	8.33	12.8	13.6	15.3	14.1	11.8	13.5	16.9
SrO	3.38	3.45	3.31	2.22	1.65	1.07	1.32	2.12	1.63	0.45
Total	96.5	98.4	98.0	98.1	97.2	97.5	97.8	98.5	97.7	96.2
Si	0.000	0.026	0.000	0.000	0.000	0.029	0.000	0.000	0.000	0.000
Ti	0.075	0.073	0.070	0.088	0.091	0.101	0.115	0.141	0.280	0.399
Al	0.222	0.212	0.192	0.198	0.200	0.184	0.190	0.182	0.167	0.172
Cr	0.000	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe ³⁺	0.634	0.629	0.692	0.762	0.820	0.891	0.878	0.882	1.034	1.132
Mn ⁴⁺	6.825	6.826	6.834	6.727	6.676	6.594	6.618	6.607	6.344	6.122
Mg	0.002	0.000	0.000	0.000	0.000	0.002	0.000	0.002	0.000	0.002
Ni	0.001	0.002	0.002	0.000	0.002	0.000	0.000	0.000	0.003	0.002
Ca	0.023	0.011	0.006	0.010	0.013	0.004	0.003	0.006	0.001	0.015
Na	0.060	0.053	0.038	0.026	0.018	0.016	0.032	0.015	0.008	0.003
K	0.335	0.326	0.317	0.125	0.111	0.047	0.121	0.229	0.191	0.027
Ba	0.430	0.417	0.429	0.673	0.725	0.819	0.749	0.616	0.719	0.931
Sr	0.262	0.261	0.252	0.173	0.130	0.085	0.104	0.164	0.129	0.037
Total	8.869	8.841	8.832	8.782	8.786	8.772	8.810	8.844	8.876	8.842

Note: Numbers of ions calculated on O=16. Total Mn as MnO₂ and Fe as Fe₂O₃.

FIG. 3. Plots of hollandite compositions in the Sr-Ba-K system.

occurs as an aggregate of subhedral and anhedral crystals and is chemically variable. The SrO content of hollandite ranges from 0.45 to 3.45 wt.%. Since Na content is very small [up to 0.06 per formula unit (pfu.) for O=16], this hollandite has Ba, Sr and K as the major A cation. The number of A cations in hollandite is nearly 1 pfu., as reported by Miura *et al.* (1987). Figure 3 shows the limited extent of replacement between Ba and Sr.

Hollandite near the core of the nodule is relatively rich in SrO (up to 3.45 wt.%) and K₂O (up to 1.97 wt.%) and poor in TiO₂ (0.74–0.75 wt.%). On the other hand, the hollandite at the outermost rim of the nodule is enriched in TiO₂ (3.77 wt.%) and is poor in SrO (0.45 wt.%) and K₂O (0.15 wt.%). From the central part to the rim of the nodule, Ba and Fe³⁺ increase [0.43 to 0.93 pfu. (Ba); 0.63 to 1.13 pfu. (Fe³⁺)] and Mn decreases (6.83 to 6.12 pfu.) (Table 2).

Substitution in hollandite

The hollandite compositions are distributed along straight lines of (Mn⁴⁺ + Ti) + Fe³⁺ = 7.6 (Fig. 4A) and K + (Ba + Sr) = 1 (Fig. 4B). The plots for the hollandite on the Mn⁴⁺ + Ti vs. K diagram (Fig. 4C) show positive correlation between K and Mn⁴⁺ + Ti, and there is positive correlation between Ba + Sr and Fe³⁺ (Fig. 4D). Minakawa (1992) also showed that there was positive correlation between Ba and Fe³⁺ of hollandite-cryptomelane series minerals from the Sanbagawa metamorphic manganese ore deposits. These data suggest that chemical variation in the hollandite can be explained by K(Mn⁴⁺, Ti⁴⁺) ⇌ (Ba, Sr)Fe³⁺ substitution. However plots on the Mn⁴⁺ +

FIG. 4. (A) $(\text{Mn}^{4+} + \text{Ti}) - \text{Fe}^{3+}$, (B) $\text{K} - (\text{Ba} + \text{Sr})$, (C) $(\text{Mn}^{4+} + \text{Ti}) - \text{K}$ and (D) $\text{Fe}^{3+} - (\text{Ba} + \text{Sr})$ plots for hollandite.

Ti vs. K and Fe^{3+} vs. Ba + Sr diagrams are more scattered than those on $\text{Mn}^{4+} + \text{Ti}$ vs. Fe^{3+} and K vs. Ba + Sr diagrams. This fact may be explained by the presence of $\text{Mn}^{3+} \rightleftharpoons \text{Fe}^{3+}$ and/or $\text{Mn}^{2+} \rightleftharpoons \text{Fe}^{2+}$ other than $\text{K}(\text{Mn}^{4+}, \text{Ti}^{4+}) \rightleftharpoons (\text{Ba}, \text{Sr})\text{Fe}^{3+}$.

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