

A barian bannisterite from Japan

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Abstract

Chemical analyses of bannisterite from the Kamo mine, Toba City, Mie Prefecture, Japan, give Ba : Ca = 69 : 31–55 : 45, yielding the ideal formula with Ba > Ca, i.e. $(\text{Ba,Ca})(\text{K,H}_3\text{O})(\text{Mn}^{2+} \cdot \text{Mg,Fe}^{2+})_{21}(\text{Si,Al})_{32}(\text{O,OH})_{92} \cdot n\text{H}_2\text{O}$, where Ba > Ca, $\text{Mn}^{2+} > \text{Mg, Fe}^{2+}$, $\text{Si} \gg \text{Al}$, and $\text{O} > \text{OH}$. The unit cell parameters calculated after the indexing of the X-ray powder pattern are: $a = 22.95$, $b = 16.52$, $c = 25.66$ Å, $\beta = 94.2^\circ$. It occurs as dark brown veinlets cutting massive caryopilite–rhodochrosite ore, which is also cut by veinlets of manganoan chlorite ($\text{Mn}/(\text{Mg} + \text{Mn} + \text{Fe}) = c. 0.30\text{--}0.39$) with minor barian orthoclase ($\text{Ba}/(\text{K} + \text{Ba}) = 0.05 \sim 0.06$).

KEYWORDS: barium, bannisterite, Japan, Kamo mine.

Introduction

DURING mineralogical studies of manganese ores from the Kamo mine, we have found bannisterite with a significant substitution of barium for calcium. The chemical and X-ray powder studies support the existence of the barium analogue of bannisterite, which is here referred to as a barian bannisterite.

Occurrence

The mineral forms dark brown veinlets in massive caryopilite–rhodochrosite ore; other associated minerals include manganoan chlorite, barian orthoclase, albite, and siegenite. It was found on the dump of a bedded manganese ore deposit at the Kamo mine, Toba City, Mie Prefecture, Japan. The ore deposit is located in weakly metamorphosed Mesozoic chert with greenstone, and the ore is a dark brick-red to brown mass composed of caryopilite, rhodochrosite and albite. Numerous veinlets of sub-millimetre width crosscut the ore, some consisting essentially of dark brown barian bannisterite which has the appearance of neotocite.

Under the microscope bannisterite forms radial aggregates, up to 0.4 mm across, composed of thin tablets which are veined by calcian rhodochrosite (CaO 8.87 wt. %) (Fig. 1). It has a strong pleochroism, brownish yellow to reddish brown. Manganoan chlorite, calcite and barian orthoclase are found in separate veinlets of similar dimensions. Siegenite occurs as minute grains in the ore.

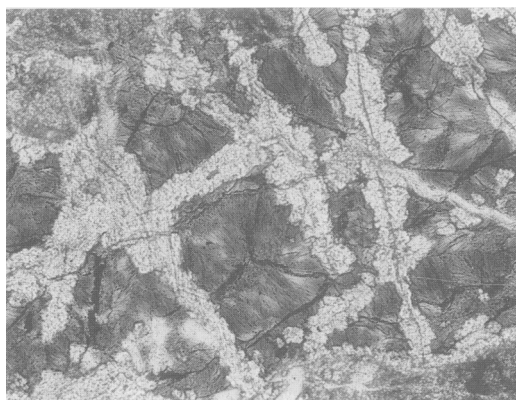


FIG. 1. Photomicrograph of bannisterite (dark grey, feathery), rhodochrosite (high relief, vein-formed), and caryopilite (grey, down right and upper left, fine-grained). Field view, approximately 0.8×0.6 mm. One polar.

Chemical analyses

The chemical analyses were made using a Link Systems energy-dispersive X-ray spectrometer. Bannisterite is chemically inhomogeneous, even in a single grain. The empirical formula of the anhydrous part of the most barium-rich analysis is $(\text{Ba}_{0.66}\text{Ca}_{0.29})_{\Sigma 0.95}\text{K}_{0.32}(\text{Mn}_{14.86}\text{Fe}_{4.69}\text{Mg}_{2.23})_{\Sigma 21.78}(\text{Si}_{27.76}\text{Al}_{3.73})_{\Sigma 31.49}\text{O}_{84}$ on the basis of $\text{O} = 84$ and total $\text{Fe} = \text{FeO}$. Na and Zn were not found. The sums of the alkali and alkaline earth cations is ideally 2 ($\text{Ca} = 1$ and $\text{K} + \text{Na} = 1$).

Table 1. Chemical analyses of bannisterite(1-3), orthoclase (4-5), and chlorite(6-7)

Weight percent(*total Fe):

	1	2	3	4	5	6	7
SiO ₂	42.69	44.59	44.36	63.16	62.99	32.01	33.85
Al ₂ O ₃	6.25	5.02	5.05	18.34	18.70	16.71	13.17
FeO*	9.61	8.50	8.96			7.70	7.72
MnO	27.29	28.81	28.04			17.06	21.41
MgO	3.61	1.97	2.40			18.52	14.82
CaO	0.56	0.41	0.43			0.36	0.20
BaO	1.84	2.16	2.71	2.58	3.41	0.59	0.61
K ₂ O	1.08	1.16	0.40	15.90	15.38	0.40	0.20
total	92.93	92.62	92.35	99.98	100.48	93.35	91.98

Empirical formulae:

1~3: bannisterite (basis: O=84 in the anhydrous part)

4~5: orthoclase (basis: O=8)

6~7: chlorite (basis: O=14 in the anhydrous part)

- (Ba_{0.45}Ca_{0.37})_{20.82}K_{0.86}(Mn_{14.39}Fe_{5.00}Mg_{3.35})_{22.74}(Si_{26.57}Al_{4.58})_{23.15}O₈₄ (anhydrous part only). The most Ba-poor analysis.
- (Ba_{0.53}Ca_{0.29})_{20.81}K_{0.93}(Mn_{15.24}Fe_{4.44}Mg_{1.84})_{22.15}(Si_{27.84}Al_{3.70})_{23.15}O₈₄ (anhydrous part only).
- (Ba_{0.66}Ca_{0.29})_{20.95}K_{0.32}(Mn_{14.86}Fe_{4.69}Mg_{2.23})_{22.17}(Si_{27.76}Al_{3.73})_{23.14}O₈₄ (anhydrous part only). The most Ba-rich analysis.
- (K_{0.95}Ba_{0.05})_{21.00}(Si_{2.96}Al_{1.01})_{23.97}O₈
- (K_{0.92}Ba_{0.06})_{20.98}(Si_{2.96}Al_{1.04})_{24.00}O₈
- (Mg_{2.71}Mn_{1.42}Al_{1.06}Fe_{0.63})_{25.82}(Si_{3.14}Al_{0.86})_{24.00}O₁₄ (anhydrous part only)
- (Mg_{2.24}Mn_{1.84}Al_{1.00}Fe_{0.85})_{25.73}(Si_{3.43}Al_{0.57})_{24.00}O₁₄ (anhydrous part only)

from the formula of Dunn *et al.* (1981), but the sums obtained from the present material are in the range 1.08-1.95, the contents being Ba = 0.45-0.66, Ca = 0.25-0.37, K = 0.21-1.15. The range of Ba/(K + Ba) in the orthoclase is 0.05-0.06. Chlorite has Mn:Mg:Fe = (39-30):(47-57):(14-13), approximately corresponding to an intermediate phase between clinocllore and pennantite, following the nomenclature of the trioctahedral chlorites (Bayliss, 1975) unless the lower Al/(Si + Al) ratio in the tetrahedral site of the present material is considered. Selected analyses of bannisterite, orthoclase, and chlorite are given in Table 1.

X-ray powder study

The X-ray powder data for bannisterite given in Table 2 are very similar to those for the original material from Franklin Furnace, New Jersey

(Smith and Frondel, 1968), though the subsidiary diffraction lines are not visible in the present data. The indexing requires a slightly larger cell than the original, i.e. $a = 22.95$, $b = 16.52$, $c = 25.66$ Å, $\beta = 94.2^\circ$, in terms of the original setting (space group $B2/b$; Smith and Frondel, 1968). The noticeable expansion of all the cell edges reflects the substitution of barium for calcium.

Discussion

The ideal formula of bannisterite was proposed by Dunn *et al.* (1981) as CaK(Mn,Fe,Mg,Zn)₂₁(Si,Al)₃₂O₇₆(OH)₁₆·12H₂O after new chemical analyses. The variation of (Ba + Ca) in the present material is over the range 0.80-0.95 with Ba:Ca = 69:31-55:45, indicating the likely substitution of Ba for Ca. The variation of K content, 0.21-1.15, may be explained by the substitution of H₃O

Table 2. X-ray powder data for bannisterite

I	d _{obs.}	d _{calc.}	hkl	I	d _{obs.}	d _{calc.}	hkl
100	12.4	12.5	002	12	2.998	2.996	426
10	6.32	6.42	311	10	2.786	2.794	246
		6.23	004			2.782	800
5	4.53	4.53	133	12	2.646	2.646	447
8	4.29	4.28	511			2.636	820
15b	4.15	4.15	006	5b	2.486	2.489	0.0.10
		4.13	040			2.485	048
5	3.83	3.83	333	3	2.263		
8	3.69	3.71	600	2	2.070		
6	3.40	3.40	117	3	1.800		
			531	5b	1.625		
6	3.37	3.37	515	2b	1.574		
10	3.14	3.16	416	2	1.557		
		3.13	533				

b=broad

a=22.95. b=16.52. c=25.66 Å. β=94.2°. B2/b

or H₂O as structurally indicated by Threadgold (1979). The low K analyses in Table 1 favour this interpretation. If a structural study reveals the nature of the interlayer cations as well as the

substitution relations, including H₃O, the status of this mineral will be settled. We describe the present material as a barian bannisterite prior to the designation of a new species, since the analyses show the possibility of differentiation into at least two species based on the fluctuating potassium content. Provided that the fluctuation is due to the substitution of H₃O, the proposed anhydrous formula is (Ba,Ca)(K,H₃O)(Mn,Fe,Mg)₂₁(Si,Al)₃₂O₈₄ where Ba > Ca, Mn > Fe,Mg, and Si >> Al, without any reference to H₂O content which has not yet been measured, except for the interlayer H₃O.

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