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Bannisterite: new chemical data and empirical formulae

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Abstract

Bannisterites from Franklin, New Jersey, and Broken Hill, Australia, are re-examined using chemical analytical techniques. The data suggest that Ca is essential in bannisterite. Mg and Zn may be ordered in Franklin bannisterite, but are not essential; Mn is the dominant cation. An empirical formula, based on 106 oxygen atoms, is: $Ca_{0.88}(K_{0.84}Na_{0.11})_{\Sigma 0.95}(Mn_{12.55}Fe^{2+}_{3.00}Mg_{2.93}Zn_{2.15}Fe^{3+}_{0.68})_{\Sigma 21.31}(Si_{29.32}Al_{3.14})_{\Sigma 32.46}O_{80}(OH)_{12.71} \cdot 13.28H_2O$ with $Z = 4$. An alternative formula, based on 168 negative charges, from previously proposed structural arguments is: $Ca_{0.86}(K_{0.82}Na_{0.11})_{\Sigma 0.93}(Mn_{12.21}Fe^{2+}_{2.92}Mg_{2.85}Zn_{2.09}Fe^{3+}_{0.66})_{\Sigma 20.73}(Si_{28.53}Al_{3.05})_{\Sigma 31.58}O_{76}(OH)_{16} \cdot 12.2H_2O$.

Introduction

Bannisterite was first found in the Franklin mine prior to 1933 and was described as an uncommon form of ganophyllite (Foshag, 1936). Subsequent examination of this material by Smith and Frondel (1968) established it as a new species, related to ganophyllite and the stilpnomelane group. A highly ferroan bannisterite was described from the Zinc Corporation Mine at Broken Hill, New South Wales, Australia, by Plimer (1977). Despite several descriptions, a chemical formula has not been proposed which is compatible with the chemical analytical data.

The present chemical analytical study was undertaken to examine a large number of bannisterite samples, establish their composition, determine the limits of solid solution of the cations, and derive a satisfactory empirical formula.

Sample descriptions

At Franklin, bannisterite occurs as broad plates up to 6 cm in breadth with a dark brown color similar to yeatmanite and lamprophyllite. The bannisterite, with intimately associated barite and calcite, composes masses up to 250 cm^3. Other associated minerals are rhodonite, sphalerite, quartz, zincian amphi-

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bole, manganoan calcite, and several fine-grained manganese silicates which may be mixtures of bementite, caryopilite and some ill-defined manganese silicates. Plimer (1977) has noted the occurrence of rhodonite, quartz, sphalerite, fluorite, galena and apophyllite as minerals associated with the Australian bannisterite.

In addition to analyzing a large number of previously unstudied samples, we have re-examined several previously analyzed specimens. The first described bannisterite, designated by Foshag (1936) as #R6724, was found to have been subjected to a poor analysis, which is not repeated here. The holotype bannisterite, analyzed by Ito in Smith and Frondel (1968) has been reanalyzed and its composition confirmed. Two samples of the Broken Hill bannisterite, one obtained from Dr. Plimer, were reanalyzed. We confirm the composition reported by Plimer, but note below that the sample may have a higher water content than he reported. Two samples, used but not analyzed by Smith and Frondel (1968), have been analyzed (HU#91863 and 91862). Densities were redetermined for both Franklin and Broken Hill samples.

Analytical procedures

All the samples were analyzed using an ARL-SEMQ electron microprobe with an operating voltage of 15 kV and a beam current of 0.15 μA. The standards used were analyzed hornblende for Si, Al, Fe, Mg, and Ca; manganite for Mn; and synthetic ZnO for Zn. The data were corrected using standard Bence–Albee factors. We encountered the same difficulties with potassium microprobe determinations as were reported by Plimer (1977). Accordingly, K_2O and Na_2O were determined by flame photometry. In the analyses for Fe^{2+}, each sample was decomposed with HF and H_2SO_4 in a reducing atmosphere and titrated with $K_2Cr_2O_7$. For Fe^{3+}, each sample was dissolved with HF, HNO_3, and H_2SO_4, reduced by passing through a silver column, and titrated with $K_2Cr_2O_7$. For samples 142982 and 142894, H_2O^- was determined in weighing bottles by drying at 110°C. The samples were then allowed to re-equilibrate at room temperature and analyzed for total H_2O by the Penfield method. H_2O^+ is the difference between the value for total H_2O and H_2O^-. Separate portions of samples C5096 and C6253 were used to determine H_2O^+ and H_2O^-.

Because the H_2O^- determinations varied by as much as 0.64 weight percent, and because of the variance between the water determinations of Ito in Smith and Frondel (1968) and Plimer (1977), we performed a DTA-TGA analysis for water. The DTA-TGA analysis of sample #R6724 indicates that this particular bannisterite contains 9.3 weight percent of H_2O, of which 3.9 percent is given up under vacuum at 20°C. Plimer (1977) found infrared evidence for loosely bound H_2O and/or (OH) and our data confirms his observation. The remainder of the H_2O is lost between 20° and 935°C. Penfield determinations had assumed water driven off under 110°C is moisture and non-essential, but the available evidence indicates that bannisterite does contain very loosely held H_2O.

Discussion

Although the original analysis of bannisterite (Foshag, 1936) indicated many octahedral cations were present (Mn, Fe, Zn, Mg, Ca), the recent description of Broken Hill bannisterite by Plimer (1977) indicates that Zn and Mg are non-essential. The abundance of Zn and Mg at Franklin in general, and the associated sphalerite and amphibole, explain their presence in bannisterite. The other elements reported for bannisterite may be essential constituents.

Ions per unit cell (Table 1) were calculated for Franklin bannisterites (analyses 1–4) using the unit cell parameters of Smith and Frondel (1968) (a = 22.20, b = 16.32, c = 24.70Å, β = 94°20′) and a newly determined density of 2.83 g/cm^3. Ions per unit cell for Broken Hill bannisterites (analyses 16 and 17) were calculated using the unit cell parameters of Threadgold (1979) (a = 22.317, b = 16.397, c = 24.687Å, β = 94°21′) and a newly determined density of 2.83 g/cm^3.

Examination of the data presented in Table 1 indicates that Franklin, New Jersey, bannisterites are remarkably consistent in chemical composition. This might argue for a localized occurrence within the Franklin mine, but the associations and textures of the available specimens are too varied to support such an argument. Analyses 14 and 15 are of slightly altered material and are deficient in calcium and manganese and enriched in magnesium, relative to other specimens. Aside from these two anomalous analyses, the others are quite similar.

Aluminum and calcium are present in bannisterite, except for the previously mentioned altered specimens, in nearly constant amounts. The rather consistent abundance of Ca, Al and (K and Na) suggests they are essential constituents. Their concentrations in terms of numbers of ions per unit cell approximate multiples of equipoints 4 and 8 as required by space

Table 1. Chemical analyses of bannisterite

SAMPLE NUMBER	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	MnO	ZnO	K_2O	Na_2O	H_2O^+	H_2O^-	ΣH_2O	Total	LOCALITY
1. NMNH C5096	46.2	3.8	0.79*	5.49*	3.3	1.2	23.3	4.5	1.04§	0.08§	6.19†	2.73	8.92	98.6	Franklin, N.J.
2. NMNH C6253	46.6	3.9	0.77*	5.60*	3.1	1.2	23.7	4.4	1.10§	0.08§	5.80†	3.37	9.17	99.6	Franklin, N.J.
3. NMNH R6724	46.3	4.2	1.44*	5.67*	3.1	1.3	23.4	4.6	1.04§	0.09§			9.3††	100.4	Franklin, N.J.
4. NMNH 145728/H 108571	46.20	4.74		6.40	1.99	1.52	23.02	4.67	1.21§	0.29§			9.74	99.78	Franklin, N.J.††††
5. NMNH 145728/H 108571	47.0	3.8		6.7**	3.3	1.2	23.4	4.6							Franklin, N.J.
6. NMNH 102731	44.7	5.1		5.5**	2.6	1.4	26.7	3.0							Franklin, N.J.
7. NMNH C5097	46.5	4.1		5.7**	3.0	1.3	24.9	4.4							Franklin, N.J.
8. NMNH 145729/H 91863	47.4	3.7		6.6**	3.2	1.2	22.9	4.7							Franklin, N.J.
9. NMNH 145730/H 91862	47.2	4.1		6.9**	3.2	1.4	23.8	4.5							Franklin, N.J.
10. Parker 410	46.3	3.7		6.1**	3.0	1.2	23.7	4.4							Franklin, N.J.
11. Hauck-E	44.7	5.1		5.7**	2.5	1.4	26.6	3.0							Franklin, N.J.
12. Hauck 342	46.8	4.0		6.4**	3.2	1.2	23.6	4.6							Franklin, N.J.
13. SG # 1133	46.8	4.0		6.6**	3.2	1.3	23.7	4.6							Franklin, N.J.
14. SG # 1132	45.4	5.0		7.0**	7.3	0.2	17.2	5.0							Franklin, N.J.
15. BAUM-S	45.3	5.6		6.8**	5.2	0.6	21.6	4.4							Franklin, N.J.
16. NMNH 142892	45.8	4.0		17.4**	0.3	1.5	20.8	0.3	0.65§	0.25§	4.90†	3.82†	8.72	99.7	Broken Hill, N.S.W.
17. NMNH 142984	45.2	4.1		18.2**	0.3	1.4	19.9	0.4	0.80§	0.30§	4.76†	3.77†	8.53	99.1	Broken Hill, N.S.W.
18. Plimer (1977) †††	45.4	3.84	2.1	16.5	0.47	1.55	19.9	0.0	0.92	0.51			7.82	99.0	Broken Hill, N.S.W.

Ions per unit cell π

	Si	Al	Fe^{3+}	Fe^{2+}	Mg	Ca	Mn	Zn	K	Na
NMNH C5096	116.95	11.34	1.50	11.62	12.45	3.25	49.95	8.41	3.36	0.39
NMNH C6253	117.97	11.64	1.47	11.85	11.70	3.25	50.81	8.22	3.55	0.39
NMNH R6724	117.21	12.53	2.74	12.00	11.70	3.52	50.17	8.60	3.36	0.44
NMNH 145728/H 108571	116.95	14.14		13.55	7.51	4.12	49.35	8.73	3.90	1.42
NMNH 142892	117.06	12.05		37.18	1.14	4.10	45.02	0.57	2.12	1.24
NMNH 142984	115.53	12.35		38.90	1.14	3.83	43.07	0.75	2.61	1.49

*------Oxidation state of iron determined as described in text.
**-----Determined as total iron and then calculated as FeO.
†------Determined by the Penfield method.
††-----Determined by DTA-TGA.
†††----Determined by AAS and flame photometry; Mg, Zn and Al by microprobe.
††††---Analysis by Jun Ito *in* Smith and Frondel (1968).

§- Determined by flame photometry.
π- Calculated as described in text.

group *A*2/*a* of Smith and Frondel (1968) and Threadgold (1979), and suggest that they might be ordered. Although Plimer (1977) has shown that Zn and Mg are not essential to bannisterite, and Threadgold (1979) has suggested, for Broken Hill material, that the octahedral cations are completely disordered, their concentrations in Franklin material in multiples of 4 or 8 atoms per unit cell does suggest that Zn and Mg, together with Fe, might have preferences for certain sites in bannisterite. The role of Fe^{3+} is ambiguous. It is present in the four analyses in which it was sought and may substitute for aluminum or divalent cations, or may play some other role, as yet unclear. In all the bannisterites examined in this study, the dominant M^{2+} cation is Mn, but it is not known to exceed 50 of the reported 80 atoms per unit cell. Franklin bannisterite has an average M^{2+} cation content near $Mn_{12}Zn_2Mg_3Fe^{2+}_3$ and that of Broken Hill bannisterite is approximately $Mn_{11}Fe^{2+}_8Mg_1$. The calculated densities for the compositions are 2.80 g/cm^3 (Franklin) and 2.84 g/cm^3 (Broken Hill), in good agreement with the value of 2.83 g/cm^3 observed for specimens from both localities.

These data provide an adequate basis for the postulation of an empirical formula, assuming limited substitutions among Si/Al, Fe^{3+}/Al, M^{2+}, K/Na and O/OH for charge balance. An empirical formula for analysis #3, calculated on the basis of 106 oxygen atoms, yields:

$$Ca_{0.88}(K_{0.84}Na_{0.11})_{\Sigma 0.95}(Mn_{12.55}Fe^{2+}_{3.00}Mg_{2.93}Zn_{2.15}Fe^{3+}_{0.68})_{\Sigma 21.31}$$

$$(Si_{29.32}Al_{3.14})_{\Sigma 32.46}O_{80}(OH)_{12.71} \cdot 13.28H_2O \text{ with } Z = 4.$$

An unambiguous chemical formula for bannisterite must await the publication of the full details of its crystal structure. In an abstract, Threadgold (1979) states that:

> "Bannisterite is essentially a 2-layer, 2:1 trioctahedral layer silicate . . . A quarter of the tetrahedra are inverted so that they are directed away from the octahedral sheet and share their apical oxygens with cations of similarly inverted tetrahedra from adjacent layers . . . Aluminum is concentrated into three of the four inverted tetrahedra . . ."

He states that the formula for partly dehydrated ferroan bannisterite from Broken Hill, Australia, calcualted from microprobe analysis and derived from single-crystal intensity data, is close to:

$$8[K_{0.5}Ca_{0.5}(H_2O)_2(Fe_{5.1}Mn_{4.8}Mn_{0.1})_{\Sigma 10.0}$$

$$(OH)_8(Si_{14.4}Al_{1.6})_{\Sigma 16.0}O_{38}.]$$

If we assume that the formula of Threadgold (1979) is largely correct, we derive a formula for analysis #3, on the basis of 168 negative charges, and with Al totally in tetrahedral coordination, of: $Ca_{0.86}(K_{0.82}Na_{0.11})_{\Sigma 0.93}(Mn_{12.21}Fe^{2+}_{2.92}Mg_{2.85}Zn_{2.09}Fe^{3+}_{0.66})_{\Sigma 20.73}(Si_{28.53}Al_{3.05})_{\Sigma 31.58}O_{76}(OH)_{16} \cdot 12.2H_2O$.

In addition to the greater number of water molecules in the fully hydrated material, there are other differences between our empirical formula and the one derived from the model of Threadgold (1979). An interesting feature of the numerous analyses presented herein is the near constancy of proportion of aluminum, at about 3 atoms per formula unit. Threadgold's (1979) model requires that ¼ of the tetrahedra be inverted and that Al be concentrated in ⅜ of these, which should be 6 sites in the formula we present, or 24 in the unit cell. The lower concentration of Al which we have found remains somewhat enigmatic. We have tentatively grouped Fe^{3+} with the octahedral cations and note that they sum to nearly 21 per formula unit instead of the 20 previously proposed. However, there is a possibility of Fe^{3+}/Si substitution on a small scale, as is known in cronstedtite. If the small amount of Fe^{3+} in bannisterite is in tetrahedral coordination, the formula would have approximately 20 M^{2+} cations and approximately 32 tetrahedral cations, thereby conforming quite closely to the model of Threadgold.

The contradiction between the amounts of Al predicted structually and those determined analytically, together with the ambiguity concerning the role of Fe^{3+}, and the possibility of H_3O/K substitutions, indicates that the fine details of the bannisterite structure remain unresolved.

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