Bannisterite: new chemical data and empirical formulae

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Abstract

Bannisterite 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$_{0.11}$Mg$_{32.97}$Fe$_{32.03}$Si$_{32.46}$O$_{106}$·13.28H$_2$O.

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

In addition to analyzing a large number of pre-
viously unstudied samples, we have re-examined sev-
eral previously analyzed specimens. The first de-
scribed 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 con-
firmed. 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 con-
tent than he reported. Two samples, used but not an-
alyzed by Smith and Frondel (1968), have been ana-
lyzed (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$_2$O and 
Na$_2$O were determined by flame photometry. In the 
analyses for Fe$^{2+}$, each sample was decomposed with 
HF and H$_2$SO$_4$ in a reducing atmosphere and titrated 
with K$_2$Cr$_2$O$_7$. For Fe$^{3+}$, each sample was dissolved with 
HF, HNO$_3$, and H$_2$SO$_4$, reduced by passing 
through a silver column, and titrated with K$_2$Cr$_2$O$_7$. 
For samples 142982 and 142894, H$_2$O$^+$ was deter-
mined in weighing bottles by drying at 110°C. The 
samples were then allowed to re-equilibrate at room 
temperature and analyzed for total H$_2$O by the Pen-
field method. H$_2$O$^+$ is the difference between the 
value for total H$_2$O and H$_2$O$^-$. Separate portions of 
samples C5096 and C6253 were used to determine 
H$_3$O$^+$ and H$_2$O$^-$. 

Because the H$_2$O$^-$ determinations varied by as 
much as 0.64 weight percent, and because of the vari-
ance between the water determinations of Ito in 
Smith and Frondel (1968) and Plimer (1977), we per-
fomed 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$_2$O, of which 3.9 percent is given up under vacuum 
at 20°C. Plimer (1977) found infrared evidence for 
loosely bound H$_2$O and/or (OH) and our data con-
forms his observation. The remainder of the H$_2$O is 
lost between 20°C and 935°C. Penfield determinations 
had assumed water driven off under 110°C is mois-
ture and non-essential, but the available evidence in-
dicates that bannisterite does contain very loosely 
held H$_2$O.

Discussion

Although the original analysis of bannisterite 
(Foshag, 1936) indicated many octahedral cations 
were present (Mn, Fe, Zn, Mg, Ca), the recent de-
scription 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 spalereite and amphibole, explain 
their presence in bannisterite. The other elements re-
ported 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 param-
eters of Threadgold (1979) (a = 22.317, b = 16.397, c 
= 24.687Å, β = 94°21') and a newly determined den-
sity of 2.83 g/cm$^3$.

Examination of the data presented in Table 1 in-
dicates 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 speci-
mens, in nearly constant amounts. The rather consist-
tent 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

<table>
<thead>
<tr>
<th>SAMPLE NUMBER</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>MnO</th>
<th>ZnO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>H₂O⁺</th>
<th>H₂O⁻</th>
<th>H₂O</th>
<th>Total</th>
<th>LOCALITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NMNH C5096</td>
<td>46.2</td>
<td>3.8</td>
<td>0.79*</td>
<td>5.49*</td>
<td>3.3</td>
<td>1.2</td>
<td>23.3</td>
<td>4.5</td>
<td>1.04</td>
<td>0.08s</td>
<td>6.19</td>
<td>2.73</td>
<td>8.92</td>
<td>98.6</td>
<td>Franklin, N.J.</td>
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<tr>
<td>2. NMNH C6253</td>
<td>46.6</td>
<td>3.9</td>
<td>0.77*</td>
<td>5.60*</td>
<td>3.1</td>
<td>1.2</td>
<td>23.7</td>
<td>4.4</td>
<td>1.10</td>
<td>0.08s</td>
<td>5.80</td>
<td>3.37</td>
<td>9.17</td>
<td>99.6</td>
<td>Franklin, N.J.</td>
</tr>
<tr>
<td>3. NMNH R6724</td>
<td>46.3</td>
<td>4.2</td>
<td>1.44*</td>
<td>5.67*</td>
<td>3.1</td>
<td>1.3</td>
<td>23.4</td>
<td>4.6</td>
<td>1.04</td>
<td>0.09s</td>
<td>9.3</td>
<td>100.4</td>
<td>Franklin, N.J.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 4. NMNH 145728/H 108571 | 46.2 | 4.74 | 6.40 | 1.99 | 1.52 | 23.02 | 4.67 | 1.21 | 0.29s | 9.74 | 99.78 | Franklin, N.J.+
| 5. NMNH 145725/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 | 0.25s | 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 | 0.30s | 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

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Al</th>
<th>Fe³⁺</th>
<th>Fe²⁺</th>
<th>Mg</th>
<th>Ca</th>
<th>Mn</th>
<th>Zn</th>
<th>K</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMNH C5096</td>
<td>116.95</td>
<td>11.34</td>
<td>1.50</td>
<td>11.62</td>
<td>12.45</td>
<td>3.25</td>
<td>49.95</td>
<td>8.41</td>
<td>3.36</td>
<td>0.39</td>
</tr>
<tr>
<td>NMNH C6253</td>
<td>117.97</td>
<td>11.64</td>
<td>1.47</td>
<td>11.85</td>
<td>11.70</td>
<td>3.25</td>
<td>50.81</td>
<td>8.22</td>
<td>3.55</td>
<td>0.39</td>
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<tr>
<td>NMNH R6724</td>
<td>117.21</td>
<td>12.53</td>
<td>2.74</td>
<td>12.00</td>
<td>11.70</td>
<td>3.52</td>
<td>50.17</td>
<td>8.60</td>
<td>3.36</td>
<td>0.44</td>
</tr>
<tr>
<td>NMNH 145728/H 108571</td>
<td>116.95</td>
<td>14.14</td>
<td>13.55</td>
<td>7.51</td>
<td>4.12</td>
<td>49.35</td>
<td>8.73</td>
<td>3.90</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>NMNH 142892</td>
<td>117.06</td>
<td>12.05</td>
<td>37.18</td>
<td>1.14</td>
<td>4.10</td>
<td>45.02</td>
<td>0.57</td>
<td>2.12</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>NMNH 142984</td>
<td>115.53</td>
<td>12.35</td>
<td>38.90</td>
<td>1.14</td>
<td>3.83</td>
<td>43.07</td>
<td>0.75</td>
<td>2.61</td>
<td>1.49</td>
<td></td>
</tr>
</tbody>
</table>

*-----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.
+++------Determined by flame photometry.
+++------Analysis by Jun Ito in Smith and Frondel (1968).
group A2/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 do suggest that Zn and Mg, together with Fe, might have preferences for certain sites in bannisterite. The role of Fe* 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* 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* cation content near Mn,Mg,Fe,Mg and that of Broken Hill bannisterite is approximately Mn,Mg,Fe,Mg. The calculated densities for the compositions are 2.80 g/cm³ (Franklin) and 2.84 g/cm³ (Broken Hill), in good agreement with the value of 2.83 g/cm³ 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*/Al, M*, K/Na and O/OH for charge balance. An empirical formula for analysis #3, calculated on the basis of 106 oxygen atoms, yields:

$$\text{Ca}_{0.88}(\text{K}_{0.48}\text{Na}_{0.11})(\text{Si}_{0.97}\text{Al}_{0.03})\text{O}_{3.10}(\text{Mn}_{12.35}\text{Fe}_{5.00}\text{Mg}_{2.99})\text{Zn}_{1.15}\text{Fe}_{10.88}\text{Si}_{21.31}$$

$$\text{(Si}_{39.32}\text{Al}_{1.68})\text{O}_{16}(\text{OH})_{12.71} \cdot 13.28\text{H}_2\text{O}$$ 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, calculated from microprobe analysis and derived from single-crystal intensity data, is close to:

$$8[\text{K}_{0.5}\text{Ca}_{0.5}(\text{H}_{2}\text{O})_{2}](\text{Fe}_{5.1}\text{Mn}_{4.8}\text{Mn}_{0.1})\text{Si}_{10.0}$$

$$\text{(OH)}_{6}(\text{Si}_{14.4}\text{Al}_{1.6})\text{O}_{38}$$

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:

$$\text{Ca}_{0.88}(\text{K}_{0.48}\text{Na}_{0.11})\text{Zn}_{0.97}(\text{Mn}_{12.35}\text{Fe}_{5.00}\text{Mg}_{2.99})\text{Si}_{21.31}$$

$$\text{(Si}_{39.32}\text{Al}_{1.68})\text{O}_{16}(\text{OH})_{12.71} \cdot 13.28\text{H}_2\text{O}$$

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 3/4 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** 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**/Si substitution on a small scale, as is known in cronstedtite. If the small amount of Fe** in bannisterite is in tetrahedral coordination, the formula would have approximately 20 M** cations and approximately 32 tetrahedral cations, thereby conforming quite closely to the model of Threadgold.

The contradiction between the amounts of Al predicted structurally and those determined analytically, together with the ambiguity concerning the role of Fe**, and the possibility of H₂O/K substitutions, indicates that the fine details of the bannisterite structure remain unresolved.

Acknowledgments

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