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Mössbauer spectroscopic study of some iron and antimony – containing minerals

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Abstract Iron-57 Mössbauer spectra have been recorded from three minerals containing both iron and antimony. Schafarzikite of composition FeSb₂O₄ contains Fe²⁺. The ¹²¹Sb Mössbauer spectrum shows only the presence of Sb³⁺. The ⁵⁷Fe Mössbauer spectrum corresponds with that recorded from a material of identical composition synthesised by a solid state reaction during the course of this work. Apuanite of formulation Fe₂₀Sb₁₆O₄₈S₄ contains both Fe²⁺ and Fe³⁺ in the ratio 1:3.35. The result is consistent with crystal structure determinations and the formulation of apuanite as Fe²⁺Fe⁶³⁺Sb₁₆O₄₈S₄. Versiliaite of composition Fe₁₂Sb₁₂O₃₂S₂ contains Fe²⁺ and Fe³⁺ in the ratio 1:2.12 and, also consistent with structural characterisations, can be formulated Fe⁶²⁺Fe⁸³⁺Sb₁₂³⁺O₃₂S₂.

1. Introduction
The application of Mössbauer spectroscopy for the characterisation of minerals has been known for many years [1]. We are beginning a programme of synthesis and characterisation of inorganic solids containing iron and antimony and have become aware of minerals containing these elements which appear to have received sparse attention in the past. As a preliminary to the main body of work we have examined, for the first time, the ⁵⁷Fe Mössbauer spectra from three minerals containing iron and antimony.

Schafarzikite was first identified in the Slovak Republic in 1921 [2] and was subsequently shown to adopt the composition FeSb₂O₄[3]. The mineral has been characterised by X-ray diffraction and described [4] in terms of columns of edge-sharing iron-containing octahedra connected by corner sharing to parallel chains of three-coordinate pyramidal antimony. The mineral is rare but after no findings for over eighty years has recently been found near Pernek also in the Slovak Republic [5]. Schafarzikite is the parent phase of apuanite, Fe₂₀Sb₁₆O₄₈S₄, and versiliaite, Fe₁₂Sb₁₂O₃₂S₂, found in the Apuan Alps in Italy. Apuanite and versiliaite are derived from schafarzikite by substitution on some antimony sites by iron [6,7] and the insertion of sulphide bridges between these iron ions. We report...
here on the characterisation of the iron oxidation states in schafarzikite and a synthetic analogue made
during the course of this work and in apuanite and versiliaite by Mössbauer spectroscopy.

2. Experimental
Schafarzikite from the Kriznica mine, Pernek, Slovak Republic [5] was obtained from Systematic
Mineralogy, Czech Republic. Apuanite and versiliaite from the Bucca della Vena Mine, Alpuan Alps,
Italy [6,7] were obtained from Roger's Minerals, Canada. A sample of FeSb₂O₄ was prepared by
heating a stoichiometric mixture of α–iron(III) oxide and antimony(III) oxide in air at 925°C for 24
hours to produce iron antimonate (FeSbO₄). The iron antimonate was heated with an appropriate
amount of elemental antimony in an evacuated sealed silica tube at 600°C for 24 hours. The product
was ground and heated again in an evacuated sealed silica tube at 600°C for 24 hours to give single
phase FeSb₂O₄.
Mössbauer spectra were recorded at 298K (⁵⁷Fe) and 77K (¹²¹Sb) with a constant acceleration
spectrometer in transmission geometry using a 400 MBq ⁵⁷Co/Rh and a 0.6 mCi Ca¹²³SnO₃ source.
The drive velocity was calibrated with the ⁵⁷Co/Rh source and a natural iron foil. All the chemical
isomer shift data are reported relative to that of metallic iron at 298K.

3. Results and discussion
3.1 Schafarzikite
The ⁵⁷Fe Mössbauer spectra recorded from schafarzikite, apuanite, versiliaite and the synthesised
FeSb₂O₄ are shown in Figures 1-3. The ⁵⁷Fe Mössbauer parameters are collected in Table 1.
The ⁵⁷Fe Mössbauer spectrum recorded here from the recently discovered sample of schafarzikite
[5] (Figure 1a) was dominated by a quadrupole split absorption characteristic of Fe²⁺. The ¹²¹Sb
Mössbauer spectrum showed a resonance, δ = -11.84 mms⁻¹, characteristic of Sb³⁺. The result is
consistent with the structural description of earlier [4] and recently [5] found samples of schafarzikite
from which chains of FeO₆ octahedra, held together by chains of 3-coordinate antimony in which the
lone pairs of electrons on Sb³⁺ point into the channels, can be envisaged. A doublet corresponding to
Fe³⁺ was observed in the spectrum but, given that schafarzikite is found with other iron-containing
minerals [2,5], we associate this with a minority impurity phase. Indeed X-ray powder diffraction
showed weak reflections not attributable to schafarzikite but which could not be unequivocally
associated with another Fe³⁺-bearing mineral.
The spectrum recorded from the synthesised material of composition FeSb₂O₄ (Figure 1b) showed a
single quadrupole split absorption with a chemical isomer shift characteristic of Fe²⁺.

3.2 Apuanite
The ⁵⁷Fe Mössbauer spectrum is shown in Figure 2. The spectrum was best fitted to two components
characteristic of Fe²⁺ and Fe³⁺. The peak area ratio of the Fe²⁺ to Fe³⁺ components was ca. 1: 3.35
(Table 1). The result validates the structural description [6,7] in terms of the substitution of every
third antimony cation in the pyramidal chains of schafarzikite by an Fe³⁺ ion with pairs of these ions
being linked by the sulphide anions; charge balance is achieved by oxidation of some Fe²⁺ within the
chains. The results recorded here are consistent with the formulation of apuanite as Fe₄²⁺Fe₁⁶³⁺Sb₁⁶³⁺O₄S₄
Figure 1a. $^{57}$Fe Mössbauer spectrum recorded from schafarzikite

Figure 1b. $^{57}$Fe Mössbauer spectrum recorded from FeSb$_2$O$_4$

Figure 2. $^{57}$Fe Mössbauer spectrum recorded from apuanite

Figure 3. $^{57}$Fe Mössbauer spectrum recorded from versiliaite
3.3 Versiliaite
The $^{57}$Fe Mössbauer spectrum is shown in Figure 3. The spectrum was again fitted to two components characteristic of Fe$^{2+}$ and Fe$^{3+}$ but with a peak area ratio of 1:2.12 (Table 1). This result is also consistent with the structural description of versiliaite [6, 7] involving the substitution of every fourth Sb$^{3+}$ cation in the pyramidal chains of schafarzikite by an iron ion and the insertion of sulphide anions with corresponding oxidation of Fe$^{2+}$. The results recorded here are consistent with the formulation of versiliaite as Fe$_4$$^{2+}$Fe$_8$$^{3+}$Sb$_{12}$$^{3+}$O$_3$S$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta$ 0.02/mms$^{-1}$</th>
<th>$\Delta$ 0.02/mms$^{-1}$</th>
<th>Area ±2 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schafarzikite</td>
<td>Fe$^{2+}$ 1.08</td>
<td>Fe$^{3+}$ 0.38</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe$^{2+}$ 1.08</td>
<td>20</td>
</tr>
<tr>
<td>FeSb$_2$O$_4$</td>
<td>Fe$^{2+}$ 0.99</td>
<td>Fe$^{3+}$ 0.32</td>
<td>100</td>
</tr>
<tr>
<td>Apuanite</td>
<td>Fe$^{2+}$ 0.99</td>
<td>Fe$^{3+}$ 0.32</td>
<td>23</td>
</tr>
<tr>
<td>Versiliaite</td>
<td>Fe$^{2+}$ 0.85</td>
<td>Fe$^{3+}$ 0.25</td>
<td>32</td>
</tr>
</tbody>
</table>

4. Conclusions
A material of composition FeSb$_2$O$_4$ containing only Fe$^{2+}$ identical to that of the mineral schafarzikite has been prepared. $^{57}$Fe Mössbauer spectroscopy shows the minerals apuanite and versiliaite to contain both Fe$^{2+}$ and Fe$^{3+}$ consistent with predictions from crystal structure determinations.

5. References