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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  $\text{FeSb}_2\text{O}_4$  contains  $\text{Fe}^{2+}$ . The  $^{121}\text{Sb}$  Mössbauer spectrum shows only the presence of  $\text{Sb}^{3+}$ . The  $^{57}\text{Fe}$  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  $\text{Fe}_{20}\text{Sb}_{16}\text{O}_{48}\text{S}_4$  contains both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the ratio 1:3.35. The result is consistent with crystal structure determinations and the formulation of apuanite as  $\text{Fe}_4^{2+}\text{Fe}_{16}^{3+}\text{Sb}_{16}\text{O}_{48}\text{S}_4$ . Versiliaite of composition  $\text{Fe}_{12}\text{Sb}_{12}\text{O}_{32}\text{S}_2$  contains  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the ratio 1:2.12 and, also consistent with structural characterisations, can be formulated  $\text{Fe}_4^{2+}\text{Fe}_8^{3+}\text{Sb}_{12}^{3+}\text{O}_{32}\text{S}_2$ .

### 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  $^{57}\text{Fe}$  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  $\text{FeSb}_2\text{O}_4$ [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,  $\text{Fe}_{20}\text{Sb}_{16}\text{O}_{48}\text{S}_4$ , and versiliaite,  $\text{Fe}_{12}\text{Sb}_{12}\text{O}_{32}\text{S}_2$ , 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  $\text{FeSb}_2\text{O}_4$  was prepared by heating a stoichiometric mixture of  $\alpha$ -iron(III) oxide and antimony(III) oxide in air at  $925^\circ\text{C}$  for 24 hours to produce iron antimonate ( $\text{FeSbO}_4$ ). The iron antimonate was heated with an appropriate amount of elemental antimony in an evacuated sealed silica tube at  $600^\circ\text{C}$  for 24 hours. The product was ground and heated again in an evacuated sealed silica tube at  $600^\circ\text{C}$  for 24 hours to give single phase  $\text{FeSb}_2\text{O}_4$ .

Mössbauer spectra were recorded at 298K ( $^{57}\text{Fe}$ ) and 77K ( $^{121}\text{Sb}$ ) with a constant acceleration spectrometer in transmission geometry using a 400 MBq  $^{57}\text{Co}/\text{Rh}$  and a 0.6 mCi  $\text{Ca}^{121\text{m}}\text{SnO}_3$  source. The drive velocity was calibrated with the  $^{57}\text{Co}/\text{Rh}$  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

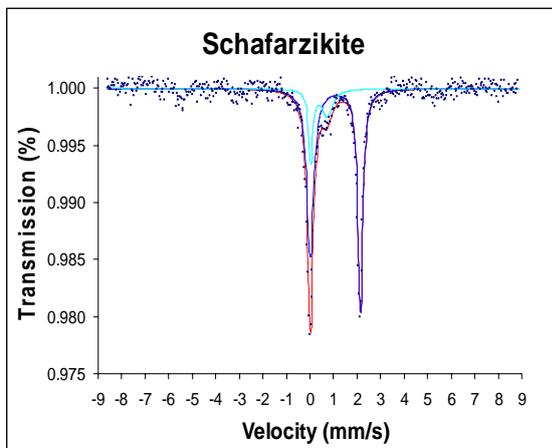
The  $^{57}\text{Fe}$  Mössbauer spectra recorded from schafarzikite, apuanite, versiliaite and the synthesised  $\text{FeSb}_2\text{O}_4$  are shown in Figures 1-3. The  $^{57}\text{Fe}$  Mössbauer parameters are collected in Table 1.

The  $^{57}\text{Fe}$  Mössbauer spectrum recorded here from the recently discovered sample of schafarzikite [5] (Figure 1a) was dominated by a quadrupole split absorption characteristic of  $\text{Fe}^{2+}$ . The  $^{121}\text{Sb}$  Mössbauer spectrum showed a resonance,  $\delta = -11.84 \text{ mms}^{-1}$ , characteristic of  $\text{Sb}^{3+}$ . The result is consistent with the structural description of earlier-[4] and recently-[5] found samples of schafarzikite from which chains of  $\text{FeO}_6$  octahedra, held together by chains of 3-coordinate antimony in which the lone pairs of electrons on  $\text{Sb}^{3+}$  point into the channels, can be envisaged. A doublet corresponding to  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$ -bearing mineral.

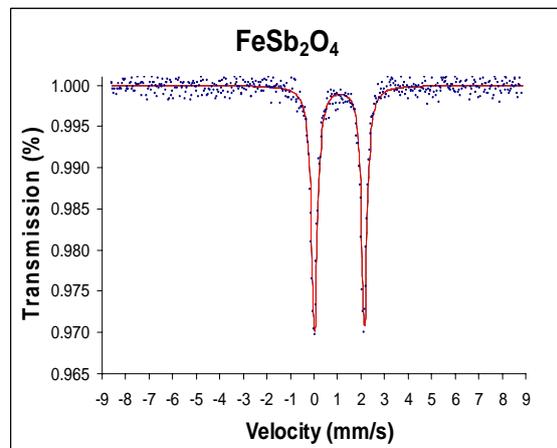
The spectrum recorded from the synthesised material of composition  $\text{FeSb}_2\text{O}_4$  (Figure 1b) showed a single quadrupole split absorption with a chemical isomer shift characteristic of  $\text{Fe}^{2+}$ .

### 3.2 Apuanite

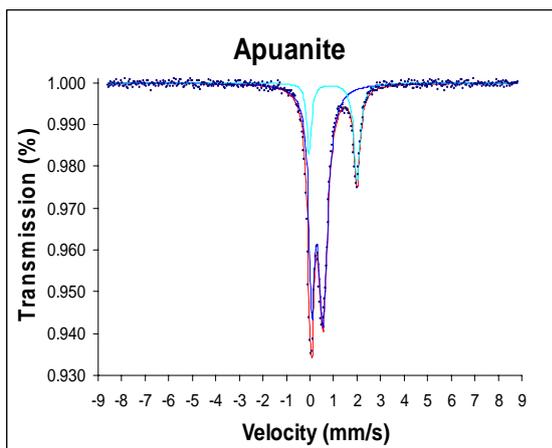
The  $^{57}\text{Fe}$  Mössbauer spectrum is shown in Figure 2. The spectrum was best fitted to two components characteristic of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . The peak area ratio of the  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  components was *ca.* 1: 3.35 (Table 1). The result validates the structural description [6,7] in terms of the substitution of every third antimony cation in the pyramidal chains of schafarzikite by an  $\text{Fe}^{3+}$  ion with pairs of these ions being linked by the sulphide anions; charge balance is achieved by oxidation of some  $\text{Fe}^{2+}$  within the chains. The results recorded here are consistent with the formulation of apuanite as  $\text{Fe}_4^{2+}\text{Fe}_{16}^{3+}\text{Sb}_{16}^{3+}\text{O}_{48}\text{S}_4$



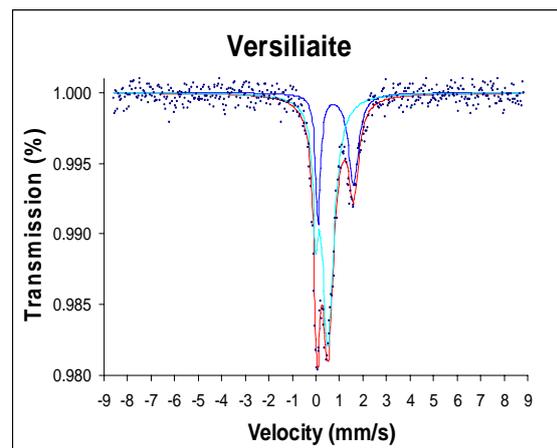
**Figure 1a.**  $^{57}\text{Fe}$  Mössbauer spectrum recorded from schafarzikite



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



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



**Figure 3.**  $^{57}\text{Fe}$  Mössbauer spectrum recorded from versiliaite

### 3.3 Versiliaite

The  $^{57}\text{Fe}$  Mössbauer spectrum is shown in Figure 3. The spectrum was again fitted to two components characteristic of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  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  $\text{Sb}^{3+}$  cation in the pyramidal chains of schafarzikite by an iron ion and the insertion of sulphide anions with corresponding oxidation of  $\text{Fe}^{2+}$ . The results recorded here are consistent with the formulation of versiliaite as  $\text{Fe}_4^{2+}\text{Fe}_8^{3+}\text{Sb}_{12}^{3+}\text{O}_{32}\text{S}_2$ .

**Table 1.**  $^{57}\text{Fe}$  Mössbauer parameters recorded at 298K from schafarzikite-related structures.

Sample		$\delta \pm 0.02/\text{mms}^{-1}$	$\Delta \pm 0.02/\text{mms}^{-1}$	Area $\pm 2\%$
Schafarzikite	$\text{Fe}^{2+}$	1.08	2.13	80
	$\text{Fe}^{3+}$	0.38	0.69	20
$\text{FeSb}_2\text{O}_4$	$\text{Fe}^{2+}$	1.08	2.11	100
Apuanite	$\text{Fe}^{2+}$	0.99	2.03	23
	$\text{Fe}^{3+}$	0.32	0.47	77
Versiliaite	$\text{Fe}^{2+}$	0.85	1.50	32
	$\text{Fe}^{3+}$	0.25	0.51	68

## 4. Conclusions

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

## 5. References

- [1] Bancroft G M 1973 *Mössbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemists* Maidenhead: McGraw-Hill
- [2] Krenner J A 1921 *Z. Kristallogr.* **56** 198
- [3] Zemann J 1951 *Tschermaks Mineral. Petrog. Mitt.* **2** 166
- [4] Fischer R and Pertlik F 1975 *Tschermaks Mineral. Petrog. Mitt.* **22**, 236
- [5] Sejkora J, Ozdin D, Vitalos J, Tucek P, Cejka J and Duda R. 2007 *Eur. J. Mineral.* **19** 419
- [6] Melini M, Merlino S and Orlandi P *Amer. Min.* **64** 1230
- [7] Mellini M and Merlino S 1979 *Amer. Min.* **64** 1235