A ^{57}Fe MÖSSBAUER SPECTROSCOPIC STUDY OF SUGILITE, KNa$_2$(Fe^{3+},Mn^{3+},Al)$_2$Li$_3$Si$_{12}$O$_{30}$

Charles A. Geiger[§]

Institut für Geowissenschaften, Abteilung Mineralogie, Universität Kiel, Olshausenstr. 40, D–24098 Kiel, Germany

Abstract

Sugilite, ideally KNa$_2$(Fe^{3+},Mn^{3+},Al)$_2$Li$_3$Si$_{12}$O$_{30}$, from the Wessels mine, Kalahari, South Africa, was studied using ^{57}Fe Mössbauer spectroscopy. The spectra confirm published electron-microprobe data and X-ray single-crystal results, which indicate that Fe^{3+} is ordered at the *A* octahedral site. The magnitude of the quadrupole splitting, ΔE_Q for Fe^{3+} at both 84 K and room temperature is 0.00 mm/s. This value is very low for a silicate; reported ΔE_Q values for octahedrally coordinated Fe^{3+} are generally greater than 0.20 mm/s. Octahedron distortion, calculated from published X-ray-diffraction data, gives an octahedron-angle variance of 7 and a mean elongation of the octahedron of 1.002. This indicates nearly regular octahedral geometry, and hence a symmetric electric-field gradient around Fe^{3+}. A crystal-chemical interpretation for the regular octahedral geometry and the resulting low ΔE_Q value for Fe^{3+} in the Mössbauer spectrum of sugilite is that structural strain is largely "taken up" by weak Li–O bonds. They permit highly distorted LiO$_4$ tetrahedra, whose variance in the O–Li–O angle, 502, and mean elongation of the tetrahedron, 1.148, are among the largest observed values for inorganic crystal structures. Weak Li–O bonds allow the edge-shared, more strongly bonded Fe^{3+}O$_6$ octahedra to remain regular in geometry.

Keywords: sugilite, ring silicate, Mössbauer spectroscopy, iron, hyperfine parameters, site distortion.

Sommaire

La sugilite, dont la formule idéale est KNa$_2$(Fe^{3+},Mn^{3+},Al)$_2$Li$_3$Si$_{12}$O$_{30}$, provenant de la mine Wessels, Kalahari, en Afrique du Sud, a été étudiée par spectroscopie de Mössbauer de l'ion ^{57}Fe. Les spectres confirment les données obtenues avec une microsonde électronique et les résultats de l'affinement de la structure sur monocristal, qui indiquent une distribution ordonnée de l'ion Fe^{3+} sur le site octaédrique *A*. La valeur du dédoublement quadrupolaire, ΔE_Q, du Fe^{3+} à 84 K et à température ambiante est 0.00 mm/s. C'est une valeur très faible pour un silicate; les valeurs habituelles de ΔE_Q pour le Fe^{3+} en coordinence octaédrique dépassent 0.20 mm/s. La distorsion des octaèdres, calculée à partir des données publiées de diffraction X, donnent une variance de l'angle des octaèdres de 7, et un allongement moyen des octaèdres de 1.002. Ces résultats indiqueraient une géométrie presque complètement régulière, et donc un gradient du champ électrique symétrique autour du Fe^{3+}. La géométrie régulière des octaèdres et les faibles valeurs de ΔE_Q pour le Fe^{3+} dans le spectre Mössbauer de la sugilite mènent à l'interprétation cristallochimique que la déformation structurale est largement accommodée par les faibles liaisons Li–O. Ces liaisons permettent aux tétraèdres LiO$_4$ de se déformer, de sorte que l'écart dans l'angle O–Li–O atteint 502, et l'allongement moyen des tétraèdres atteint 1.148, valeurs qui sont parmi les plus élevées qui soient connues parmi les structures cristallines inorganiques. Les faibles liaisons Li–O permettent aux octaèdres Fe^{3+}O$_6$, à arêtes partagées et à liaisons plus fortes, de demeurer géométriquement réguliers.

(Traduit par la Rédaction)

Mots-clés: sugilite, cyclosilicate, spectroscopie de Mössbauer, fer, paramètres hyperfins, distorsion des sites.

[§] *E-mail address*: chg@min.uni-kiel.de

INTRODUCTION

For many petrological and geochemical studies, it is necessary to obtain a crystal-chemical description of the Fe cations in minerals. Although much has been learned about the intracrystalline partitioning behavior and oxidation state of Fe in various silicates, there still remain gaps of knowledge concerning the nature of Fe^{2+} and Fe^{3+} in certain silicate groups. This is the case for both single- and double-ring structures (*i.e.*, those of the milarite type), the latter of which have the general formula $^{VI}A_2{}^{IX}B_2{}^{XII}C^{XVIII}D^{IV}(T2)_3{}^{IV}(T1)_{12}O_{30}$ (Forbes *et al.* 1972). In this regard, the double-ring silicate sugilite, of ideal formula $KNa_2(Fe^{3+},Mn^{3+},Al)_2Li_3Si_{12}O_{30}$ (Armbruster & Oberhänsli 1988b), requires further investigation. Quantitative determinations of the site occupancy and intracrystalline partitioning behavior of Fe^{2+} and Fe^{3+} are, in any case, not simple for several reasons. First, site assignments based on considerations of ideal stoichiometry can be fraught with uncertainty, because ring silicates may be nonstoichiometric in composition (*e.g.,* Armbruster & Oberhänsli 1988a, Geiger *et al.* 2000a, 2000b). Electron-microprobe analysis alone is therefore insufficient to differentiate between Fe^{2+} and Fe^{3+} and, thus, to determine their amounts and partitioning behavior. Second, with X-ray-diffraction measurements, one cannot distinguish quantitatively between different oxidation states of Fe at sites containing several atoms.

In order to further characterize the crystal chemistry and to address the valence state of Fe and its intracrystalline partitioning behavior in ring silicates, a ^{57}Fe Mössbauer spectroscopic study of a well-characterized sample of sugilite was undertaken.

EXPERIMENTAL METHODS

Sample description

A sample of sugilite from the Wessels mine, Kalahari, South Africa, was chosen for study. A description of its crystal structure and composition is found in Armbruster & Oberhänsli (1988b) and Gnos *et al.* (2003, sample N8). About 100 mg of crystals were hand-picked and characterized by X-ray powder diffraction, which showed only peaks that could be indexed as belonging to sugilite.

^{57}Fe Mössbauer spectroscopy

Spectra were measured at room temperature and 84 K with a nominal 50 mC $^{57}Co/Rh$ source using the experimental set-up described in Geiger *et al.* (2000a).

RESULTS: ^{57}FE MÖSSBAUER SPECTRA

The Mössbauer spectra at both 84 K and RT are simple (Figs. 1a, 1b). Both show a single resonance line that can be fit with the hyperfine parameters given in Table 1.

DISCUSSION

Sugilite, $KNa_2(Fe^{3+},Mn^{3+},Al)_2Li_3Si_{12}O_{30}$, is a double-ring silicate of the milarite type with general formula $^{VI}A_2{}^{IX}B_2{}^{XII}C^{XVIII}D^{IV}(T2)_3{}^{IV}(T1)_{12}O_{30}$. This group of phases is interesting for crystal-chemical reasons, among which the ring-connecting tetrahedral site, $T2$, can contain Al, B, Fe^{2+}, Fe^{3+}, Be, Zn, Mg, and Li (Strunz & Nickel 2001). Consider the crystal structure of sugilite (Fig. 2a), which has been analyzed by Armbruster & Oberhänsli (1988b). Here the ring-connecting $T2$ site contains Li, and the A cation resides at Wyckoff site 4c, with point symmetry 32. The six A–O distances are identical, 1.972(2) Å, and the O–A–O angles lie between 85.72° and 92.27°. The Mössbauer spectra confirm the site occupancy and valence state of Fe in sugilite from the Wessels mine, as given by single-crystal X-ray and electron-microprobe analysis (Armbruster & Oberhänsli 1988b). All Fe is trivalent and is located solely at the A site. The RT spectrum shows a single resonance line with an isomer shift (I.S.) of 0.38 mm/s and a quadrupole splitting value, ΔE_Q, which is effectively 0.00 mm/s. The spectrum at 84 K is similar in appearance. This is one of the lowest, if not the lowest, value for ΔE_Q reported for octahedral Fe^{3+} in silicates.

In the case of the isostructural osumilite, ideally $K(Mg,Fe^{2+},Mn)_2(Al,Fe^{3+})_3(Si,Al)_{12}O_{30}$, Fe can occur as both Fe^{2+} and Fe^{3+} (Goldman & Rossman 1978, Armbruster & Oberhänsli 1988a, C.A. Geiger, unpubl. data), and the A–O distances are 2.118(2) Å (Armbruster & Oberhänsli 1988a). The Mössbauer spectrum and the exact partitioning behavior and site locations for Fe^{2+} and Fe^{3+} in osumilite are not fully understood. Generally, most Fe is Fe^{2+}, and it resides at the A site. The Mössbauer spectrum of a sample of osumilite richer in Fe^{3+} (*i.e.*, Obsidian Cliffs, in Goldman & Rossman 1978) shows a small doublet with an I.S. = 0.40 mm/s and $\Delta E_Q = 0.60$ mm/s, the latter of which is considerably greater than that observed in sugilite. This could be an indication of octahedrally coordinated Fe^{3+}.

Cordierite, $[Na,K]_y(Mg,Fe^{2+},Mn^{2+},Li)_2(Al,Be,Mg,Fe^{2+},Fe^{3+})_4Si_5O_{18}\bullet x[H_2O, CO_2]$, is a single-ring silicate,

TABLE 1. SUGILITE: MÖSSBAUER FIT PARAMETERS[a]

Temp. K	I.S.* mm/s	Q.S. (ΔE_Q) mm/s	Γ mm/s	χ^2
84	0.48	0.00	0.37	0.39
298	0.38	0.00	0.35	0.53

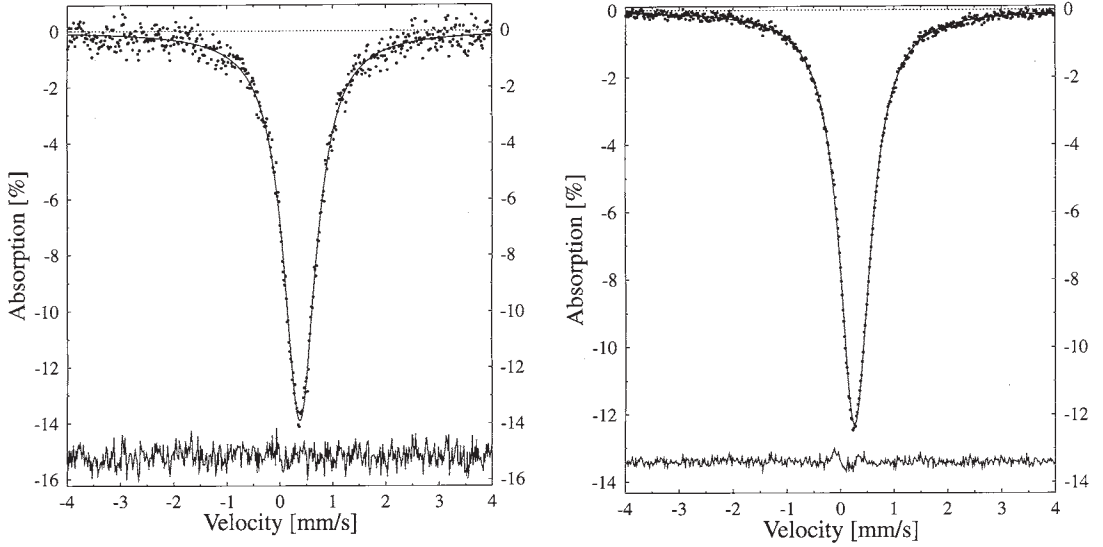[a] Estimated errors in the hyperfine parameters <0.02 mm/s. * Relative to Fe metal.

FIG. 1. ^{57}Fe Mössbauer spectra of sugilite from the Wessels mine at a) 84 K and b) room temperature.

but it is related in structure to the milarite-type phases, and the nature of Fe in it has been analyzed (Geiger *et al.* 2000a, 2000b). Cordierite crystallizes in space group *Cccm*; most Fe^{2+} occurs in octahedral coordination, at the Wyckoff site 8*g* of point symmetry 2. The tetrahedron that connects the rings, *T*11, of point symmetry 2, contains dominant Al, but in some cases, minor Fe^{2+} and even smaller amounts of Fe^{3+} can be present. The ΔE_Q value for Fe^{2+} at T11 is 2.31 mm/s, but the hyperfine parameters for Fe^{3+} are not known quantitatively (Geiger *et al.* 2000b).

In terms of Mössbauer hyperfine parameters, quadrupole splitting results from the interplay between the nuclear quadrupole moment and the surrounding electric-field gradient (efg). Splitting of the energetic states of the nucleus results when the quadrupole moment of Fe, for example, interacts with a noncubic component of the efg. The magnitude, ΔE_Q, is given by:

$$\Delta E_Q = -\frac{e}{2} Q V_{zz} \left(1 + \frac{\eta^2}{3}\right)^{1/2} \qquad (1)$$

where Q is the electric quadrupole moment of the first excited state of the nucleus, V_{zz}, the negative z component of the electric-field gradient, and η, the asymmetry parameter. It is defined as

$$\eta = (V_{zz} - V_{yy})/V_{zz}, \qquad (2)$$

where $|V_{zz}| > |V_{yy}| \geq |V_{xx}|$. The asymmetry parameter takes a value in the interval $0 < \eta < 1$, and it describes the deviation of the efg from axial symmetry. Ingalls (1964) analyzed the nature of ΔE_Q for octahedral coordination and considered that its magnitude is a function of two contributions. The first, the valence-term contribution, reflects the asymmetry from the charge distribution arising from the valence electrons. In the case of Fe^{3+} with five *d* electrons, this should be small to negligible (Fe^{3+} is spherically symmetrical in the free state). The second contribution, which is different in sign, is the lattice term, and it is a function of the deviation of the local environment (*i.e.,* here the crystal field around the Fe atom) from cubic symmetry. This contribution is linear, such that the values of ΔE_Q decrease with decreasing distortion of the surrounding field and tend to zero with no distortion (*e.g.*, McCammon 2004).

The measured values of ΔE_Q at both 84 K and room temperature for octahedrally coordinated Fe^{3+} in sugilite are effectively 0.00 mm/s within the resolution of the experimental spectrum. This value is one of the lowest observed for a silicate, where for octahedrally coordinated Fe^{3+}, one observes ΔE_Q greater than 0.20 mm/s (McCammon 1995). Apparently, the efg around Fe^{3+} at the *A* site is nearly symmetric. In terms of polyhedron distortion, calculated from the data of Armbruster & Oberhänsli (1988b), the variance in the octahedron angle is 7, and the mean elongation of the octahedron is 1.002 (Robinson *et al.* 1971). Both values are very low. Common silicates (*e.g.*, olivine, garnet, pyroxene, amphibole, humite) show a range of values between 0 and 220 for variance of the octahedron angle
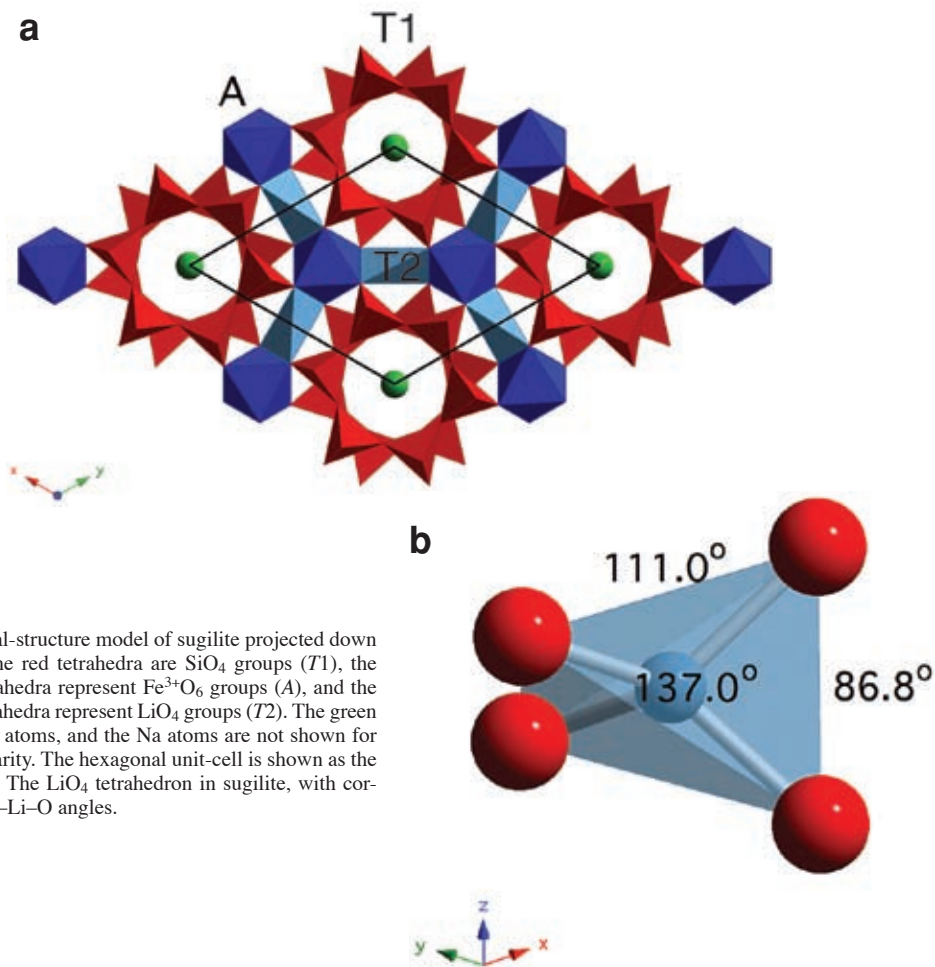
FIG. 2.   a) Crystal-structure model of sugilite projected down the c axis. The red tetrahedra are SiO_4 groups ($T1$), the dark blue octahedra represent $Fe^{3+}O_6$ groups (A), and the light blue tetrahedra represent LiO_4 groups ($T2$). The green spheres are K atoms, and the Na atoms are not shown for the sake of clarity. The hexagonal unit-cell is shown as the solid lines. b) The LiO_4 tetrahedron in sugilite, with corresponding O–Li–O angles.

and between 1.000 and 1.070 for mean elongation of the octahedron, with garnet-group phases showing the lowest values (Robinson *et al.* 1971). A simple crystal-chemical interpretation that could allow for the low distortion of the octahedron in sugilite is that structural strain is "taken up" by the weakly bound LiO_4 tetrahedra, whose Pauling electrostatic bond-strength for Li–O is 0.25 valence units (*vu*). This could allow the edge-shared octahedra (Fig. 2a), with stronger Fe^{3+}–O bonds (*i.e.*, bond strength 0.50 *vu*), to remain regular in geometry. The LiO_4 tetrahedron is highly distorted (Fig. 2b) having an O–Li–O tetrahedron-angle variance of 502 and a mean elongation of the tetrahedra of 1.148. Analogous values for $T2$ in osumilite are 239 and 1.07, respectively, using data of Armbruster & Oberhänsli (1988a). The variance of the octahedron angle for osumilite is 114, and the mean elongation of the octahedra is 1.03. The largest reported values for tetrahedron-angle

variance and mean tetrahedron-elongation in Robinson *et al.* (1971) for a number of different tetrahedra (*i.e.,* containing Cr, Ge, Be, B, P, S, W, Mn, Mo, Zn, *etc.*) are about 100 and 1.025, respectively.

The absorption line in the Mössbauer spectra of sugilite is slightly broadened, having a half-width of about 0.35 mm/s (Fig. 1). Values of 0.24–0.28 mm/s for Fe at a single crystallographic site are typical for silicates (McCammon 2004). Three explanations are possible. First, the single absorption line may actually consist of a very closely spaced doublet. Second, slight broadening may arise from the nature of the local structural environment around the A site. In sugilite, the Na atoms are disordered at the B sites, with up to about 50% of them being occupied, and they are located less than 4.1 Å from the Fe^{3+} atoms (Armbruster & Oberhänsli 1988b). Local variations of the Na cations could give rise to a distribution of slightly different efg around the respec-

tive Fe^{3+} atoms. Third, sugilite from the Wessels mine shows some compositional heterogeneity, and crystals can be zoned (Armbruster & Oberhänsli 1988b). This also could give rise to line broadening.

Hematite, α-Fe_2O_3, is an oxide phase whose Mössbauer spectrum shows a small ΔE_Q value of 0.12 mm/s at 298 K (Greenwood & Gibb 1971). The absorption line, compared to that in sugilite, is broad and asymmetric, and a relatively complex line-shape arises on cooling down to 200 K. Note that Fe^{3+}-bearing halide phases have also been reported (*e.g.*, FeF_3) that contain Fe^{3+} in an almost regular octahedron. The phase FeF_3 is antiferromagnetic below 363 K. Above this temperature, its spectrum shows a single narrow resonance line with an isomer shift of 0.489 mm/s (Greenwood & Gibb 1971).

REFERENCES

ARMBRUSTER, T. & OBERHÄNSLI, R. (1988a): Crystal chemistry of double-ring silicates: structural, chemical, and optical variation in osumilites. *Am. Mineral.* **73**, 585-594.

ARMBRUSTER, T. & OBERHÄNSLI, R. (1988b): Crystal chemistry of double-ring silicates: structures of sugilite and brannockite. *Am. Mineral.* **73**, 595-600.

FORBES, W.C., BAUR, W.H. & KAHN, A.A. (1972): Crystal chemistry of milarite-type minerals. *Am. Mineral.* **57**, 463-472.

GEIGER, C.A., ARMBRUSTER, T., KHOMENKO, V. & QUARTIERI, S. (2000a): Cordierite I: the coordination of Fe^{2+}. *Am. Mineral.* **85**, 1255-1264.

GEIGER, C.A., RAGER, H. & CZANK, M. (2000b): Cordierite III: the coordination and concentration of Fe^{3+}. *Contrib. Mineral. Petrol.* **140**, 344-352.

GNOS, E., ARMBRUSTER, T. & VILLA, I.M. (2003): Norrishite, $K(Mn_2^{3+}Li)Si_4O_{10}(O)_2$, an oxymica associated with sugilite from the Wessels mine, South Africa: crystal chemistry and ^{40}Ar–^{36}Ar dating. *Am. Mineral.* **88**, 189-194.

GOLDMAN, D.S. & ROSSMAN, G.R. (1978): The site distribution of iron and anomalous biaxiality in osumilite. *Am. Mineral.* **62**, 490-498.

GREENWOOD, N.N. & GIBB, T.C. (1971): *Mössbauer Spectroscopy.* Chapman and Hall Ltd., London, U.K.

INGALLS, R. (1964): Electric-field gradient tensor in ferrous compounds. *Phys. Rev.* **133**, A787-A795.

MCCAMMON, C.A. (1995): Mössbauer spectroscopy of minerals. Mineral physics and crystallography. *In* A Handbook on Physical Constants. American Geophysical Union, Washington, D.C. (332-347).

MCCAMMON, C.A. (2004): Mössbauer spectroscopy: applications. *In* Spectroscopic Methods in Mineralogy (A. Beran & E. Libowitzky, eds.). *Eur. Mineral. Union, Notes in Mineralogy* **6**, 369-398.

ROBINSON, K., GIBBS, G.V. & RIBBE, P.H. (1971): Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science* **172**, 567-570.

STRUNZ, H. & NICKEL, E.H. (2001): *Strunz Mineralogical Tables* (9th ed.). E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, Germany.