A Mössbauer study of pentacoordinated ferric iron in orthoericssonite

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Abstract

Mössbauer spectra of orthoericssonite in the temperature range 78–547 K reveal very low quadrupole splittings ($QS=0.26\text{--}0.31\text{ mm/s}$) for pentacoordinated Fe^{3+} , which is shown to be a consequence of the size of the angle between equatorial bonds and the apical bond of this site. At temperatures above 298 K the Mössbauer centroid shift (CS) decreases linearly at $-8.0 (\pm 1.1) \cdot 10^{-4} \text{ mm} \cdot \text{s}^{-1} \cdot \text{deg}^{-1}$, which is in good agreement with the theoretical value of $-7.3 \cdot 10^{-4} \text{ mm} \cdot \text{s}^{-1} \cdot \text{deg}^{-1}$. In agreement with previous chemical analyses of the studied samples minor absorption doublets caused by the presence of ferrous iron were recorded in the spectra of a sample from the Hijikuzu mine, Japan. Mössbauer spectra indicate that ferrous iron substitutes for manganese randomly at all three types of octahedral sites found in the orthoericssonite structure.

Introduction

Pentacoordinated cations in silicate mineral structures are rare, although some rock-forming minerals display this feature. Consequently spectroscopic data on cations at such sites are scarce in literature. The present Mössbauer study was performed with the aim to obtain additional data on ferric iron in pentacoordination in silicates, which so far has only been reported for vesuvianite at room temperature (Olesch 1979) and andalusite (Abs-Wurmbach *et al.* 1981) at ambient temperature and at 77 K. An additional aim was to explore the possibility for thermally induced electron delocalisation between neighbouring Fe^{2+} and Fe^{3+} in orthoericssonite.

The two polymorphic minerals ericssonite and orthoericssonite were originally described from Långban, Sweden by Moore (1971), who gave the mineral formula $\text{BaMn}_2(\text{Fe}^{3+}\text{O})[\text{Si}_2\text{O}_7](\text{OH})$. The crystal structure of orthoericssonite has been determined by Matsubara (1980) on a sample from the second occurrence of the mineral at the Hijikuzu mine, Japan (Matsubara and Nagashima, 1975). The structure of the mineral consists of a quasi-silicate sheet composed of Si_2O_7 sorosilicate groups and FeO_5 square pyramids, which sandwich an octahedral sheet composed of three different types of MO_6 -octahedra. Between neighbouring composite sheets are Ba^{2+} cations located. The Fe^{3+} -site is a square pyramid

with a mean bond length of 1.960 Å. The apical bond is considerably shorter (1.834 Å) than the remaining four equatorial bonds (twice 1.989 Å and twice 1.995 Å). Angles between the apical and the equatorial bonds are 107.3 and 106.5 degrees respectively. The differences in bond lengths and bond angles for the equatorial bonds are within the experimental error and consequently the site may be regarded as essentially a square pyramid of C_4 symmetry.

Samples

In the present study one sample from each of the reported localities, were investigated. The sample from the Hijikuzu mine was separated from specimen NSM M-20799 deposited at the Department of Geology at the National Science Museum in Tokyo. Single Crystals from the same specimen were used for the crystal structure determination of orthoericssonite by Matsubara (1980). The chemistry of the sample has been reported by Matsubara and Nagashima (1975) and it may be specified as a strontian and ferroan variety of the mineral.

The specimen from Långban, Sweden consists of a typical tephroite-rhodonite-“schefferite” (manganian aegirine) skarn as described by Moore (1971) and it contains a mixture of orthoericssonite and ericssonite, with predominance of the first mentioned. The Långban sample reported by Moore (1971) did not contain detectable amounts of Sr, but minor amounts of Pb substituting for Ba were recorded. All iron was allocated as ferric.

The structural relationship between orthoericssonite and ericssonite has been explained by Matsubara (1980) in terms of twinning on $[100]$ of the monoclinic subcell. As this relationship does not involve any differences in cation site geometries, Mössbauer parameters (isomer shifts and quadrupole splittings) should be insensitive to variations in the proportions of the two polymorphs in a Mössbauer absorber, unless the chemistry of the two coexisting phases differs considerably.

Experimental

Mössbauer spectra were recorded with a constant acceleration system working in conjunction with a 512 channel MCA using a nominal 50 mCi $^{57}\text{Co}/\text{Rh}$ -source and a CO_2/Ar -filled proportional counter as detector. Absorbers were prepared from powders of carefully separated mineral concentrates, which for the room and low temperature experiments were mixed with transoptic powder. The absorber densities were in the range 3.5–5.0 mg Fe/cm^3 . A thin foil of α -Fe was used for velocity calibration and all Mössbauer parameters are given relative to α -Fe at room temperature. Low temperature spectra were recorded with the absorber in a cryogenic chamber in thermal contact with liquid nitrogen, and high temperature experiments were performed with the sample placed in the sample chamber of a resistorheated oven equipped with beryllium windows. The chamber was evacuated during thermal experiments and temperatures were continually monitored and controlled using Pt-

Pt/Rh-thermocouples. The accuracy of the temperature readings was ± 10 K. Fits of the recorded spectra were carried out using a computer program (Jernberg and Sundqvist, 1983) assuming Lorentzian line shapes, equal values of FWHM (full width at half maximum) and equal intensity of the two components of each quadrupole doublet. In addition to this FWHM-values for all doublets were constrained to be equal.

Subsequent to high temperature measurements the absorber powder was run at room temperature. This was done in order to ensure that sample changes had not occurred during the high temperature exposure. After the completion of the Mössbauer experiments, the mineral powders were recovered from the absorbers and also studied by powder XRD to ascertain that no changes had been induced by the thermal experiments.

Results

Mössbauer spectra of the two samples obtained at different temperatures are shown in figures 1 and 2 and the derived Mössbauer parameters for all measured spectra are summarized in Table 1. On the basis of the Mössbauer parameters and their temperature dependence (Figure 3) the major absorption doublet, with $CS=0.35$ and $QS=0.30$ mm/s at room temperature, is assigned to Fe^{3+} . The small CS and the very small dependence of the quadrupole splitting on temperature are typical features of high-spin ferric iron (Coey, 1984). The temperature dependence of the CS of the major Fe^{3+} quadrupole doublet is $-8.0 (\pm 1.1) \cdot 10^{-4} \text{ mm} \cdot \text{s}^{-1} \text{ deg}^{-1}$ at temperatures above 298 K. This value is in good agreement with the theoretical value of $-7.3 \cdot 10^{-4} \text{ mm} \cdot \text{s}^{-1} \text{ deg}^{-1}$. A Debye temperature related negative deviation of the second order Dopplershift from this linear relationship is observed as expected at lower temperatures (78 K).

The large CS -values and the temperature dependent quadrupole splitting of the minor absorption, which was exclusively recorded in the spectra of the Japanese sample, indicate that it is caused by ferrous iron at two or more non-equivalent sites. In high temperature Mössbauer spectra (Figure 1c) this low intensity absorption may be adequately described by a single quadrupole doublet. However, at decreasing temperature the widths of the resolved high-velocity part of this absorption increases and it deviates significantly from Lorentzian shape (figure 1a and 1b). In the spectrum recorded at 78 K two absorption maxima are clearly discernable in the high velocity range (figure 1a). Different procedures using one, two and three quadrupole doublets of Lorentzian shape were adopted to fit this low intensity feature. A distinct improvement of the spectral fit, as monitored by the χ^2 -values, was noted when introducing a second low intensity doublet in the fitting procedure. Addition of a third quadrupole doublet to this velocity region did not improve the situation significantly. An equal intensity of the two low-intensity doublets was recorded in the fits of the 78 K and 298 K spectra. As a consequence of this all spectra of the Hijikuzu mine sample were resolved by using a fitting procedure which included in total three quadrupole doublets and the

FIG. 1. Mössbauer spectra of orthoericssonite NSM-M 20799 at 78 K (A), 298 K (B) and 547 K (C). Diamonds represent experimentally obtained data, the dotted low-intensity envelopes correspond to the sum of the two computer fitted quadrupole subsets due to ferrous iron, the dashed lines represent the quadrupole due to five-coordinated ferric iron and the solid lines are delineating the sum of all three quadrupole subsets.

FIG. 2. Mössbauer spectrum of the orthoericssonite/ericssonite sample from Långban. Diamonds represent the measured spectrum and the solid line shows the quadrupole doublet due to ferric iron at the five-coordinated site.

TABLE 1. Mössbauer parameters for pentacoordinated ferric iron and octahedrally coordinated ferrous iron in orthoericssonite from the Hijikuzu mine, Japan and orthoericssonite/ericssonite from Långban, Sweden.

Sample	T	Fe^{3+}			Fe^{2+}						FWHM
		CS	QS	I	CS ₁	CS ₂	QS ₁	QS ₂	I ₁	I ₂	
		(K)	– (mm/s) –	(%)	———— (mm/s) ————				(%)	(%)	
NSM	78	0.45	0.31	74	1.28	1.29	2.65	2.07	13	13	0.30
	298	0.35	0.29	74	1.15	1.17	2.31	1.92	13	13	0.28
	393	0.27	0.28	76	1.06	1.07	2.10	1.85	12	12	0.26
	443	0.23	0.27	76	1.02	1.00	1.99	1.82	12	12	0.26
	493	0.19	0.27	78	0.97	0.94	1.86	1.78	11	11	0.27
M20799	547	0.15	0.26	78	0.93	0.93	1.71	1.71	11	11	0.26
Långban	78	0.46	0.30	100							0.26
	298	0.36	0.30	100							0.26

The estimated errors for Mössbauer parameters (CS and QS) for ferric iron is ± 0.01 mm/s, while the errors for the parameters given for the ferrous iron doublets are estimated to be ± 0.05 mm/s.

intensity of the two low-intensity doublets were constrained to be equal. In this context it must be stressed that the CS- and QS-values of the high intensity doublet due to ferric iron remained constant within the limit of error (± 0.01 mm/s) irrespective of the number of

FIG. 3. Temperature dependence of CS and QS for pentacoordinated ferric iron in orthoericssonite NSM-M 20799.

quadrupole doublets (two, three or four) used in the fitting procedure.

Discussion

The room-temperature centroid shift of 0.35 mm/s observed for the dominating quadrupole doublet indicate the presence of ferric iron at a relatively small coordination site. This CS-value is larger than those normally found for ferric iron at tetrahedral sites in silicates (Coey, 1984 and McCammon 1995). From the crystal structure determination of orthoericssonite by Matsubara (1980) it is evident that there exists only one site at which ferric iron is expected to produce the observed CS and that is the square pyramid site labelled "Fe". The observed QS-value (0.30 mm/s at RT) for this doublet is however distinctly smaller than those recorded for Fe^{3+} at five-coordinated sites in vesuvianite (1.12 mm/s; Olesch, 1979) and andalusite (0.76 mm/s; Abs-Wurbach *et al.*, 1981). As ferric iron possesses an isotropic electron distribution in the valence shell the Mössbauer QS is expected to essentially reflect the charge distribution on ions surrounding the Fe^{3+} ion. If all distances r , and polar angles ϕ and θ of all contributing ions with respect to the Mössbauer atom are known and charges q can be assigned to these ions, the lattice charge distribution may be calculated (Gütlich *et al.* 1978):

$$\text{QS} = 0.5(V_{zz})_{\text{lat}}(1 + \eta^2/3)^{0.5}eQ$$

where the $(V_{zz})_{\text{lat}}$ and η are the main tensor of the lattice contribution to the electric field

gradient and the assymetry parameter, respectively and they are defined as:

$$(V_{zz})_{lat} = \sum q_i r_i^{-3} (3 \cos^2 \theta_i - 1) \text{ and } \eta = \sum q_i r_i^{-3} (\sin^2 \theta \cos 2\phi)$$

Assuming that only the first ligand sphere contributes to $(V_{zz})_{lat}$ and that all ligand charges are equal the QS-values for doublets due to Fe^{3+} at the five-coordinated sites in vesuvianite, andalusite and orthoericssonite are calculated to relate as 1: 0.46: 0.34. The experimentally obtained values 1.12, 0.76 and 0.30 mm/s (1: 0.68: 0.27) are in good agreement with this calculated relationship.

The observed large difference in QS-values for ferric iron at the five-coordinated sites in vesuvianite and orthoericssonite may seem surprising. The site symmetry is in both cases adequately described as C_{4v} and the bond distances are comparable. In vesuvianite the apical bond length is 1.874 Å and the four equatorial bonds are 2.000 Å (Giuseppetti and Mazzi, 1983) compared to 1.834 Å and 1.992 Å, respectively, in orthoericssonite. However, the angle between the apical bond and the equatorial bonds differs significantly. In vesuvianite this angle is 99.1° , while in orthoericssonite it is distinctly larger, 106.9° . The calculated variation of $|(V_{zz})_{lat}|$, which is the main contribution to QS in the two examples, in response to changes in the angle between the apical and equatorial bonds is illustrated in figure 4. From this figure it is evident that the experimentally recorded difference in QS for ferric iron at the square pyramid sites in the two minerals is mainly an effect of θ -bond angle differences.

The minor absorption feature observed in the spectra of the sample from the Hijikuzu mine is obviously composed of a number of overlapping quadrupole doublets with large CS-

FIG. 4. Calculated $|(V_{zz})_{lat}|$ of the square pyramid sites in vesuvianite (V) and orthoericssonite (E). The lines passing through V and E represent calculated values for the same sites at varying θ -angles but constant M-O distances and ϕ -angles.

and QS-values. This absorption feature can be satisfactorily fit with just two doublets characterized by high CS-values of 1.15 and 1.17 mm/s and QS-values of 2.31 and 1.92 mm/s, respectively at room temperature. The quadrupole splitting of one of these two doublets is strongly dependent on temperature (Fe^{2+} -subset 1 in Table 1). In the crystal structure of orthoericssonite (Matsubara, 1980) there are three different octahedral sites, which are mainly Mn^{2+} -centered. Two of these sites, Mn2 and Mn3, are geometrically very similar showing four long bond distances of 2.244 and 2.281 Å, respectively and two shorter bond distances of 2.074 and 2.056 Å, respectively. The third octahedral site, Mnl, is less distorted displaying two long, two intermediate and two short bond distances of 2.266, 2.192 and 2.156 Å, respectively. Considering the similar mean bond distances it is unlikely that ferrous iron at these sites will give rise to quadrupole doublets with significantly different CS-values. However the Mnl site differs from the Mn2 and Mn3 sites in terms of symmetry and distortion. In analogy with the situation in orthopyroxene (Shenoy *et al.* 1969) it is likely that Fe^{2+} at the more distorted Mn2 and Mn3 sites of orthoericssonite will cause quadrupole doublets with relatively small and temperature independent QS as compared to Fe^{2+} at the Mnl site. A tentative assignment of two low-intensity quadrupole doublets resolved in the spectra of the Hijikuzu sample is that ferrous iron at the Mnl site gives rise to Fe^{2+} set 1 and ferrous iron at Mn2 and Mn3 causes set 2 (Table 1). From spectra recorded at low temperatures it is seen that the intensities of the two sets are equal. As the number of Mnl sites in the unit cell is equal to the sum of Mn2 and Mn3 sites this indicates that ferrous iron is statistically distributed over the three types of octahedral sites.

Features assignable to thermally induced electron delocalization between Fe^{2+} and Fe^{3+} at neighbouring sites were not observed in the present high temperature spectra of orthoericssonite. The absence of such effects is in agreement with the results of Amthauer & Rossman (1984), which strongly indicate that delocalization effects are exclusively observed in spectra of mineral structures in which Fe^{2+} - and Fe^{3+} -centered sites share at least polyhedral edges. In addition to this the structures should be characterized by a high degree of Fe-site polymerization. In orthoericssonite, FeO_5 square pyramids and neighbouring octahedral sites share only one ligand and the $\text{FeO}_5\text{-MO}_6$ clusters occur as isolated dimers.

Conclusions

Mössbauer spectra of orthoericssonite and ericssonite from the Hijikuzu mine, Japan and Långban, Sweden are characterized by a strong quadrupole doublet due to ferric iron at a five-coordinated site. The small quadrupole splitting displayed by this doublet is in agreement with the structural determination of the mineral by Matsubara (1980), which shows that the angle between the apical and equatorial bonds of the square pyramid site is relatively large.

Ferrous iron was only detected in the Mössbauer spectra of the Japanese sample. This

is in agreement with results of previous chemical analyses of orthoericssonite and ericssonite from the two localities (Matsubara and Nagashima, 1975; Moore, 1971). Based on a tentative assignment of the computer resolved quadrupole doublets caused by ferrous iron it is suggested that Fe^{2+} substitutes for Mn^{2+} in a disordered manner at all three types of octahedral sites in orthoericssonite.

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