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^{57}Fe Mössbauer spectroscopy, X-ray single-crystal diffractometry, and electronic structure calculations on natural sinhalites

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Abstract Natural sinhalites, $MgAlBO_4$, from the Ratnapura District, Sri Lanka, and from Bodnar Quarry near Hamburg, Sussex Co., New Jersey, USA, have been characterized by ^{57}Fe Mössbauer spectroscopy, electron microprobe, X-ray single-crystal diffractometry and by electronic structure calculations in order to determine the oxidation state and site occupancy of iron in the sinhalite structure. The samples contain about 3.35 and 1.46 wt% of total iron oxide, respectively. The structure refinement is successful and reproduces the total iron content provided that the substitution of Mg^{2+} by Fe^{2+} on the M2 position only is assumed. The ^{57}Fe Mössbauer spectra at 77, 293, 573 and 773 K can be resolved into two doublets with hyperfine parameters common for octahedrally coordinated high-spin Fe^{2+}. There is no evidence for iron in the tetrahedral site. Electronic structure calculations in local spin density approximation yield hyperfine parameters for Fe^{2+} on the M2-site at 0, 293, 573 and 773 K in quantitative agreement with experiments. Calculated spectroscopic properties for Fe^{2+} on the M1-site are at variance with the experimental data and, thus, indicate that substitution of Al^{3+} by Fe^{2+}, if occurring at all, must be accompanied by considerable local expansion and distortion of the M1-octahedron.

Keywords Sinhalite · Mössbauer spectroscopy · Electronic structure calculations

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Introduction

Sinhalite has the ideal chemical composition $MgAlBO_4$ and is a rare mineral occurring, e.g., in high grade scarns and gneisses. Bowden et al. (1969 and references therein) located sinhalite in scarn assemblages from contact zones of metamorphosed carbonate rocks with, for example, Archaean gneiss or granite. Sinhalite is isostructural with fayalite, alexandrite or chrysoberyl, and is the only borate with olivine structure (Strunz 1997). An early structure determination (Fang and Newnham 1965) has later been refined by Hayward et al. (1994). The sinhalite samples reported in the literature contain up to 3.5 wt% FeO as derived from microprobe analysis. Hence, iron has been assumed to be divalent and substitutes Mg (Claringbull and Hey 1952), but low Fe^{3+} contents have probably been detected in some samples (Hayward et al. 1994). Farrell and Newnham (1965) conclude that the distinctive color and optical absorption spectra are caused by small concentrations of iron and perhaps Cr. In view of these open questions, it is desirable to determine the site occupancy and oxidation state of iron in sinhalite for an improved understanding of the crystal chemistry and color of this rare mineral.

To the best of our knowledge, the localization of iron in the crystal structure by Mössbauer spectroscopic measurements has not yet been attempted. To this end, two sinhalite samples, one from metamorphic rocks of the charmichite-metamorphic type from the Ratnapura District, Sri Lanka, and the other from the scarns from Bodnar Quarry near Hamburg, Sussex Co., New Jersey, USA, (Smithsonian National Museum of Natural History, Washington, DC, USA, sample ID 145688, courtesy of Pete Dune) are investigated by microprobe analysis, X-ray single crystal diffraction, ^{57}Fe Mössbauer spectroscopy and by electronic structure calculations. Finally, sinhalite will be compared with olivine $(Fe,Mg)_2SiO_4$, alexandrite $(Al,Cr)_2BeO_4$ and kirschsteinite $CaFeSiO_4$ because sinhalite can be interpreted as the Fe^{2+} equivalent of alexandrite and chrysoberyl.

Experimental and theoretical methods

Microprobe analysis

Quantitative chemical data for two samples from each sinhalite single crystal of both locations were obtained with an electron microprobe (JEOL Superprobe JXA-8600, controlled by *Probe for Window*s system of programs, operated at 15 kV, 40 nA, 15 s counting time on peak and beam diameter 5 μm). The following standards (all synthetic except wollastonite) and corresponding K_α emission lines of the cation were selected: SiO_2, Al_2O_3, MgO, wollastonite $CaSiO_3$, NaCl, KCl, FeO and MnO. The oxygen content was calculated by stoichiometry and the theoretical amount of 27.60% B_2O_3 was taken in account for the on-line ZAF-4 procedure. Measurements were performed at ten points on the Ratnapura sample and five points on the Hamburg sample. For all samples cation numbers were calculated with respect to four oxygen atoms and one boron atom per formula unit.

Single-crystal X-ray refinement

Several small fragments were cut from a larger transparent homogeneous piece of sinhalite for single-crystal X-ray diffraction analysis. Before data collection the crystals were quenched several times in liquid nitrogen since a preliminary data set suffered from severe extinction effects. Single crystal intensity data collection was performed on a Bruker SMART APEX 3-axis CCD-diffractometer using both ω and ϕ rotation scans (frame width = 0.3°). Further details on data collection and crystal structure refinement are given below. The shape and composition (low linear absorption coefficient) of the crystal render any absorption correction unnecessary. The structure was solved and refined with the programs SHELXS-97 and SHELXL-97 (Sheldrick 1997), as implemented in the program suite WINGX 1.64 (Farrugia 1999).

Mössbauer spectroscopy

A sample of the same charge as the one used for the diffraction experiment was carefully powdered and prepared as a Mössbauer absorber with 3.81 (Ratnapura sinhalite) and 1.62 mg Fe/cm^2 (Hamburg sinhalite) and with a diameter of 7 mm by embedding it homogeneously in an epoxy resin with good thermal conductivity and fixing it in a copper ring sandwiched by aluminium foils of excellent purity. This absorber was mounted in a conventional Mössbauer apparatus (Halder Elektronik GmbH) with constant acceleration (time mode arrangement) and was exposed to a nominal 50 mCi (1.8 GBq) ^{57}Co/Rh source (Wissel GmbH). The transmitted intensities were stored in a 1024 multichannel analyzer (Halder Elektronik). An acceptable resolution and peak-to-background ratio was attained at a comparably high counting rate of about 500,000 counts and a measuring time of 5 days. High temperature Mössbauer spectroscopic measurements on sinhalite powder were performed in a self-constructed furnace at 300 and 500°C, low temperature data (77 K) were collected utilizing a gas-flow cryostat (Leybold GmbH). An α-Fe spectrum was subsequently recorded in order to determine the calibration factor. The velocity scale was then recalculated from channel numbers to mm/s.

The Mössbauer spectrum was folded to 510 channels, fitted with a conventional refinement routine with Lorentzian lines (MOESALZ, Lottermoser et al. 1993), and decomposed into subspectra with parameters of the following meaning: isomer-shift (IS) relative to α-Fe (mm/s), half width Γ of the lines with Lorentzian shape (mm/s), quadrupole splitting QS (mm/s), and area A (%) of the different subspectra. The convergence of the iteration and the χ^2-value of the final fit served as an indication of the quality of the refinement:

$$\chi^2 = \sum_{i=1}^{N} \frac{\left(Y_{i,\mathrm{calc}} - Y_{i,\mathrm{obs}}\right)^2}{Y_{i,\mathrm{obs}}} \times \frac{1}{N-K}.$$

$Y_{i,\mathrm{calc}}$ and $Y_{i,\mathrm{obs}}$ are calculated and observed intensities per channel i, respectively; N is the total number of measured intensities and K is the number of refined parameters.

Electronic structure calculations

All calculations have been performed in local spin density approximation (LSDA) by the spin-polarized self-consistent-charge-(SCC-)Xα method (Grodzicki 1980, 1985). However, the Xα-exchange potential (with $\alpha = 0.7$) is only used for the evaluation of the two- and three-center integrals while the one-center integrals are derived from fully numerical all-electron relativistic atomic calculations. Furthermore, the core electrons enter the two- and three-center integrals via a pseudopotential also derived from the relativistic atomic calculations. The method is hence ab initio in the sense that it does not contain any adjustable parameter. The valence basis set consists of 2s-, 2p-orbitals for B, O and F, 3s-, 3p-orbitals for Mg and Al, and 3d-, 4s-, 4p-orbitals for Fe.

The measured quadrupole splitting ΔE_Q is related to the components $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$ of the electric field gradient (EFG) tensor in its principal axes system by

$$\Delta E_Q = \frac{1}{2} e_0 Q V_{ZZ} \sqrt{1 + \frac{\eta^2}{3}},$$

where the asymmetry parameter $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ can take values between 0 and 1 and describes the deviation of the EFG from axial symmetry. The nuclear quadrupole moment Q of the first excited state of ^{57}Fe is assumed to be 0.16 barn (Dufek et al. 1995). The calculation of the EFG tensor $V_{\alpha\beta}$ within the framework of a valence-electron-only MO method has been described in detail previously (Grodzicki et al. 1987; Grodzicki and Amthauer 2000). In particular, the EFG tensor can be decomposed into three different contributions, viz. (1) the valence contribution related to the anisotropies of the 3d- and 4p-shell of iron, (2) the covalence contribution related to the anisotropy of the charge distribution within the iron-ligand bonds, and (3) the ligand contribution related to the anisotropy of the charge distribution of the remaining atoms of the cluster or solid. In the principal axes system of the EFG-tensor the EFG V_{ZZ} is simply the sum of these three contributions. The valence part is roughly proportional to the anisotropies of the Fe(3d)-shell and Fe(4p)-shell occupations, respectively:

$$\Delta n_d = n_{x^2-y^2} + n_{xy} - n_{z^2} - \left(\frac{n_{xz} + n_{yz}}{2}\right),$$

$$\Delta n_p = \frac{n_x + n_y}{2} - n_z.$$

Usually the anisotropy of the Fe(3d)-shell dominates the EFG for high-spin ferrous iron, whereas it is generally assumed that for high-spin ferric iron the ligand contribution should be the largest.

Results and discussion

Microprobe analysis

Preliminary examination of the Ratnapura single crystal does not yield any additional phases or inclusions in the samples. The powder diffraction pattern of sinhalite from Hamburg, New Jersey, exhibits small amounts of quartz and an additional unknown phase. Microprobe analysis of these additional phases yields, however, negligible amounts of Fe. Hence, these phases have no influence on the sinhalite Mössbauer spectra.

The results of the microprobe analysis of both sinhalite samples are listed in Table 1. All tested oxides with concentrations larger than zero are listed in the table. The oxide percentages for each of the major oxides agree with the results from other samples (Claringbull and Hey 1952; Fang and Newnham 1965; Hayward et al. 1994; Pitman et al. 1995) within experimental error, whereas the amounts of FeO of both samples are in the upper part of the range common for sinhalite. Other elements are below the detection limit of the microprobe analysis. The structural formula, calculated on the basis of four oxygen atoms and an assumed B_2O_3-content of 27.60 wt%, yields an average chemical composition of $Al_{0.99}Mg_{0.92}Fe_{0.06}B_{1.03}O_4$ for the Ratnapura sinhalite and of $Al_{1.00}Mg_{0.96}Fe_{0.03}B_{1.02}O_4$ for the Hamburg sinhalite. The variation of the chemical composition with respect to different measurement points is in the range of the experimental error so that the crystals appear to be chemically homogeneous. Finally, the comparison of the two specimens yields a correlation between the decrease of MgO and an increasing FeO content which suggests the substitution of Mg by Fe.

Single-crystal X-ray diffraction

Preliminary investigations of the intensity data sets did not show any evidence for twinning. The analysis of systematic extinctions confirms that sinhalite crystallizes in the space group *Pnma* with Z = 4. The details on data collection and crystal structure refinement together with the fractional coordinates and selected bond distances are summarized in Tables 2, 3, 4, 5. The unit cell parameters of both samples are in the range reported for other sinhalites and seem to decrease with decreasing iron content. A schematic view of the sinhalite structure is shown in Fig. 1. As in all crystals with olivine structure the oxygen atoms approximately form distorted hexagonally close-packed arrays. Al^{3+} occupies the special position 4*a* [M1-site, symmetry $\bar{1}$] and Mg^{2+} is at the special position 4c [M2-site, symmetry *m*]. Both sites are octahedrally coordinated. The M2-octahedron has the larger mean M-O bond length (2.09 Å) typical for Mg octahedra, while the smaller M-O bond length of the M1-site (1.90 Å) is representative for an Al octahedron. Accordingly, Al is assigned to the M1-position and Mg to the M2-position. Finally, the M2 octahedron is more distorted than M1, evidenced by significantly larger polyhedral distortion parameters (Table 5). The tetrahedra occupied exclusively by boron are isolated from each other and crosslink the octahedral chains of different layers along the *c*-axis. The B-tetrahedra have an average B–O bond length of 1.50 Å and are too small for incorporating iron in detectable amounts. Indeed, tetrahedrally coordinated iron in such a small tetrahedron has not yet been observed in minerals. In fact, from the unsuccessful attempts to prepare sinhalite-forsterite solid solutions, Werding et al. (1981) concluded that the tetrahedral site in sinhalite does not accept substitutions for boron even by silicon or aluminium.

Table 1 Chemical composition of two specimens of sinhalite

Sample	Al_2O_3	MgO	Na_2O	CaO	K_2O	FeO	MnO	B_2O_3	Total
The oxide partition with the assumption of 27.6 wt% B_2O_3									
Ratnapura	39.1 (1)	28.6 (2)	0.01 (1)	0.02 (3)	0.04 (3)	3.35 (9)	0.06 (2)	27.60	99.2 (2)
Hamburg	39.7 (3)	30.1 (2)	0.0 (0)	0.01 (1)	0.01 (1)	1.46 (4)	0.03 (2)	27.60	98.88 (37)
Sample	**Al**	**Mg**	**Na**	**Ca**	**K**	**Fe**	**Mn**	**B**	**Total**
Cations pfu calculated for four oxygen atoms									
Ratnapura	0.99	0.92	0.00	0.00	0.00	0.06	0.00	1.03	2.99
Hamburg	1.00 (1)	0.96 (1)	0.00	0.00	0.00	0.03	0.00	1.02	3.00

After structure refinement with full anisotropic displacement parameters the occupancy factors of the M1 and M2 sites were released yielding unity for Al on M1, and values of 0.048 and 0.018 for Fe and of 0.952 and 0.982 for Mg on the M2 position, respectively, for the Ratnapura and Hamburg sinhalite. Additional attempts of refinement assuming an iron distribution over both the M1 and M2 sites were not successful but yield negative occupancy for Fe^{2+} on the M1 position and similar occupations for the M2 site. Accordingly, only the refinement described above turns out to be successful and is, moreover, consistent with the concentration of iron as derived from the microprobe analysis. Hence, with regard to the results of the structure refinement Fe^{2+} substitutes for Mg^{2+} on the M2 position only.

Mössbauer spectroscopy

The Mössbauer spectra of both sinhalite samples at 293 K (RT) are displayed in Fig. 2. Both spectra exhibit two asymmetric absorption lines with the low velocity peak having the lower intensity and the larger line width. Therefore, these spectra have been fitted with two doublets, and the fit without any constraints yields a χ^2 of 1.62 and 0.82 for the Ratnapura and the Hamburg sinhalite, respectively. The resulting isomer shifts of 1.17 and 1.07 mm/s and quadrupole splittings of 2.78 and 2.97 mm/s, respectively, are in the range typical for high-spin Fe^{2+} in octahedral coordination at RT (Hawthorne 1988; Burns 1994; McCammon 2004) though an isomer shift of 1.07 mm/s appears to be rather small. The area ratios are 68% for doublet 1 and 32% for doublet 2. While there is no evidence for iron at a third position, e.g., in the tetrahedral site, and in an additional oxidation state, the assignment of the doublets is not clear at first glance. On one side, the asymmetry of the Mössbauer absorption lines might indicate the existence of two different iron sites whereas, on the other side, in the X-ray structure refinement using the results of the microprobe analysis iron has been located exclusively on the M2-site, and iron amounts corresponding to the intensity of doublet 2 are certainly detectable by these methods. Accordingly, the following alternative will be considered.

Based on the geometric argument that the quadrupole splitting of octahedrally coordinated high-spin Fe^{2+} generally decreases with increasing distortion of the coordination octahedron, and the isomer shift increases with increasing bond length (Burns 1994), doublet 1 may be assigned to high-spin Fe^{2+} substituting Mg^{2+} on the M2-position (mean bond length 2.09 Å), whereas doublet 2 might be assigned to the more symmetric M1-site (mean bond length 1.90 Å) substituting, thus, Al^{3+} with the lower site occupancy of 32%. In this case, however, the Al octahedron of sinhalite must expand considerably as will be demonstrated by the electronic structure calculations in the subsequent section. The charge compensation is given because the M2-site may be occupied either by trivalent cations (Al^{3+}, Cr^{3+}) or by vacancies (Hayward et al. 1994) so that it is possible that Fe^{2+} occupies the M1 position, as well.

Alternatively to this interpretation, the Mössbauer spectra may be fitted with one broadened doublet assigned to Fe^{2+} on a single site, and the asymmetry being caused by other mechanisms as, e.g., next-nearest neighbor interactions, texture, magnetic relaxation or anisotropic recoil free fractions (Gol′danski-Karyagin effect).

In order to obtain more information about the origin of the two doublets, additional measurements have been carried out at 77, 573 and 773 K. The spectra for the sinhalite from Ratnapura are displayed in Fig. 3, and the resulting hyperfine parameters are listed in Table 6. The area ratios of the absorption lines are virtually constant for all spectra, i.e., they are temperature-independent. Hence, the asymmetry is not correlated with the Gol′danski-Karyagin effect yielding a decrease of the asymmetry with decreasing temperature. Magnetic relaxation can be excluded, as well, because this should result in an increase in asymmetry with decreasing temperature.

The temperature dependence of the isomer shift (shown in Fig. 4a) is attributed to the second order Doppler shift.

Table 2 Details on data collection and structure refinement on natural sinhalites (this work) and alexandrite (Weber et al. 2007b)

	Sinhalite, Ratnapura District	Sinhalite, Hamburg, New Jersey	Alexandrite, Malishevo
Crystal data			
Chemical formula	$Al_{0.99}Mg_{0.92}Fe_{0.06}B_{1.03}O_4$	$Al_{1.00}Mg_{0.96}Fe_{0.03}B_{1,02}O_4$	$Al_{1.98}Cr_{0.02}BeO_4$
M_r	127.62	126.67	126.48
Cell setting, space group	Orthorhombic, *Pnma*	Orthorhombic, *Pnma*	Orthorhombic, *Pnma*
Temperature (K)	293 (2)	293 (2)	293 (2)
a, b, c (Å)	9.906 (1), 5.691 (1), 4.337 (1)	9.875, 5.576, 4.327	9.4082 (2), 5.4790 (2), 4.4288 (4)
V (Å^3)	244.5	242.5	228.29 (2)
Z	4	4	4
D_x (Mg m^{-3})	3.64	3.67	3.68
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	2.23	2.23	1.97
Crystal form, color	Cuboid, yellow	Cuboid, yellow	Cuboid, colorless
Crystal size (mm)	0.19 × 0.18 × 0.14	0.19 × 0.18 × 0.14	0.25 × 0.17 × 0.10
Data collection			
Diffractometer	Bruker SMART APEX	Bruker SMART APEX	Bruker SMART APEX
Data collection method	ω and ϕ scans	ω and ϕ scans	ω and ϕ scans
Absorption correction	None	None	None
No. of measured, independent and observed reflections	2,694, 331, 329	2,662, 328, 318	14,427, 1,468, 1,438
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.044	0.055	0.063
$\theta_{\max}$ (°)	28.7	28.4	54.5
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.066, 1.13	0.024, 0.067, 1.2	0.041, 0.090, 1.27
No. of reflections	331	328	1,468
No. of parameters	43	43	44
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o{}^2) + (0.0453P)^2 + 0.092P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 0.0877P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0296P)^2 + 0.1827P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	<0.001	<0.002	<0.0001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.30, −0.35	0.33, −0.34	1.01, −1.30
Extinction method	SHELXL	SHELXL	SHELXL
Extinction coefficient	2.74 (12)	0.081 (13)	0.52 (2)

This is indicated by the agreement of the experimentally determined isomer shift slope of about $-7.26(8) \times 10^{-4}\mathrm{mm/(s\,K)}$ with the hypothetical value of $-7.3 \times 10^{-4}\mathrm{mm/(s\,K)}$ obtained from the relationship

$$\frac{\mathrm{d}}{\mathrm{d}T}\delta_{\mathrm{SOD}}(T) = -\frac{3E_\gamma k_B}{2Mc^2},$$

which corresponds to the high-temperature limit of the Einstein model (Amthauer et al. 1976). The observed temperature dependence (shown in Fig. 4b) of the quadrupole splitting is predominantly caused by the thermal occupation of the low-lying empty t_{2g}-like levels, because the degeneracy of the t_{2g}-levels is removed by the distortion of the M2-octahedron.

The Mössbauer spectra of both specimens do not show any compelling evidence for Fe^{3+} in detectable concentrations although the occurrence of octahedrally coordinated high-spin Fe^{3+} with concentrations below 2 wt% of the total iron content cannot be excluded.

Electronic structure calculations

In order to shed more light on the assignment problem of the Mössbauer spectra electronic structure calculations

Table 3 Structural data on synthetic fayalite (Lottermoser et al. 2002) and meteoritic kirschsteinite (Falco and Mellini 1997)

	Fayalite	Kirschsteinite
Crystal data		
Chemical formula	Fe_2SiO_4	$Ca_{0.95}Fe_{0.61}Mn_{0.16}Mg_{0.26}SiO_{3.98}$
Cell setting, space group	Orthorhombic, *Pnma*	Orthorhombic, *Pbnm*
Temperature (K)	153 (2)	293 (2)
a (Å)	10.4597 (17)	4.877 (1)
b (Å)	6.0818 (15)	11.166 (1)
c (Å)	4.8150 (7)	6.448 (1)
V (Å^3)	306.20	351.1

have been performed based on the geometric data of the Ratnapura sinhalite at RT. With regard to the low iron content cluster model calculations are more suitable for computing the hyperfine parameters than band structure calculations relying on periodic boundary conditions. Previous experience has shown that clusters of about 150 atoms, corresponding to a sphere of radius about 5–6 Å around the central iron, are necessary to achieve size convergence with respect to the computed hyperfine parameters (Weber et al. 2007b and references therein). In case of sinhalite the calculations are based on a size converged cluster containing 198 atoms.

The calculated quadrupole splittings of Fe^{2+} at the M2-site for 77, 293, 573 and 773 K are given in Table 7. The

Table 4 Fractional atomic coordinates and isotropic temperature factors (Å^2), with standard deviations in the least significant digits in *parentheses*

Sinhalite	Occ.	*x*/*a*	*y*/*b*	*z*/*c*	E.s.d
Hamburg					
Al(1)	1	0.00000	0.00000	0.00000	0.009
Mg(1)	0.9818 (3)	0.27613 (6)	0.25000	−0.01476 (12)	0.009
Fe(1)	0.0181 (3)	0.27613 (6)	0.25000	−0.01476 (12)	0.009
O(1)	1	0.08054 (13)	0.25000	0.74093 (27)	0.009
O(2)	1	0.44421 (13)	0.25000	0.25655 (26)	0.009
O(3)	1	0.14870 (9)	0.03849 (17)	0.26483 (20)	0.009
B(1)	1	0.08720 (18)	0.25000	0.40847 (47)	0.010
Ratnapura					
Al(1)	1	0.00000	0.00000	0.00000	0.008
Mg(1)	0.952 (3)	0.27612 (6)	0.25000	−0.01526 (12)	0.008
Fe(1)	0.048 (3)	0.27612 (6)	0.25000	−0.01526 (12)	0.008
O(1)	1	0.08058 (13)	0.25000	0.74071 (27)	0.009
O(2)	1	0.44432 (13)	0.25000	0.25661 (25)	0.008
O(3)	1	0.14867 (9)	0.03849 (18)	0.26480 (19)	0.009
B(1)	1	0.08705 (17)	0.25000	0.40833 (47)	0.009

Sinhalite	U11	U22	U33	U12	U13	U23
Hamburg						
Al(1)	0.0096 (4)	0.0079 (4)	0.0083 (4)	0.0000 (2)	−.0004 (2)	−0.0009 (2)
Mg(1)	0.0091 (4)	0.0088 (4)	0.0092 (4)	0.0000	0.0004 (2)	0.0000
Fe(1)	0.0091 (4)	0.0088 (4)	0.0092 (4)	0.0000	0.0004 (2)	0.0000
O(1)	0.0107 (6)	0.0091 (6)	0.0077 (6)	0.0000	0.0001 (4)	0.0000
O(2)	0.0093 (6)	0.0087 (7)	0.0085 (6)	0.0000	−0.0001 (4)	0.0000
O(3)	0.0100 (5)	0.0087 (5)	0.0089 (5)	0.0000 (3)	−0.0006 (3)	−0.0001 (3)
B(1)	0.0083 (8)	0.0106 (9)	0.0096 (8)	0.0000	−.0005 (7)	0.0000
Ratnapura						
Al(1)	0.0088 (4)	0.0076 (4)	0.0077 (4)	0.0001 (2)	−0.0003 (2)	−0.0009 (2)
Mg(1)	0.0082 (5)	0.0082 (5)	0.0087 (4)	0.0000	0.0003 (2)	0.0000
Fe(1)	0.0082 (5)	0.0082 (5)	0.0087 (4)	0.0000	0.0003 (2)	0.0000
O(1)	0.0097 (6)	0.0086 (7)	0.0072 (6)	0.0000	0.0001 (4)	0.0000
O(2)	0.0088 (6)	0.0079 (7)	0.0079 (6)	0.0000	0.0003 (4)	0.0000
O(3)	0.0091 (5)	0.0083 (5)	0.0083 (5)	0.0008 (3)	−0.0004 (3)	−0.0002 (3)
B(1)	0.0080 (8)	0.0097 (9)	0.0086 (9)	0.0000	−0.0008 (7)	0.0000

For anisotropic atoms, the equivalent isotropic temperature factors are shown

Table 5 Bond lengths (in Å) and polyhedral distortion parameters of the coordination polyhedra of both sinhalite samples (this work), alexandrite (Weber et al. 2007b), synthetic fayalite (Lottermoser et al. 2002), and natural kirschsteinite (Falco and Mellini 1997)

Bond length	Sinhalite, Ratnapura	Sinhalite, Hamburg	Alexandrite, Malyshevo	Synthetic fayalite	Kirschsteinite
M(1)–O(1)	2 × 1.8865 (8)	2 × 1.8754 (9)	2 × 1.8645 (4)	2 × 2.117 (1)	2 × 2.213 (1)
M(1)–O(2)	2 × 1.8554 (7)	2 × 1.8511 (8)	2 × 1.8923 (5)	2 × 2.125 (1)	2 × 2.138 (1)
M(1)–O(3)	2 × 1.9814 (9)	2 × 1.9756 (8)	2 × 1.9142 (5)	2 × 2.233 (1)	2 × 2.194 (1)
⟨M(1)–O⟩	1.906	1.9007	1.890	2.152	2.182
BLD[a]	2.54	2.62	0.91	2.21	1.34
Vol. (Å^3)	8.97	8.9	8.87	12.70	13.15
OAV (°)[b]	67.41	67.59	37.48	126.88	123.69
OQE[c]	1.0202	1.0202	1.0102	1.0369	1.0350
M(2)–O(1)	2.2073 (10)	2.2018 (14)	1.9468 (7)	2.232 (1)	2.473 (1)
M(2)–O(2)	2.0412 (13)	2.0330 (13)	1.8625 (7)	2.105 (1)	2.306 (1)
M(2)–O(3)	2 × 2.0397 (10)	2 × 2.0352 (10)	2 × 1.8938 (5)	2 × 2.062 (1)	2 × 2.296 (1)
M(2)–O(3)	2 × 2.1256 (10)	2 × 2.1186 (10)	2 × 2.0156 (5)	2 × 2.290 (1)	2 × 2.419 (1)
⟨M(2)–O⟩	2.0965	2.0904	1.938	2.173	2.368
BLD[a]	2.69	2.67	2.82	8.50	2.91
Vol.	11.67	11.57	9.52	13.01	16.51
OAV[b]	125.25	124.63	46.58	122.50	168.78
OQE[c]	1.0358	1.0356	1.0141	1.0363	1.0490
T–O(1)	1.4429 (20)	1.4401 (20)	1.5707 (15)	1.624 (1)	1.624 (1)
T–O(2)	1.5845 (22)	1.5822 (22)	1.6914 (16)	1.653 (1)	1.656 (1)
T–O(3)	2 × 1.4862 (14)	2 × 1.4822 (15)	2 × 1.6426 (10)	2 × 1.636 (1)	2 × 1.638 (1)
⟨T–O⟩	1.5000	1.4966	1.637	1.647	1.639
BLD[a]	2.82	2.85	0.83		
Vol.	1.7015	1.6896	2.18	2.22	2.23
TAV[d]	55.74	56.29	105.22	36.09	33.93
TQE[e]	1.0131	1.0133	1.0227	1.0083	1.078

[a] BLD $= \frac{100}{n}\sum_{i=1}^{n}\frac{\left|(X-O)_i-(\langle X-O\rangle)\right|}{(\langle X-O\rangle)}\%$, n = amount of cation – anion bonds and X – O = cation – anion (oxygen) distance (Renner and Lehmann 1986)

[b] OAV $= \sigma^2_{\theta(\mathrm{oct})} = \sum_{i=1}^{12}(\Theta_i - 90^\circ)^2 \Big/ 11$ with Θ_i = O-M-O bonding angle (Robinson et al. 1971)

[c] OQE $= \langle\lambda_{\mathrm{oct}}\rangle = \sum_{i=1}^{6}\frac{(l_i/l_o)^2}{6}$ (Robinson et al. 1971)

[d] TAV $= \sigma^2_{\theta(\mathrm{tet})} = \sum_{i=1}^{6}(\Theta_i - 109.57^\circ)^2 \Big/ 5$ with Θ_i = O-T-O bonding angle (Robinson et al. 1971)

[e] TQE $= \langle\lambda_{\mathrm{tet}}\rangle = \sum_{i=1}^{4}\frac{(l_i/l_o)^2}{4}$ (Robinson et al. 1971)

sign of the quadrupole splitting is negative in all cases, but only the absolute value will be discussed since measurements in external magnetic fields that could determine the sign are not available. Regarding that neither spin-orbit coupling, reducing the quadrupole splitting by about 0.1 mm/s for high-spin Fe^{2+}, nor local distortions due to the substitution of Mg by Fe^{2+}, nor geometric changes with temperature have been accounted for, the agreement between experimental and theoretical values is very good. The dominating contribution to the temperature dependence arises from the thermal occupation $\sim\exp(-\delta\varepsilon_i/k_BT)$ of the two low-lying empty t_{2g}-like orbitals with $\delta\varepsilon_1 = 806\ \mathrm{cm}^{-1}$ and $\delta\varepsilon_2 = 1{,}919\ \mathrm{cm}^{-1}$. Both energy differences are about 15–20% larger than the corresponding values in fayalite (Lottermoser et al. 2002) yielding the first evidence for a local expansion of the octahedron due to the Fe^{2+} substitution.

The isomer shift at 0 K is obtained as 1.11 mm/s which may be compared with the measured value of 1.28 mm/s at 77 K. The deviation between both values is comparable with the results of earlier calculations on similar systems with low iron content (Weber et al. 2007a, b). Accordingly, this deviation may be traced back at least partially again to the fact that substitution of Mg^{2+} by Fe^{2+} may cause local expansion of the coordination octahedron that cannot be detected by the X-ray diffraction measurements due to the low iron content. The final evidence for such a local expansion and/or distortion is supplied by the calculated ligand field splittings of 13,800 and 15,250 cm^{-1} for the spin-down 3d-orbitals that are considerably larger than the

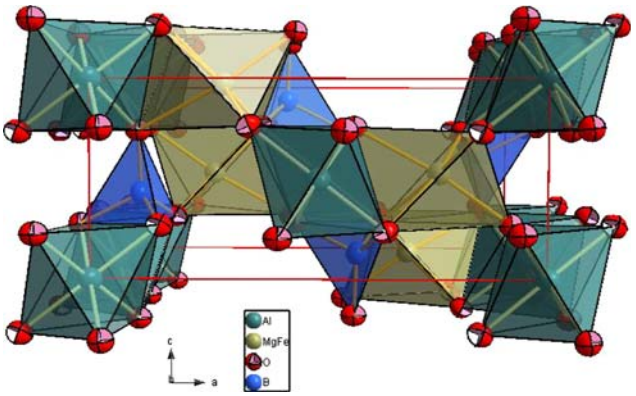

Fig. 1 Polyhedral representation of the sinhalite structure based on the data of the structure refinement of the sinhalite sample from Hamburg, New Jersey (this work)

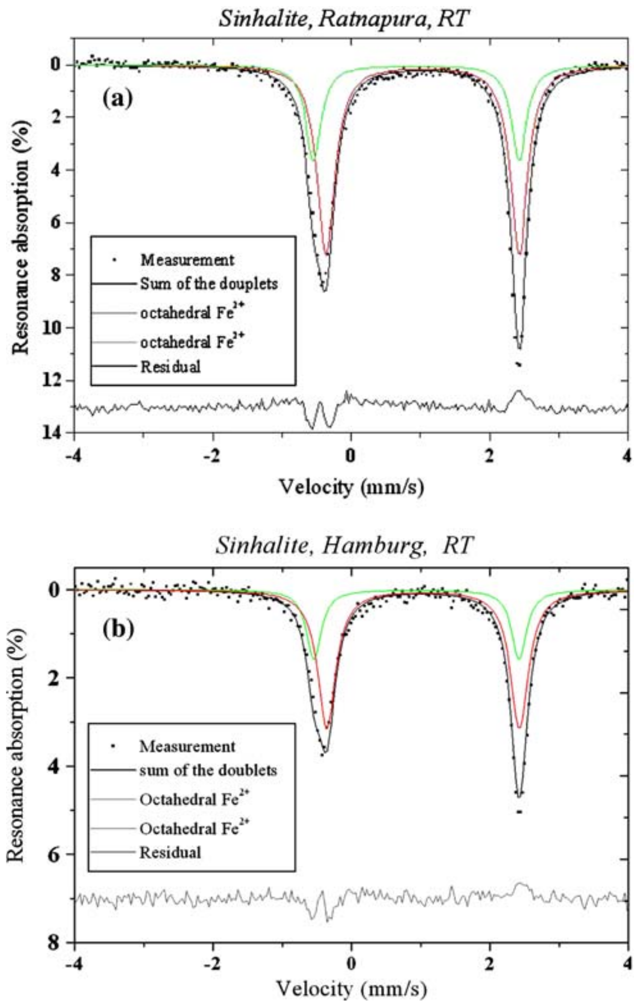

Fig. 2 Mössbauer spectra of sinhalite from Ratnapura at 293 K (**a**), and from Hamburg, New Jersey at 293 K (**b**)

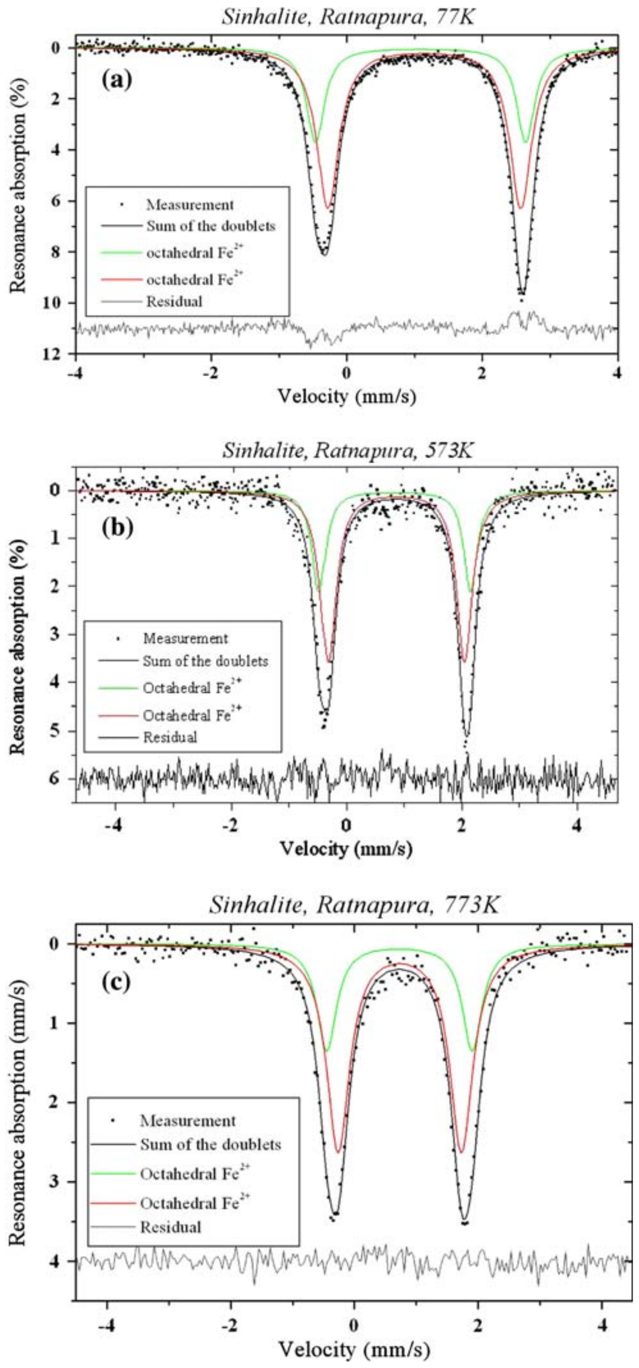

Fig. 3 Mössbauer spectra of sinhalite from Ratnapura at 77 K (**a**), 573 K (**b**) and 773 K (**c**)

measured values of about 10,000 cm^{-1} (Farrell and Newnham 1965; Hayward et al. 1994). Allowing, thus, for some expansion and distortion of the first coordination sphere of iron, the calculated value for the ligand-field splitting will decrease while that for the isomer shift will increase.

On the other hand, analogous calculations for Fe^{2+} at the M1 site yield results that are distinctly at variance with the measured hyperfine data, cf. last column of Table 7. The calculated isomer shift of 0.97 mm/s at 0 K, when corrected for the second order Doppler shift, is about

0.3 mm/s too small and the quadrupole splitting is merely two-third of the experimental value. Moreover, the ligand field splitting is more than 5 eV which is not consistent with the observed high-spin state of Fe^{2+}. Consequently, these calculations suggest that there is either no Fe^{2+} at the M1 site, at all, or iron substitution at this site must be accompanied by a considerable local expansion of the coordination octahedron, as is also consistent with the large difference in the ionic radii of 0.78 and 0.535 Å for Fe^{2+} and Al^{3+}, respectively (Shannon 1976). Although for this reason Fe^{2+} at M1 cannot conclusively be excluded on the basis of these calculations, such a possibility appears to be rather unlikely.

In summary, the following alternative is conceivable. In case of the distribution of iron over both M1 and M2 sites the second doublet may be assigned to Fe^{2+} on the substantially expanded M1 site. This is not in contradiction with the X-ray single-crystal measurements because this technique is incapable of detecting local heterogeneities caused by small amounts of iron, whereas Mössbauer spectroscopy is sensitive to the local surroundings. If, however, Fe^{2+} exclusively occupies the larger M2-site, the asymmetry may arise, e.g., from texture or from iron concentrations near the surface leading to slightly different hyperfine parameters for the M2-site. A conclusive decision is not possible on the basis of the existing data.

Comparison with other olivine structures

In summary, iron in sinhalite seems to be located at least predominantly at the M2-site. This is in accordance with the general experience that in the olivine structure larger divalent cations tend to order on M2, while smaller cations occupy the M1 site (Morozov et al. 2005). Moreover, this preference is the stronger the larger is the difference of the ionic radii of the substituting cations.

Comparison with alexandrite

The difference between the mean bond lengths $\bar{d}$ of the M1 and M2 octahedra in iron-doped alexandrite, Al_2BeO_4:Cr,Fe, $\bar{d}(M1) = 1.890\,Å$ and $\bar{d}(M2) = 1.938\,Å$ (Weber et al. 2007b), is much smaller than the respective difference in sinhalite (cf. Table 5). Because of this relatively small difference in alexandrite both trivalent and divalent iron are attributed to both Al positions though with distinct preference for the more distorted M2-site (Weber et al. 2007b), whereas Fe^{2+} in sinhalite most likely occupies almost exclusively the M2 site. The comparison of the hyperfine parameters shows that the isomer shift of Fe^{2+}(M2) in alexandrite has a value between the two isomer shift values in sinhalite. Hence, if M1 should actually be occupied by Fe^{2+}, the M1 octahedron in sinhalite is less expanded than the M2 octahedron in alexandrite. The quadrupole splitting of alexandrite is smaller than that of sinhalite so that the Fe^{2+}(M2) octahedron in alexandrite appears to be more distorted than the Fe^{2+} sites in sinhalite.

Table 6 Mössbauer parameters of natural sinhalite powders at different temperatures

Location	Temp	Dbt	IS (mm/s)	QS (mm/s)	Γ/2 (mm/s)	Area (%)
Ratnapura	77 K	1	1.26 (2)	2.85 (2)	0.20 (1)	67.6
		2	1.21 (2)	3.10 (2)	0.16 (1)	32.4
	293 K	1	1.17 (1)	2.78 (3)	0.15 (2)	68.8
		2	1.07 (3)	2.97 (7)	0.14 (1)	31.2
	573 K	1	0.96 (1)	2.37 (4)	0.17 (2)	66.4
		2	0.93 (3)	2.63 (7)	0.14 (1)	33.6
	773 K	1	0.83 (2)	1.99 (7)	0.23 (1)	69.6
		2	0.82	2.35 (7)	0.19 (1)	30.6
Hamburg	RT	1	1.16 (1)	2.78 (3)	0.16 (2)	71.0
		2	1.07	2.97 (7)	0.13 (1)	29.0

Isomer shift (*IS*) relative to α-Fe, half of half width (Γ/2), quadrupole splitting (*QS*), and relative area (*A*) of the subspectra as defined in the text

Comparison with fayalite

In fayalite, Fe_2SiO_4, the M1 and M2 octahedra have a mean bond length of 2.152 and 2.173 Å, respectively (Lottermoser et al. 2002; Hazen 1977), with a slightly more distorted M1 octahedron. The Mössbauer spectra of fayalite at RT can be fitted with two doublets with isomer shifts of 1.13 and 1.16 mm/s and quadrupole splittings of 2.72 and 2.94 mm/s for Fe^{2+} on the M1 and M2 octahedron, respectively (Lottermoser et al. 2002). The fit with two symmetric doublets reproduces the asymmetry of the two absorption lines at RT. Already at moderately elevated temperatures around 150°C and above the high velocity absorption peak exhibits a distinct splitting into two lines supplying, thus, clear evidence for the presence of two different iron sites. Whereas at RT the shape of the Mössbauer spectrum of sinhalite is similar to the fayalite spectrum at RT consisting of two asymmetric lines, as well, the high temperature spectra of sinhalite up to 500°C do not exhibit any splitting as observed in fayalite. However, the absence of an additional splitting in the sinhalite spectra does not supply sufficient evidence for the exclusive preference of iron for the M2 site, but only that in sinhalite the larger Fe^{2+} (compared to Al^{3+}) occupies predominantly the larger M2 site, whereas in fayalite Fe^{2+} occupies both the very similar M1 and M2 sites. Accordingly, there is no clear evidence for the occupancy of the M1 site by

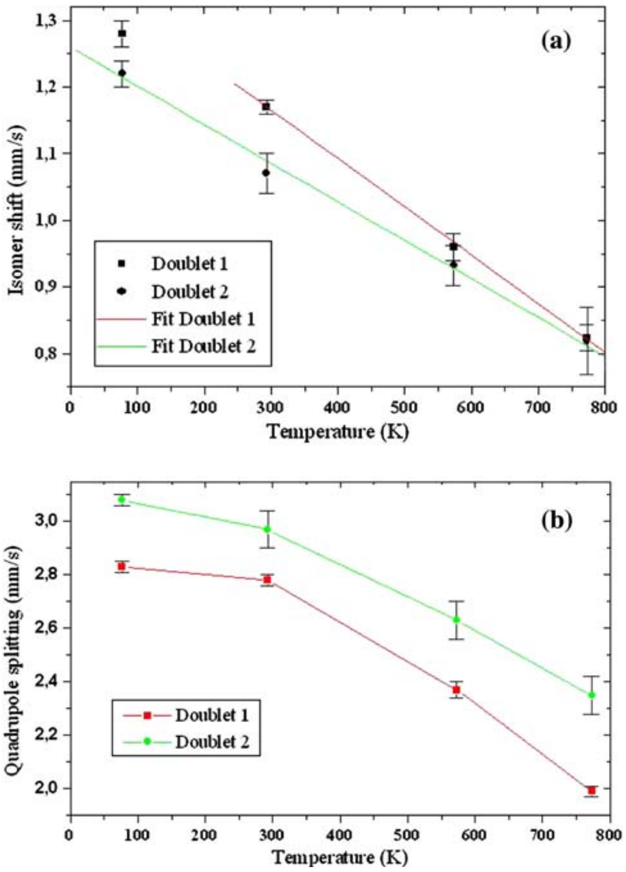

Fig. 4 Temperature dependence of the isomer shift (**a**) and of the quadrupole splitting (**b**). In **a** the *lines* represent the result of a fitting procedure whereas in **b** the *lines* just connect the measured data

Fe^{2+} in sinhalite so that the origin of the asymmetry of the absorption lines of the sinhalite Mössbauer spectra remains unclear.

Comparison with kirschsteinite

Table 7 Calculated temperature-dependent quadrupole splitting (QS) for a 198-atom cluster of the Ratnapura sinhalite

	Fe^{2+}(M2)				Fe^{2+}(M1)
Temperature (K)	77	293	573	773	293
QS_{calc} (mm/s)	−2.92	−2.88	−2.33	−1.97	+2.06
QS_{exp} (mm/s)	2.85	2.78	2.37	1.99	(2.97)

In kirschsteinite, $CaFeSiO_4$, the M1 and M2 sites are very different with mean bond lengths of 2.182 and 2.368 Å, respectively (Falco and Millini 1997), and Fe^{2+} occupies exclusively the smaller M1 octahedron. The RT Mössbauer spectrum consists of two symmetric absorption lines with smaller line width and without any additional splitting, which was interpreted as indication for the exclusive occupancy of the M1 site by Fe^{2+}. Therefore, the spectrum has been fitted with a single symmetric doublet with a quadrupole splitting of 2.18 mm/s (Eibschütz and Ganiel 1967) which is considerably smaller than all the other measured quadrupole splittings of Fe^{2+} in minerals with olivine structure, and may be related to the strong tetragonal compression of the M1 octahedron. The sinhalite Mössbauer spectra exhibit no indication for such a doublet, and this is not expected because such a great compression of the M1 octahedron is not present in the sinhalite structure. In summary, kirschsteinite is an example for the exclusive occupation of Fe^{2+} on the M1 site confirming the trend that larger divalent cations prefer the M2 site while the smaller ones prefer the M1 site. While in sinhalite Fe^{2+} is the larger cation, Fe^{2+} is the smaller cation in kirschsteinite.

Conclusion

The oxidation state and the site occupancy of iron in two natural sinhalites were determined in order to characterize the crystal chemistry of sinhalite. The iron in both samples is divalent. Whereas the structure refinement and electronic structure calculations uniformly show that, most likely, Fe^{2+} occupies the larger M2-site only, Mössbauer spectroscopy yields an asymmetric doublet supplying some evidence for a distribution of iron over both sites. The comparison of the crystal chemistry and Mössbauer hyperfine parameters of the sinhalite samples with those of fayalite, alexandrite, and kirschsteinite yields that, in general, the preference of the larger cation on the M2 site in the olivine structure seems to be the stronger the larger are the differences in the mean bond lengths within the M1 and M2 octahedra.

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