

Cordierite I: The coordination of Fe²⁺

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ABSTRACT

The incorporation of Fe²⁺ was investigated in four natural cordierite samples. ⁵⁷Fe Mössbauer, single-crystal UV-VIS optical absorption, and X-ray absorption spectroscopies, as well as X-ray single-crystal diffraction were used. Mössbauer, optical, and XAS spectroscopy show that Fe²⁺ is incorporated on two different structural sites in two Mg-rich samples. Mössbauer measurements give the best quantitative measure of the amounts of Fe²⁺, but the optical spectra are the most sensitive for determinations at low concentrations and at high-bulk Fe²⁺ concentrations in cordierite. The spectroscopic data are most consistent with small amounts of Fe²⁺ (i.e., 0.02 of Fe²⁺ per formula unit) being located on a tetrahedral site rather than in the center (or off center) of the six-membered tetrahedral rings or in channel cavities. X-ray single-crystal refinements on two Mg-rich cordierites show a very small excess electron density on T₁1 and not in the channels. A third refinement on a slightly more iron-rich sample shows, in contrast, no excess electron density on T₁1. We interpret these data as indicating that small amounts of Fe²⁺ (0.01 to 0.02 atoms per formula unit) replace tetrahedral Al₁1 in cordierite, where charge balance is achieved by placing Na in the center of the six-membered rings. This substitution is consistent with the known chemistry of natural cordierites and with simple structural energetics. The identification and assignment of small amounts of Fe²⁺ on T₁1 requires spectroscopic determination or careful X-ray single-crystal refinements and cannot be achieved from composition data and structural formula calculations.

INTRODUCTION

Cordierite has the ideal formula (Mg,Fe)₂Al₄Si₅O₁₈·x(H₂O, CO₂). The composition of natural cordierites can be considerably more complicated and a more complete formula has been proposed as [^{Ch}(Na,K,Fe²⁺,Fe³⁺)₀₋₁^{V1}(Mg,Fe²⁺,Mn²⁺,Li)₂^{IV}(Si,Al,Be,Fe³⁺)₉O₁₈·x^{Ch}(H₂O,CO₂,Ar...)] (Schreyer 1985). One of the complications concerns the role of Fe²⁺. It is well known that most Fe²⁺ occupies the octahedral M-site (Byström 1942). However, several spectroscopic studies have shown that some Fe²⁺ can occupy an additional structural site. Some investigators argued that this additional Fe²⁺ is located in channel cavities or in the six-membered rings that are parallel to the *c* axis (Duncan and Johnston 1974; Goldman et al. 1977). Other investigators proposed that the Fe²⁺ replaces Si⁴⁺ or Al³⁺ in one of the tetrahedral sites (Vance and Price 1984). The experimental measurements are open to different interpretations and the arguments are difficult to test.

We investigated natural cordierites using several different spectroscopic methods, some of which have not been used in

the past, and X-ray single-crystal diffraction. One question is how Fe²⁺ is incorporated in the cordierite structure. The question of Fe²⁺ in cordierite is pertinent, because the distribution of Fe²⁺ and Mg between cordierite and coexisting ferromagnesian minerals, such as garnet, is of petrological relevance. In addition, from a crystal chemical point of view, the presence of Fe²⁺ in coordination sites in silicates smaller than sixfold, especially those occupied predominantly by Si⁴⁺ or Al³⁺, is rather unusual and thus deserves investigation.

EXPERIMENTAL METHODS

Sample description

About 40 rock and mineral samples from a wide variety of petrologic environments were initially collected. Cordierite separates were made from all samples and their room-temperature ⁵⁷Fe-Mössbauer spectra recorded. X-ray powder diffraction and examination under a binocular were used to ascertain the purity of the samples, which is better than 99% cordierite. Four samples were chosen for detailed study here. A description of the four cordierites is given in Table 1. Their compositions determined by electron-microprobe analysis are given in Table 2.

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TABLE 1. Cordierite samples

Sample label	Rock type	Mineral	Location assemblage	P-T estimate	Fe/(Fe + Mg)*
42/IA†	Silica-deficient Granulite	Crd-Ged-Sill-Co-Plag-Sa-Sp	Tamil Nadu (Kiranur), India	750 ± 40 °C 7 ± 0.4 Kb	0.09
C005	Migmatitic Schist	Crd-Bt-Qtz-Plag-Gt	Sundsvall, Sweden	?	0.26
DA-1	Metamorphic ?	?	Rhodesia	?	0.08
TUB-1	Granitic	?	Dolni Bory, Czech Republic	?	0.84
Sekaninaite	Pegmatite				

* Fe = Fe²⁺ + Mn²⁺.

† Lal et al. (1984).

TABLE 2. Chemical composition of cordierites

Sample	TUB-1	C005	DA-1	42/IA
SiO ₂	45.34	48.93	49.66	49.41
TiO ₂	0.02	0.01	0.01	0.01
Al ₂ O ₃	32.11	33.11	33.34	33.57
MgO	2.23	10.66	12.73	12.69
FeO	16.89	4.78	2.21	2.50
MnO	0.79	0.09	0.02	0.03
CaO	0.05	0.01	0.01	0.01
K ₂ O	0.00	0.00	0.01	0.00
Na ₂ O	0.56	0.12	0.34	0.35
Total	97.99	97.71	98.33	98.57
Cations				
Si	4.91	4.99	4.98	4.95
Al	4.10	3.98	3.94	3.97
Fe ²⁺	—	—	0.02	0.02
Σ (tet.)	9.01	8.97	8.94	8.94
Mg	0.36	1.62	1.90	1.90
Fe ²⁺	1.53	0.41	0.17	0.19
Mn ²⁺	0.07	0.01	0.00	0.00
Σ (oct.)	1.96	2.04	2.07	2.09
Na	0.12	0.03	0.07	0.07
K	0.00	0.00	0.00	0.00
Σ (channel)	0.12	0.03	0.07	0.07

Notes: Calculated on the basis of 18 O atoms per anhydrous formula unit and using the Mössbauer results.

⁵⁷Fe Mössbauer spectroscopy

The four cordierites were measured at room temperature and 77 K with a nominal 50 mC ⁵⁷Co/Rh source. Ground cordierite powders were pressed together with corn starch into pellets of diameter 12.0 mm with approximately 5 mg Fe²⁺/cm². Mirror-image spectra were collected on a 512 multichannel analyzer and then folded. The spectra were fitted with the program MÖSALZ. The low-temperature measurements were made with an Oxford cryostat with the absorber held at approximately 77 K. Such measurements permit a better resolution of the Fe²⁺ doublets and a more accurate estimate of their relative areas due to the closer similarities of the recoil-free fractions at lower temperatures. Either one or two symmetric doublets were fit to the spectra.

Single-crystal optical absorption spectroscopy

Selected fragments of cordierite crystals from Dolni Bory (TUB-1) and Kiranur (42/IA) were oriented parallel to (100), (010), and/or (001) and ground and polished on both sides to a thickness of 0.10–0.35 mm. These orientations allow polarized spectra with E||a, E||b, and E||c to be measured and contain all Fe²⁺ spin-allowed absorption bands.

Polarized spectra were measured at room temperature in the spectral range 30 000–1500 cm⁻¹ using a single-beam microscope spectrometer model UMSP 80 from Zeiss (30 000–12 000 cm⁻¹) and a FTIR Bruker spectrometer model IFS 66 (13 000–1500 cm⁻¹). For the Zeiss spectrometer, a 10× Ultrafluars served as the objective and condenser. The measuring diameter was 32 μm and the spectral-slit width and step width were both 1 nm. Polarized radiation was achieved by using a Glan-Thompson-type calcite polarizer. Experimental details are described by Langer (1988). With the FTIR-Bruker spectrometer, equipped with an IR-microscope and polarizer, the polarized spectra were obtained with a measuring diameter of 90 μm and a spectral resolution of 2 cm⁻¹. Spectra were averaged over at least 100 scans, with the reference spectra being measured in air.

Spectra were deconvoluted using a program provided by Bruker (OPUS 2.2 1995), which is based on the Levenberg-Marquardt algorithm. Straight baselines with fixed slopes and Gaussian band shapes were used in the first step of fitting. In the second step, the slopes of the baselines and the shapes of the bands were left unconstrained. In spite of this, band shapes were still found to be Gaussian in shape or close to it (i.e., <30% Lorenzian). Different deconvolutions using the same procedure gave differences in band positions of less than 0.4%.

X-ray absorption spectroscopy

All four samples were investigated at the ESRF in Grenoble, France. An olivine standard from Ivrea Verbano, Italy of composition Fo₉₁Fa₉ was also measured. The samples were finely ground and sedimented on a Millipore membrane by a sonication technique. A layer thickness was adopted so as to obtain the best absorption contrast at the Fe-K edge. The Fe-K edge XANES spectra were collected in transmission mode at GILDA-CRG operated at 6 GeV. A dynamically sagittally-focussing monochromator with Si(311) crystals (Pascarelli et al. 1996) was used. Harmonics were eliminated by a pair of grazing-incidence mirrors. The incident and the transmitted flux were measured using argon-filled ionization chambers. The XANES data were recorded at an interval of 0.1 eV. Energy calibration was achieved with a Fe-foil standard supplied by the Gilda beamline. The position of the first inflection point was taken at 7112.0 eV.

X-ray single-crystal diffraction

Cordierites from Kiranur, India, (42/IA) and Rhodesia (DA-1) were studied because both are compositionally simple and showed two well-resolved Fe²⁺ doublets in their Mössbauer spectra. A cordierite from Sundsvall, Sweden, (C005) was cho-

sen for a “reference” refinement, because it showed only one well-defined Fe²⁺ doublet. Single-crystals were mounted on glass fibers and diffraction data were collected at room temperature with an ENRAF NONIUS CAD4 X-ray single-crystal diffractometer with graphite monochromated MoK α X-radiation at 55 kV and 32 mA. Cell dimensions were refined from the angular settings of 22 reflections with $20^\circ < \theta < 22^\circ$ yielding orthorhombic symmetry. Diffraction data were collected up to $\theta = 40^\circ$. Experimental details are in Table 3. Data reduction, including background and Lorenz polarization correction, was carried out with the SDP program system (Enraf Nonius 1983). An empirical absorption correction using the ψ -scan technique was applied. Systematic absences confirmed the space group *Cccm*. Structure solution via direct methods and refinement were performed with neutral-atom scattering factors and the programs SHELXS-97 and SHELXL-97 (Sheldrick 1997). Mg and Fe were assigned to the octahedral M-site and the corresponding populations were allowed to vary. Vacancies were refined on the partially occupied channel sites CH0(Na), CH1(O,C), and CH2(O). Subsequently, population factors of the tetrahedral sites were alternately allowed to vary. These refinements, weighted $1/\sigma^2$, yielded significant vacancy concentrations on all tetrahedral sites for the 42/IA and DA-1 cordierites. For them ca. 2.0(1)% vacancies on Al₂6, Si₂3, Si₂1, and Si₁6 (notation modified from Cohen et al. 1977, such that T = Al or Si) were determined, whereas on Al₁1 vacancies were significantly below 1%. The refined vacancy concentrations are artifacts of the refinement procedure related to errors associated in estimating correctly the true valence of Si and Al (neutral atoms were assumed) and by the bonding electrons between Si, Al, and O. To reduce the influence of valence electrons on the refined populations, a weighting factor of $\exp[5 \cdot (\sin\theta/\lambda)^2]/\sigma^2$ was empirically determined. Increasing the weighting of high-angle reflections will, in general, give more reliable population estimates though with increased standard deviations. CH0, CH1, and CH2 populations and their corresponding displacement parameters were fixed in the high-angle refinements, because high-angle diffraction data are not sensitive to partially occupied channel sites. As in the $1/\sigma^2$ refinement routine, tetrahedral vacancies were alternately allowed to vary.

TABLE 3. Data collection and refinement parameters

Sample	DA-1	42/IA	C005
Crystal size (mm ³)	0.10 × 0.20 × 0.08	0.20 × 0.10 × 0.15	0.20 × 0.18 × 0.10
No. reflections measured	3274	3271	3271
Unique reflections > 2 σ (<i>I</i>)	1758	1861	1858
cell dimensions (Å)			
<i>a</i>	17.072(1)	17.069(1)	17.101(1)
<i>b</i>	9.727(1)	9.725(1)	9.736(1)
<i>c</i>	9.351(1)	9.347(1)	9.331(1)
<i>R</i> (int) after empirical absorption correction	1.35%	1.30%	1.35%
<i>R</i> (σ)	2.16%	1.98%	2.06%
<i>R</i> 1, <i>F</i> _o > 4 σ (<i>F</i> _c)	1.95%	1.91%	1.84%
<i>wR</i> 2 (on <i>F</i> ²)	4.88%	5.01%	4.59%

Notes: $R1 = (\sum |F_o| - |F_c|) / (\sum |F_o|)$ and $wR2 = \sqrt{(\sum (F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)}$.

h, *k*, *l* limits $-1 \leq h \leq 30$, $-1 \leq k \leq 17$, $-1 \leq l \leq 16$.

Space group is *Cccm* (No. 66).

Number of least squares fitting parameters is 80.

RESULTS

⁵⁷Fe Mössbauer spectra

Cordierites C005 from Sundsvall, Sweden, and TUB-1 from Dolni Bory, the Czech Republic show only one Fe²⁺ doublet (Figs. 1a and 1b) with an isomer shift value of 1.34 ± 0.01 mm/s that can be assigned to Fe²⁺ in octahedral coordination. Close examination of the iron-rich Dolni Bory spectrum (Fig. 1b) shows a slight misfit in the high-velocity line, which probably results from not including a very small unobserved overlapped peak. This aspect will be discussed further below. The spectra of the cordierites from Kiranur (42/IA) and Rhodesia (DA-1) must be fit with two doublets (Figs. 1c and 1d). The best fits were obtained when the low-velocity peak of the weaker overlapped component of the smaller Fe²⁺ doublet was at a lower velocity than that of the more intense peak. This model was found to be statistically better (see also Vance and Price 1984) than one where the smaller peak has a slightly higher velocity. Hyperfine parameters are listed in Table 4.

Single-crystal optical absorption spectra

In the optical spectra of cordierites TUB-1 and 42/IA (Fig. 2), Fe²⁺ ions produce a doublet consisting of two overlapping bands appearing in the α -polarization orientation (*Ellc*) between 11 000 and 8000 cm⁻¹, and a strong, single band near 10 000 cm⁻¹ in the γ -polarized and β -polarized spectra. The doublet consists of two bands that are situated at about 10 000 and 8000 cm⁻¹ in the Dolni Bory cordierite and they are shifted 100–300 cm⁻¹ to higher energy in the Kiranur sample. The half width of these bands is about 2000 cm⁻¹. The integral intensity of the doublet in the Dolni Bory spectrum is greater than that in the Kiranur cordierite and is proportional to the Fe-content, whereas the intensity of the γ - and β -polarized band at 10 000 cm⁻¹ is larger in the Kiranur sample. The fitted spectroscopic parameters are summarized in Table 5. The accuracy of these values depends on the curve-fitting procedures adopted, i.e., the positions of the band maxima. Errors are estimated to be not greater than 1%.

In the visible region a very broad band centered at about 20 000 cm⁻¹, which is assigned to Fe²⁺-Fe³⁺ charge transfer

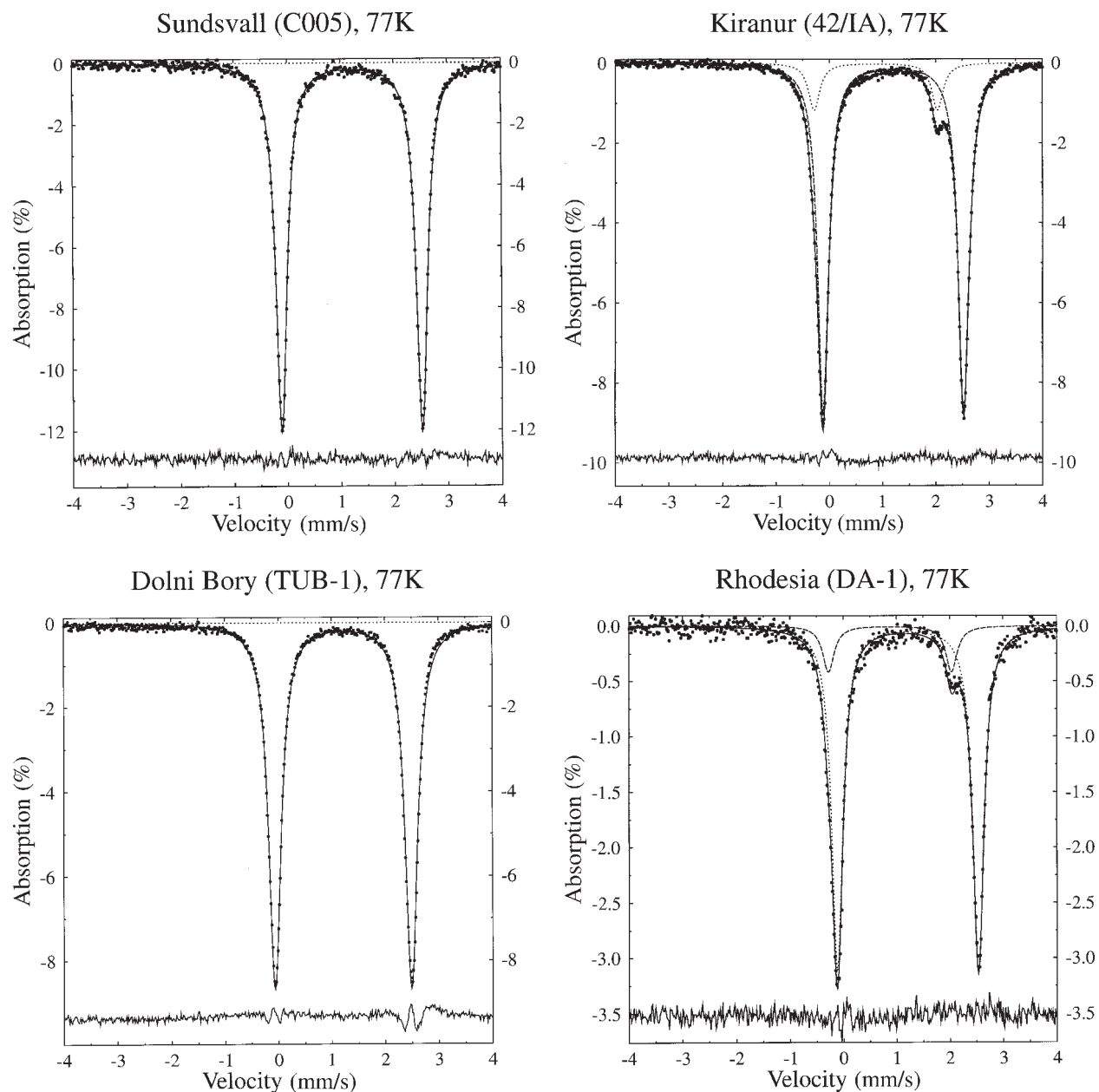


FIGURE 1. (a–d) ⁵⁷Fe Mössbauer spectra of the four cordierites at 77 K.

TABLE 4. ⁵⁷Fe Mössbauer parameters at 77 K

Sample	No. of Fe ²⁺ doublets	I. S.* (mm/s)	Q. S. (mm/s)	Half width (mm/s)	Absorption (%)
C005	1	1.34	2.63	0.13	100.0
TUB-1	1	1.34	2.56	0.14	100.0
42/IA	2	1.00	2.32	0.13	12.3
		1.34	2.64	0.12	87.7
DA-1	2	1.01	2.31	0.13	12.2
		1.34	2.65	0.13	87.8

* Relative to Fe metal.

TABLE 5. Parameters of Fe²⁺ optical absorption bands

Sample	Polarization	Band position (cm ⁻¹)	Integral intensity (cm ⁻²)	Half width (cm ⁻¹)
TUB-1	α	8020	28760	1550
		10010	49930	2370
		10020	15100	2080
	γ	10010	26220	2190
42/IA	α	8340	3150	1460
		10160	7280	2190
		10740	24500	2450

(Goldman et al. 1977; Vance and Price 1984), appears in the β -polarized and γ -polarized spectra. Sharp, intense bands related to the internal stretching bands of molecular H₂O are present in the IR and NIR between 3000 and 8000 cm⁻¹. They are superimposed on a relatively weak and broad band, whose position and polarization dependence cannot be defined accurately due to strong deformation caused by the H₂O stretching bands.

X-ray absorption spectra

X-ray absorption spectroscopy has been used to probe the oxidation and structural state of Fe in minerals and glasses (e.g., Waychunas et al. 1983, 1986; Calas and Petiau 1983; Brown et al. 1988; Henderson et al. 1995). However, a study of the Fe oxidation state and its site distribution in cordierite is not an easy task. This is due to both the low-total amount of Fe normally present and to the extremely low percentage of Fe that may be found on an additional site beside the octahedral one.

The raw Fe-K edge XANES spectra of the cordierites and a reference olivine were treated prior to examination by subtracting the pre-edge background and normalizing the absorption coefficient on the high-energy side of the curve. The normalized spectra are shown in Figure 3. Since the four cordierites contain only, or predominantly, Fe²⁺ in sixfold coordination,

the spectra are virtually identical in the edge and post-edge regions, while a careful analysis of the pre-edge region showed interesting differences.

An analysis of the pre-edge region was performed by least-squares fitting of Gaussian peaks to the pre-edge spectral envelope. The best fits for all samples were obtained by using three Gaussian components, in agreement with the Fe²⁺ pre-edge analysis performed by Calas and Petiau (1983). The fits are shown in Figure 4a-e and Table 6 lists the energies of the XANES features of the four cordierites and olivine.

X-ray single-crystal diffraction

Atomic coordinates and displacement parameters from the high-angle refinements of cordierites DA-1, 42/IA and C005 are given in Tables 7, 8, and 9¹. Cordierite DA-1 has 0.14(1) Fe pfu in octahedral coordination, 0.09 Na pfu in the center of the six-membered tetrahedral rings, and 0.12 CO₂ and 0.20 H₂O

¹For a copy of Table 9, document item AM-00-049, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site (<http://www.minsocam.org>).

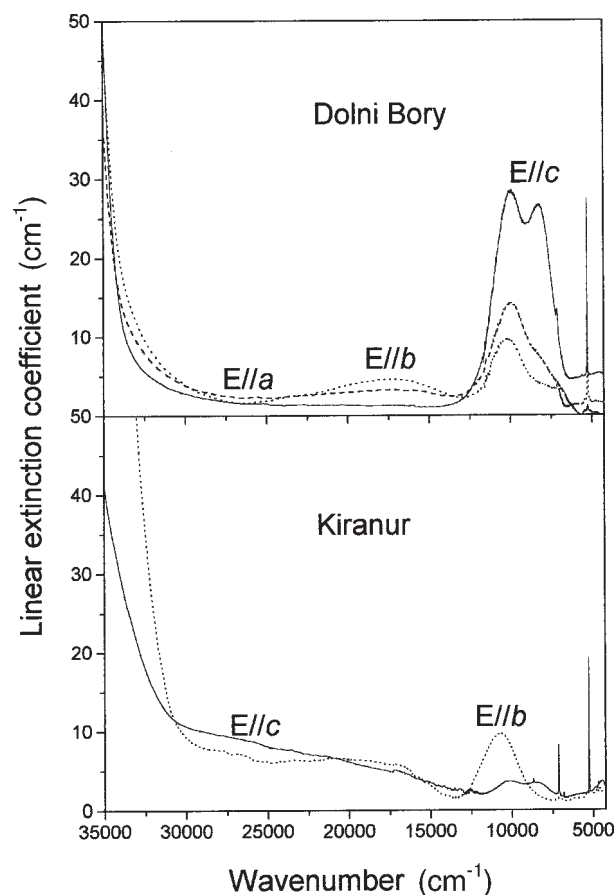


FIGURE 2. Room-temperature polarized optical-absorption spectra of the Dolni Bory (TUB-1) and the Kiranur (42/IA) cordierites. a, b, and c give the polarization directions.

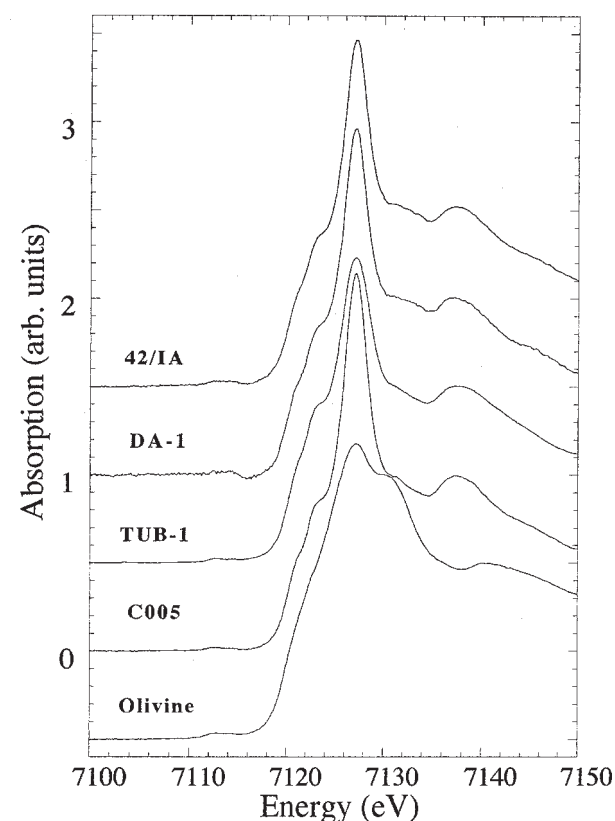


FIGURE 3. XAS spectra of the four cordierites and olivine at room temperature.

pfu in the cage between adjacent six-membered rings. Cordierite 42/IA has 0.16(1) Fe pfu in octahedral coordination, and 0.07 Na pfu, 0.14 CO₂, and 0.17 H₂O pfu in the channel cavities. Both crystals (DA-1 and 42/IA) are chemically and structurally very similar. In contrast, cordierite C005 has 0.40(1) Fe pfu in octahedral coordination, and 0.07 Na pfu, 0.08 CO₂, and 0.12 H₂O pfu in the channel cavity. The CO₂ molecules are aligned parallel to the *a* axis and show librational disorder within (001) as shown by Armbruster (1985b). The mean M-O distances for the first two cordierites are 2.107 Å (42/IA) and 2.108 Å (DA-1); mean tetrahedral Si₂1, Si₁6, Si₂3, Al₂6, and Al₁1 distances are 1.615, 1.629, 1.616, 1.740, 1.756 Å (42/IA) and 1.615, 1.628, 1.616, 1.741, 1.757 Å (DA-1), respectively. The site-population refinements on tetrahedral sites (Table 10) in these two cordierites show a slightly increased scattering

power on Al₁1 compared to Al₂6, Si₂3, Si₁6, and Si₂1. This is not the case for cordierite C005.

DISCUSSION

The spectroscopic measurements show that Fe²⁺ can be located on different structural sites in cordierite. This possibility has been known for some time now (Duncan and Johnston 1974; Goldman et al. 1977; Vance and Price 1984). The Mössbauer spectra indicate that small amounts of Fe²⁺, about 10% of the total iron in the Kiranur and Rhodesia samples, is not located on the octahedral site. The isomer shift value associated with this Fe²⁺ doublet is about 0.87 mm/s at 298 K and is within the range of reported values for Fe²⁺ in tetrahedral coordination (about 0.6 to 1.15 mm/s), but this range is large and not unique (Hawthorne 1988). If Fe²⁺ occupies the site in the center of the six-membered ring, it would have nearly a sixfold planar coordination at *z* = 0 and possibly neighboring oxygen atoms of H₂O molecules above and below. If it is bonded to a single H₂O molecule, it could be slightly displaced from the center of the ring. Another possibility was given by Duncan and Johnson (1974), who argued for a bipyramidal coordination of Fe²⁺ along the inner wall of a channel cavity. The hyperfine parameters for such coordinations around Fe²⁺ in silicates are not known. However, the bonding in all such cases should be weaker than in tetrahedral coordination. One should expect a large change in the hyperfine parameters with changing temperature. This is not observed. Vance and Price (1984) calculated the Debye temperatures for both Fe²⁺ Mössbauer doublets based on a series of spectra obtained between 4.2 to 290 K. The effective Debye temperatures for Fe²⁺ on the octahedral site and the second Fe²⁺ site were about 350 K and 275 K, respectively. The value for the latter is more typical for a substitutional site than in a loosely bonded six-member ring. Hence, they proposed that this Fe²⁺ substitutes for either Si⁴⁺ or Al³⁺. The second weak doublet was not observed or is extremely weak in the Dolni Bory cordierite. However, its absence can be explained if one takes into account the high Fe(oct)/Fe(non-oct) ratio of the samples and the strong overlap of the doublets.

Goldman et al. (1977) assigned the doublet in the α -polarized optical spectra (Fig. 2) to spin-allowed transitions between split low-symmetry ⁵T₂- and ⁵E-states of Fe²⁺ ions on the octahedral site. This was based on a good correlation between total Fe-content and the doublet band intensities. Our data are consistent with this assignment (Table 5), which explains both the

TABLE 6. Energies (eV) of the XANES features in cordierite and olivine

Sample	Pre-edge	1 st Shoulder	2 nd Shoulder	Edge
C005	7112.4 7113.4 7114.3	7120.5	7123.2	7127.0
TUB-1	7112.4 7113.3 7114.3	7120.3	7123.2	7127.0
42/IA	7112.5 7113.6 7114.4	7120.6	7123.3	7127.0
DA-1	7112.7, 7113.7, 7114.4	7120.7	7123.0	7127.0
Olivine*	7112.4, 7113.5, 7114.2	7119.7	7122.8	7126.9

* Fo₉₁Fa₉.

TABLE 7A. Atomic positional parameters and B_{eq} (Å²) values for cordierite DA-1

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	B_{eq}
Si ₂ 1	0.30746(2)	0.07779(3)	0	0.382(3)
Si ₁ 6	0	0	1/4	0.425(4)
Si ₂ 3	0.36489(2)	0.23727(3)	1/2	0.388(3)
Al ₂ 6	0.05090(2)	0.19210(4)	0	0.411(4)
Al ₁ 1	1/4	1/4	0.25021(4)	0.488(5)
MgM*	0.16264(2)	0	1/4	0.515(7)
O ₁ 6	0.06225(3)	0.08387(6)	0.15115(7)	0.635(6)
O ₁ 1	0.25272(4)	0.10278(6)	0.14116(7)	0.648(6)
O ₁ 3	0.32679(4)	0.31010(7)	0.64158(7)	0.684(6)
O ₂ 1	0.37770(6)	0.1845(1)	0	0.97(1)
O ₂ 6	0.45699(5)	0.2475(1)	1/2	0.99(1)
O ₂ 3	0.33548(6)	-0.0793(1)	0	0.93(1)
CH0†	1/2	0	1/2	3.49
CH1‡	1/2	0	1/4	6.26
CH2§	0.440	0	1/4	5.74

* 0.930(5) Mg + 0.070(5) Fe.

† 0.09 Na.

‡ 0.32 O + C.

§ 0.13 O.

TABLE 7B. Atomic displacement parameters for cordierite DA-1

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si ₂ 1	0.0050(1)	0.0039(1)	0.0056(1)	-0.00013(7)	0	0
Si ₁ 6	0.0051(1)	0.0059(1)	0.0051(1)	0	0	0
Si ₂ 3	0.0047(1)	0.0044(1)	0.0056(1)	-0.00059(7)	0	0
Al ₂ 6	0.0045(1)	0.0052(1)	0.0059(1)	-0.00040(9)	0	0
Al ₁ 1	0.0072(1)	0.0052(1)	0.0061(2)	-0.00169(9)	0	0
MgM	0.0056(2)	0.0059(2)	0.0081(2)	0	0	0.0000(1)
O ₁ 6	0.0068(2)	0.0091(2)	0.0082(2)	-0.0010(1)	-0.0001(1)	0.0031(2)
O ₁ 1	0.0104(2)	0.0067(2)	0.0075(2)	-0.0005(1)	0.0036(2)	-0.0007(1)
O ₁ 3	0.0090(2)	0.0088(2)	0.0082(2)	-0.0013(1)	0.0020(2)	-0.0029(2)
O ₂ 1	0.0097(3)	0.0100(3)	0.0171(4)	-0.0063(2)	0	0
O ₂ 6	0.0050(3)	0.0158(3)	0.0166(4)	-0.0025(2)	0	0
O ₂ 3	0.0133(3)	0.0048(3)	0.0173(4)	0.0029(2)	0	0
CH0	0.04118	0.02585	0.06546	0.00249	0	0
CH1	0.09435	0.09373	0.04963	0	0	0
CH2	0.04386	0.13710	0.03721	0	0	-0.01927

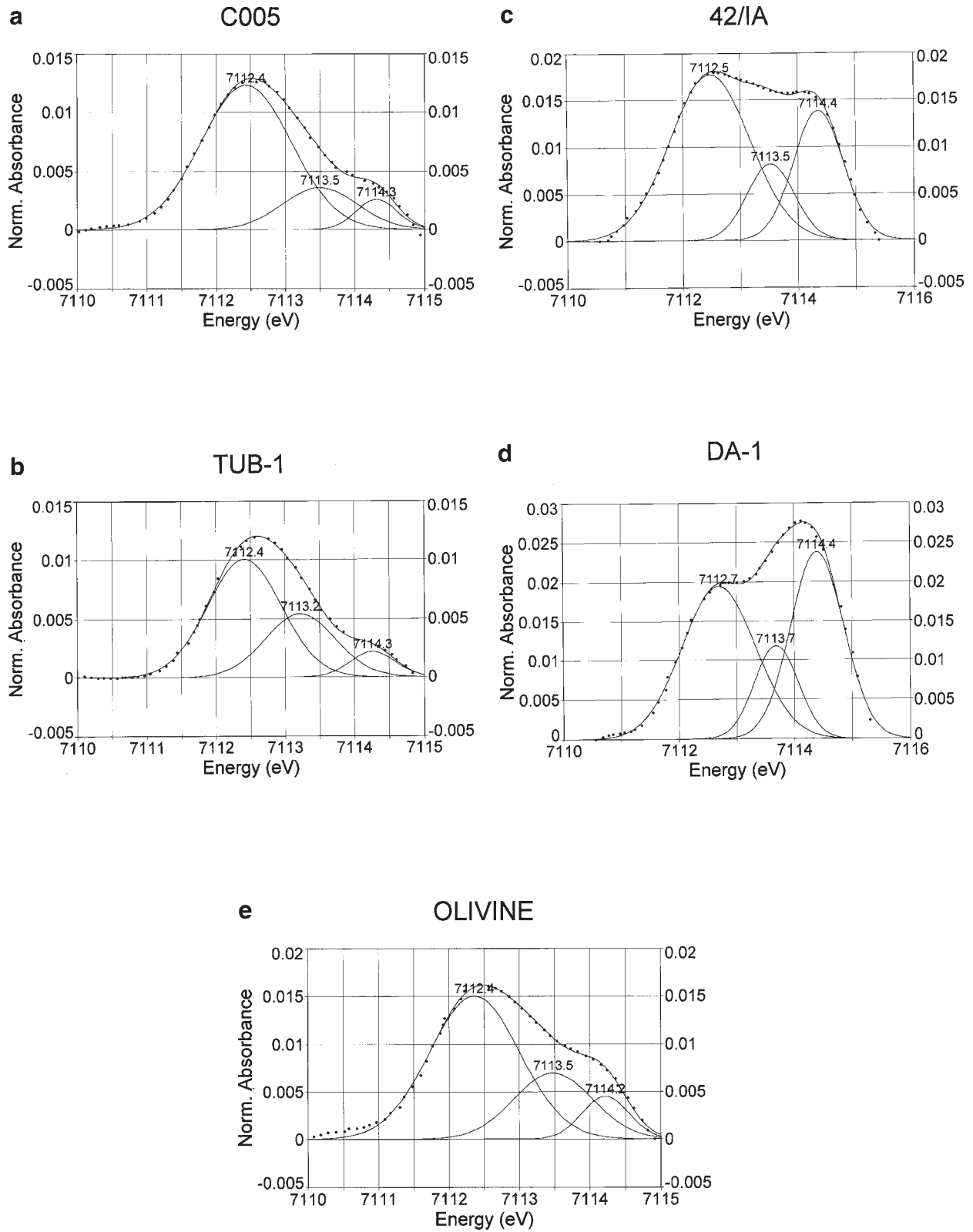


FIGURE 4. (a–e) Fe²⁺ pre-edge spectra of the four cordierites and olivine between 7110 and 7115–7116 eV.

band energies and the polarization of the doublet as well. An interpretation of the single, strong band in the γ -polarized and β -polarized spectra is more problematic. Its intensity does not correlate with Fe content, nor with the intensity of the doublet in the α -polarized spectrum. Thus, this band originates from Fe²⁺ ions on a site other than the octahedron. Goldman et al. (1977) attributed this band, together with a minor spectral feature at ≈ 4500 cm⁻¹, to a channel position in the center of the six-membered ring. The optical spectra alone could perhaps be interpreted as indicating that Fe²⁺ is in an off-centered ring site or an interstitial site. However, neither the X-ray refinement data nor the Mössbauer spectra support this. Vance and Price (1984) interpreted their optical spectra as indicating that Fe²⁺ replaces Al³⁺ or Si⁴⁺. The polarized electronic absorption spectra presented in Figure 2 show that the weak and broad absorption band at 4000–5000 cm⁻¹ is so distorted by the internal stretching bands of H₂O that it is difficult to interpret. If this spectral feature is caused by Fe²⁺, we cannot be sure of whether it is composed of a single band or a weak doublet consisting of two closely overlapped bands related to Fe²⁺ on T₁1. The large splitting between it and the band at 10 000 cm⁻¹ could be due to the nature of the small and distorted site. The mineral osumilite, in which tetrahedral Fe²⁺ is present in significant concentrations (Hesse and Seifert 1982), shows a similar optical absorption spectrum to cordierite. Here there is also a large

energy splitting between Fe²⁺ tetrahedral bands. Here, we note simply that both the polarization and the very high molar absorptivity of the band at 10 000 cm⁻¹ in the γ -polarized and β -polarized spectra are not what one would expect for Fe²⁺ located in a planar centrosymmetric site of the six-membered ring. Therefore, it is difficult to argue in favor of an channel site (center or off center) against a tetrahedral one based on the number, position and, especially, polarization of the absorption bands caused by non-octahedral Fe²⁺ ions. Both the very high molar absorptivity and polarization of the 10 000 cm⁻¹ band in the γ -polarized and β -polarized spectra are consistent with Fe²⁺ on T₁1. Using the integral intensities of the optical absorption bands attributed to non-octahedral Fe²⁺ in the Kiranur and Dolni Bory cordierites (Table 5), and the Fe concentration from the Mössbauer measurements in the former sample (Table 4), we estimate the amount of Fe²⁺ ions on the non-octahedral position in the Dolni Bory cordierite to be about 0.01 pfu.

The energy values of the XANES features (Table 6) for all cordierites are similar to those of olivine, hence confirming the dominant presence of octahedral Fe²⁺. Figures 4a–4e show that, although the pre-edge features of the spectra of cordierite and olivine can be fitted by three Gaussians with the same energies, there are differences in the relative intensities of the fit components. The relative intensities of the Gaussians used to fit the pre-edge features of cordierites C005 and TUB-1 are very similar to those of olivine, whereas in the cordierites from Kiranur (42/IA) and Rhodesia (DA-1) we observe a strong enhancement of the Gaussian at about 7114.3 eV. Moreover, we see that the total pre-edge intensity of these two cordierites is slightly higher than that in C005 and TUB-1. These differences could suggest the presence of a small percentage of Fe atoms on a different coordination state in 42/IA and DA-1. An unambiguous identification of this site is difficult due to the dominant presence of the sixfold coordinated Fe²⁺. Fe²⁺ on the tetrahedral site does not have an inversion center and this may produce a prepeak enhancement (Calas and Petiau 1983; Waychunas et al. 1983) with respect to sixfold coordinated Fe²⁺. Hence, we consider T₁1 as a more probable site for Fe²⁺ compared to a site in the six-membered ring, where it should be in a rather symmetric local geometry.

The X-ray diffraction data can give direct information on the site occupations provided that special care is used in the data collection and refinement procedures. Electron microprobe analysis yielded ca. 0.2 Fe²⁺ pfu for samples 42/IA and DA-1

TABLE 8a. Atomic positional parameters and B_{eq} (Å²) values for cordierite 42/IA

Atom	x/a	y/b	z/c	B_{eq}
Si ₂ 1	0.30750(2)	0.07774(3)	0	0.367(3)
Si ₁ 6	0	0	1/4	0.413(4)
Si ₂ 3	0.36487(2)	0.23734(3)	1/2	0.383(3)
Al ₂ 6	0.05089(2)	0.19218(4)	0	0.396(3)
Al ₁ 1	1/4	1/4	0.25025(4)	0.470(4)
MgM*	0.16262(2)	0	1/4	0.515(6)
O ₆	0.06224(3)	0.08396(6)	0.15096(6)	0.628(6)
O ₁	0.25279(3)	0.10285(5)	0.14133(6)	0.649(5)
O ₃	0.32678(3)	0.31029(6)	0.64167(6)	0.666(6)
O ₂ 1	0.37769(5)	0.1844(1)	0	0.925(9)
O ₂ 6	0.45701(5)	0.2475(1)	1/2	0.96(1)
O ₂ 3	0.33551(5)	-0.07960(9)	0	0.90(1)
CH0†	1/2	0	1/2	2.62
CH1‡	1/2	0	1/4	5.68#
CH2§	0.446	0	1/4	7.64#

* 0.918(5) Mg + 0.082(5) Fe.

† 0.07 Na.

‡ 0.31 O + C.

§ 0.14 O.

These atoms were refined isotropically.

TABLE 8b. Atomic displacement parameters for cordierite 42/IA

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si ₂ 1	0.00472(9)	0.00409(9)	0.0052(1)	-0.00028(7)	0	0
Si ₁ 6	0.0047(1)	0.0063(1)	0.0047(1)	0	0	0
Si ₂ 3	0.00417(9)	0.0050(1)	0.0054(1)	-0.00073(7)	0	0
Al ₂ 6	0.0042(1)	0.0055(1)	0.0053(1)	-0.00066(8)	0	0
Al ₁ 1	0.0069(1)	0.0053(1)	0.0057(1)	-0.00143(8)	0	0
MgM	0.0055(2)	0.0061(2)	0.0079(2)	0	0	0.00004(9)
O ₆	0.0067(2)	0.0098(2)	0.0074(2)	-0.0013(1)	0.0001(1)	0.0036(1)
O ₁	0.0103(2)	0.0072(2)	0.0072(2)	-0.0007(1)	0.0033(1)	-0.0009(1)
O ₃	0.0084(2)	0.0093(2)	0.0076(2)	-0.0014(1)	0.0017(1)	-0.0023(2)
O ₂ 1	0.0097(3)	0.0102(3)	0.0153(3)	-0.0056(2)	0	0
O ₂ 6	0.0050(2)	0.0159(3)	0.0158(3)	-0.0020(2)	0	0
O ₂ 3	0.0132(3)	0.0049(2)	0.0161(3)	0.0029(2)	0	0
CH0	0.02378	0.02869	0.04720	0.00059	0	0

and Mössbauer spectroscopy shows that ca. 10% of the total Fe²⁺ (0.02 Fe²⁺ pfu) is probably in tetrahedral coordination. The standard deviation for a refined Fe-site population from high-angle diffraction data is about 0.01 Fe²⁺ pfu. Thus, routine X-ray site-population refinements are not sufficient to locate such low Fe concentrations. However, the separately refined scattering powers on the various tetrahedral sites (Table 10) suggest that T₁1 has ca. 0.1–0.2 electrons more than expected for complete occupation by Al. This estimate is at the edge of 3σ significance, but there is a clear trend in both cordierites for increased scattering power at this site alone. Considering that Fe²⁺ has twice as many electrons as Al³⁺, one may conclude that the T₁1 site in 42/IA and DA-1 is occupied by 1–2% Fe²⁺. Taking into account the site multiplicity of T₁1, this leads to 0.02–0.04 Fe²⁺ pfu in tetrahedral coordination. This amount is in agreement with the concentration of tetrahedral Fe²⁺ determined by Mössbauer spectroscopy. In addition, the refinement results on cordierite C005 reinforce this interpretation. In this sample we did not detect any excess electron density on T₁1 and this is consistent with the Mössbauer spectrum which does not show a second Fe²⁺ doublet.

Little to no Fe³⁺ is observable in the Mössbauer spectra of our cordierites. Parkin et al. (1977) reported the appearance of a weak doublet with an isomer shift of about 0.39 mm/s occurring in Mössbauer spectra recorded at 77 K, that they assigned to Fe³⁺ in tetrahedral coordination in cordierites from Dolni Bory and Madagascar. Surprisingly, their spectra at 298 K showed no such Fe³⁺ doublet. The spectra of the samples studied herein show little difference between 298 K and 77 K. Parkin et al. (1977) discussed this unusual temperature behavior of the Fe³⁺ doublet and possible reasons for it, for which we have no explanation. Based on our Mössbauer measurements we consider their spectra and estimates of Fe³⁺ contents in cordierite to be suspect. Some older chemical analyses made on cordierite using wet-chemical methods or determinations of structural formulae based on simple stoichiometric considerations have given Fe₂O₃ contents greater than 1 wt% (e.g., see Schreyer 1965 and Leake 1960 for a review and discussion). We consider such high values also suspect. The amount of Fe³⁺ in nearly all natural cordierites is low, probably being less than 2.0% of the total iron. In the Mg-rich cordierites the upper limit of Fe³⁺ on T₁1 would be 0.004 cations per formula unit. The intensity of the charge transfer (CT) Fe²⁺-Fe³⁺ band near 18 000 cm⁻¹ observed in the electronic absorption spectra of cordierite (Smith and Strens 1976; Goldman et al. 1977) varies greatly even in samples with similar total Fe amounts indicating considerable variations in Fe³⁺ content. The molar absorptivity of the CT band is 2 to 3 orders of magnitude larger than those of the dd-bands. Therefore, we can conclude that the amount of Fe³⁺ in all cordierites studied is comparatively low and in agreement with the Mössbauer measurements. The polarization of this CT band (β:γ = 2.7) is constant and coincides well with the predicted value for a tetrahedral-octahedral intervalence transition. With most Fe²⁺ allocated to the octahedra, this interaction requires Fe³⁺ on the T₁1-tetrahedra. Such an interpretation was suggested by Smith and Strens (1976) and is supported by independent EPR data (Hedgecock and Chakravarty 1966). A cavity site for Fe³⁺ (Goldman et al. 1977) is unlikely to cause

TABLE 10. Site occupancies from site population refinements for the tetrahedral sites

Sample	DA-1	42/IA	C005
Al ₁ 1	1.008(4)	1.004(4)	0.997(4)
Al ₂ 6	0.996(4)	0.992(4)	0.996(4)
Si ₂ 3	0.992(4)	0.998(4)	0.998(4)
Si ₁ 6	0.988(6)	0.990(6)	0.997(5)
Si ₂ 1	0.992(4)	0.994(4)	0.991(4)

the observed CT band, because CT-interactions only take place between ions in edge- or face-shared polyhedra (e.g., Burns 1993).

Fe²⁺ occurs seldom in tetrahedral coordination in silicates where it replaces Al³⁺ or Si⁴⁺. However, Fe²⁺ does replace tetrahedral Al in the double-ring silicate osumilite (Hesse and Seifert 1982) and the structurally related chayesite (Alietti et al. 1994), both of which are similar structurally to cordierite. Synthetic double-ring silicates with mixed octahedral and tetrahedral Fe²⁺-Mg occupation also exist (Nguyen et al. 1980). Merlino (1969) described the structure of tuhualite (Na,K)Fe²⁺Fe³⁺Si₆O₁₅, which is related to a double ring structure and here Fe³⁺ occupies an octahedral site edge shared to Fe²⁺-tetrahedra. The T₁1 site in cordierite is large and distorted (Gibbs 1966; Armbruster 1985a). From simple crystal-chemical grounds, Fe²⁺ should be energetically preferred in this site compared to the other tetrahedral sites in cordierite. Armbruster (1985a) showed that the T₁1-O distance decreases with increasing ionic radius (Fe content) on the octahedral M-site. This suggests that Mg-rich cordierites could be more favorable structurally for the incorporation of a large cation on T₁1 (i.e., Fe²⁺).

The simplest substitution that can account for tetrahedral Fe²⁺ is:



This substitution is consistent with the known chemistry and structure of cordierite. It accounts, in part, for the greater than 11 cations per-formula-unit observed in many cordierite analyses, Al³⁺ cation totals slightly less than 4.0 pfu, and divalent cation totals greater than 2.0. However, substitution (1) cannot account for all Na⁺ in cordierite, because its cation totals per-formula-unit are greater than the number of tetrahedral Fe²⁺ pfu. Other substitution mechanisms must also be operating to account for the compositional variations observed in natural cordierites (Schreyer 1985). We give a new modified general structural formula for natural cordierites as [{}^{Ch}(Na, K)₀₋₁ {}^{VI}(Mg, Fe²⁺, Mn²⁺, Li)₂ {}^{IV}(Si, Al, Be, Fe³⁺, Fe²⁺)₉ O₁₈ X {}^{Ch}(H₂O, CO₂, Ar...)]. Only Na⁺, and to a lesser extent K⁺, are allocated inside the six-membered rings. The channel cavities contain only molecules. Note that Fe²⁺ can replace Al³⁺ even in mineral assemblages that are saturated with Al₂O₃ as in the case of the cordierite from Kiranur. Thus, its incorporation is not due to some unusual bulk composition of the parent rock.

One consequence of this investigation is that microprobe analyses of cordierite are not of sufficient quality to determine quantitative structural formulas, if Fe²⁺ on T₁1 is present. Difficulties also exist in detecting Li and Be (see Černý et al. 1997). The question of tetrahedral Fe²⁺ pertains to the study of Fe²⁺-Mg

partitioning between cordierite and other ferromagnesian minerals. Microprobe analyses are, in general, of insufficient precision to be able to assign small amounts of Fe²⁺ to the T₁1 site. Mössbauer or other spectroscopic measurements are required.

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