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Cordierite III: the site occupation and concentration of Fe³⁺

Received: 3 May 2000 / Accepted: 16 August 2000

Abstract Cordierite has the ideal formula $(\text{Mg,Fe})_2\text{-Al}_4\text{Si}_5\text{O}_{18}\cdot x(\text{H}_2\text{O,CO}_2)$, but it must contain some Fe^{3+} to account for its blue color and strong pleochroism. The site occupation and concentration of Fe^{3+} in two Mg-rich natural cordierites have been investigated by EPR and ^{57}Fe Mössbauer spectroscopy. In addition, powder IR spectroscopy, X-ray diffraction, and TEM examination were used to characterize the samples. Single-crystal and powder EPR spectra indicate that Fe^{3+} is located on T₁1 in natural cordierites and not in the channels. The amount in Mg-rich cordierites is very small with an upper limit set by Mössbauer spectroscopy giving less than 0.004 cations per formula unit (pfu). Fe^{3+} in cordierite can, therefore, be considered insignificant for most petrologic calculations. Heat-treating cordierite in air at 1,000 °C for 2 days causes an oxidation and/or loss of Fe^{2+} on T₁1, together with an expulsion of Na^+ from the channels, whereas heating at the Fe–FeO buffer produces little Fe^{3+} in cordierite. Heating at 1,000 °C removes all class I H₂O, but small amounts of class II H₂O remain as shown by the IR measurements. No evidence for channel Fe^{2+} or Fe^{3+} in the heat-treated samples was found. The blue color in cordierite arises from a broad absorption band (E//b and weaker with E//a) around 18,000 cm⁻¹ originating from charge-transfer between Fe^{2+} in the octahedron and Fe^{3+} in the edge-shared T₁1 tetrahedron. It therefore appears that all natural cordierites contain some tetrahedral

Fe^{3+} . The brown color of samples heated in air may be due to the formation of very small amounts of submicroscopic magnetite and possibly hematite. These inclusions in cordierite can only be identified through TEM study.

Introduction

Although cordierite has the ideal formula $(\text{Mg,Fe})_2\text{Al}_4\text{-Si}_5\text{O}_{18}\cdot x(\text{H}_2\text{O,CO}_2)$, it has been inferred that all natural samples contain some Fe^{3+} . Directionally dependent charge transfer between it and Fe^{2+} causes the blue color and strong pleochroism that are characteristic of cordierite (Faye et al. 1968; Smith and Strens 1976; Goldman et al. 1977). However, the structural location of Fe^{3+} is uncertain, as is the amount which can be incorporated. Some investigators have argued that Fe^{3+} is located in the channel cavities that are parallel to the *c*-axis (Goldman et al. 1977), while an early single-crystal EPR investigation proposed that it is located on the T₁1 site (Hedgecock and Chakravartty 1966). The early optical absorption studies also suggested Fe^{3+} on T₁1 (Faye et al. 1968; Smith and Strens 1976), although they could not show this directly. In addition, a ^{57}Fe Mössbauer study proposed that Fe^{3+} occurs in octahedral coordination (Pollak 1976).

The amounts of Fe_2O_3 reported for natural cordierites have mostly been determined from older wet-chemical analyses and they vary considerably, with some samples having no Fe_2O_3 , while others have as much as 3–4 wt% Fe_2O_3 (Leake 1960; Schreyer 1965; Smith and Strens 1976). Such amounts have not been confirmed by recent analyses using ^{57}Fe Mössbauer spectroscopy and it is doubtful that wet-chemical analyses are quantitative in this regard (Geiger et al. 2000; Khomenko et al., unpublished). It is difficult to determine by microprobe analysis and stoichiometric considerations the amount of Fe^{3+} , because of the presence of light elements (Li, Be) and deviations from nominal stoichiometry often

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shown by natural cordierites. There has been a small amount of experimental work done on synthetic Mg-cordierite regarding the incorporation of Fe^{3+} , which was shown to be limited (Abs-Wurmbach et al. 1989). However, the concentrations and site occupation of Fe^{3+} in natural cordierite are poorly understood.

As a continuation of our mineralogical and crystal-chemical investigation of natural cordierites (i.e., Geiger et al. 2000; Kolesov and Geiger 2000; Khomenko et al., unpublished), we have addressed these questions. Understanding the site partitioning and concentration of Fe^{3+} in cordierite are important in petrologic investigations of oxygen fugacities, F_{O_2} 's, occurring during metamorphism and for studies of iron–magnesium partitioning between cordierite and other ferromagnesian phases. Important crystal-chemical questions concern the structural location of Fe^{3+} and its charge-transfer interaction with Fe^{2+} . It is also not clear whether cations with charges greater than one can be incorporated in the channel cavities of cordierite.

Experimental methods

Sample description and heating experiments

Two Mg-rich cordierites were chosen for investigation. They are from Kiranur, India (42/IA), and an unknown locality from Zimbabwe (DA-1 – labeled Rhodesia in Geiger et al. 2000). A sample (TUB-1) from Dolni Bory, the Czech Republic, was also chosen initially, but it proved to be too iron rich to obtain interpretable EPR spectra and was not studied further. The sample from Kiranur is a large aggregate crystal mass and the sample from Zimbabwe was available in aggregate form and also as large single crystals. A description of the two samples is given in Table 1 of Geiger et al. (2000).

Prior to the different measurements to be described below, an optically clean Kiranur sample was ground and sized to produce a grain fraction between 0.335 and 0.125 mm. About 300 mg were heated at 1 atm and 1,000 °C in air for about 48 h and a second fraction at the same temperature and for the same time period at an oxygen fugacity fixed by the Fe–FeO buffer. This was achieved by holding the sample in a ceramic crucible in a vertical tube furnace under a predetermined flow of CO/CO_2 .

^{57}Fe Mössbauer spectroscopy

The two cordierites studied (DA-1 and 42I/A) were measured previously at 293 and 77 K with a nominal 50 mC $^{57}\text{Co}/\text{Rh}$ source (Geiger et al. 2000). The 77 K measurements herein were made as

in that study, except that a new source was used in which the ^{57}Co is embedded in a Cr-metal matrix. The unheated Kiranur and Zimbabwe samples were therefore remeasured, and the two heat-treated Kiranur samples were measured for the first time. For the determination of the amounts of Fe^{3+} it is assumed that the recoil-free fractions of Fe are the same on all sites.

Powder IR spectroscopy

The powder IR spectra of the different Kiranur cordierites were measured in the wavenumber region of the H_2O stretching vibrations ($4,000\text{--}3,400\text{ cm}^{-1}$) at room temperature using the KBr method with a Bruker IR spectrometer. 2.0 mg of ground cordierite were combined with 200 mg of KBr and then pressed under vacuum to a pellet. The spectra were recorded with 512 scans and at a resolution of 2 cm^{-1} .

Microprobe analysis

Microprobe analyses were made on the untreated and heated Kiranur samples using the same setup as in Geiger et al. (2000). Between 7 and 10 random spot analyses were made on two different crystallites of all samples and averaged to give the final composition.

X-ray powder diffraction

The untreated and two heat-treated cordierites from Kiranur were characterized by X-ray powder diffraction methods using an automated Siemens D5000 diffractometer. The powder patterns were recorded with a Si standard (NBS) between 10 and $100^\circ 2\theta$ using $\text{Cu K}\alpha$ radiation. Cell refinements were undertaken with more than 40 reflections using least-squares methods.

Transmission electron microscopy

For TEM examination a Philips EM 400 T microscope was used. It is operated at 100 kV and equipped with a rotation-tilt holder (360° and $\pm 60^\circ$). Both the natural and the in-air-heated Kiranur cordierite were finely ground separately under ethanol absolute in an agate mortar and a drop of this suspension was deposited on a grid covered with a perforated amorphous carbon film and allowed to dry. Crystallites thin enough for bright-field (BF) and dark-field (DF) diffraction contrast imaging could be obtained in this way. An energy-dispersive X-ray system (KeveX 7000) allowed qualitative chemical analyses of inclusions.

EPR spectroscopy

The spectra were recorded at room temperature with a Varian X-band spectrometer and 100 kHz modulation. The external magnetic field, \mathbf{B} , could be varied between 0 and 1 T and was monitored by a Gauss meter (Bruker B-H 15). The resonance frequency was about

Table 1 ^{57}Fe Mössbauer parameters at 77 K

Sample	No. of doublets	I.S. ^a (mm/s)	Q.S. (mm/s)	Γ (mm/s)	Absorption (%)
DA-1	Two Fe^{2+} doublets	1.33	2.62	0.13	88.3
		1.01	2.26	0.13	11.7
42/IA (unheated)	Two Fe^{2+} doublets	1.34	2.64	0.13	89.6
		1.02	2.29	0.13	10.4
42/IA (Fe–FeO)	Two Fe^{2+} doublets	1.33	2.62	0.13	93.4
		1.06	2.25	0.15	6.6
42/IA (air)	One Fe^{2+} doublet	1.33	2.62	0.13	80.3
	One Fe^{3+} doublet	0.35	1.25	0.46	19.7

^a Relative to Fe metal

9.51 GHz and was determined precisely by a frequency counter (HP 5340). The powder and single-crystal spectra of cordierite DA-1 from Zimbabwe were recorded, as were the powder spectra of the three different Kiranur samples.

In order to measure the EPR angular dependence of cordierite DA-1, a single crystal was oriented by the X-ray precession method and mounted on a quartz rod. That way the crystal could be rotated around one of the crystallographic *a*, *b* or *c* axes, and the angular dependence of the EPR could be measured with the applied magnetic field, **B**, in (100), (010), or (001). The accuracy of the crystal orientation was better than 0.50°.

Results

Heating experiments

The untreated, sized Kiranur cordierite sample is of a light sky-blue color. After heating in air at 1,000 °C for 48 h it turned into a cloudy brownish color to the eye. Under the binocular, however, the cores of many crystallites appeared to have a dark gray-bluish tint, but this is difficult to quantify. The surface and along cracks of grains appeared to be especially brownish or oxidized. A very small number of grains appeared to be heavily oxidized or converted to another phase assemblage. They were removed by hand picking. The sample heated at the Fe–FeO buffer remained bluish, but appeared to be a little lighter in color than the original unheated sample. The heated samples were not measurably magnetic using a hand magnet.

⁵⁷Fe Mössbauer spectra

The fitted 77 K Mössbauer spectra of the natural Zimbabwe and Kiranur cordierites and the Kiranur samples after heating in air and at the Fe–FeO buffer are shown in Fig. 1a–d. The Kiranur sample heated in air (Fig. 1d) has a spectrum where the smaller Fe²⁺ doublet is not present or very weak, but instead a doublet centered around 0.6 mm/s with a high-energy line at about 1.1 mm/s appears (Fig. 2). Its lower energy partner is hidden under the low-energy line of the octahedral Fe²⁺ doublet. It is not possible to fit a narrow doublet to this small feature because of its broad and weak nature, but it is assigned to Fe³⁺ because of its low isomer shift value and the EPR results (see below). The spectra of the natural unheated samples must be fitted with two Fe²⁺ doublets (Geiger et al. 2000). The Kiranur cordierite heated at the Fe–FeO buffer (Fig. 1c) has a spectrum similar to the unheated sample, except that the intensity of the smaller Fe²⁺ doublet is somewhat smaller. The fitted hyperfine parameters at 77 K of the four samples are listed in Table 1. Our observations agree well with those of Vance and Price (1984). As discussed in Geiger et al. (2000), we are of the opinion that the Mössbauer measurements of the Fe³⁺ contents of the natural cordierites of Parkin et al. (1977) are spurious and their conclusions are, therefore, not considered further herein.

Powder IR spectroscopy

The powder IR spectra of the Kiranur samples are shown in the wavenumber region from 4,000 to 2,500 cm⁻¹ (Fig. 3). The background was corrected for H₂O occurring in the KBr. The untreated sample shows three major H₂O stretching modes and two weaker ones. Their assignment is based on the classification proposed by Kolesov and Geiger (2000). The band at 3,709 cm⁻¹ corresponds to the asymmetric stretch of class I – type III H₂O and the band at 3,691 cm⁻¹ to the asymmetric stretch of class I – type I or type II H₂O. The broad band at 3,632 cm⁻¹ belongs to the asymmetric stretch of class II H₂O and that at 3,578 cm⁻¹ is its symmetric stretch partner. The very weak shoulder at about 3,600 cm⁻¹ is the symmetric stretch of class I H₂O. The two heated samples, in comparison, show a complete loss of class I H₂O, but some class II H₂O remains after heating to 1,000 °C. There appears to be slightly more class II H₂O in the sample heated at the Fe–FeO buffer compared to that heated in air based on a comparison of the peak intensities. The weak bands around 2,900 cm⁻¹ are due to hydrocarbons probably arising from surface contamination. The incorporation and degassing of CO₂ are not considered herein.

Powder X-ray diffraction

The X-ray patterns show only cordierite peaks. At the sensitivity level of our measurements, we did not detect any hematite/magnetite or other phases in the sample heated in air. The unit-cell dimensions of the unheated Kiranur sample are *a* = 17.082 (0.005) Å, *b* = 9.736 (0.005) Å, and *c* = 9.354 (0.005) Å and the unit-cell volume is 1,555.7 (1.2) Å³. The cordierite heated at the Fe–FeO buffer showed *a* = 17.102 (0.007) Å, *b* = 9.738 (0.006) Å, and *c* = 9.355 (0.005) Å with the volume being 1,558.1 (1.4) Å³. The sample heated in air showed *a* = 17.107 (0.006) Å, *b* = 9.736 (0.006) Å, and *c* = 9.357 (0.006) Å with the volume being 1,558.6 (1.5) Å³. A measurement of the ordering state (Δ) in the three samples using the equation (Miyashiro 1957):

$$\Delta = 2\theta_{131} - \frac{2\theta_{511} + 2\theta_{421}}{2}$$

gives identical values of 0.21 for all three cordierites and indicates a highly ordered distribution of Al and Si on the tetrahedral sites.

There are no measurable structural differences between the different samples.

Microprobe analysis

The results of the microprobe analyses are given in Table 2. Heating causes a loss of H₂O/CO₂ (by difference of the analyzed totals) and Na₂O, with the sample heated in air losing slightly more of the latter. There are no other major compositional differences between the two heated cordierites.

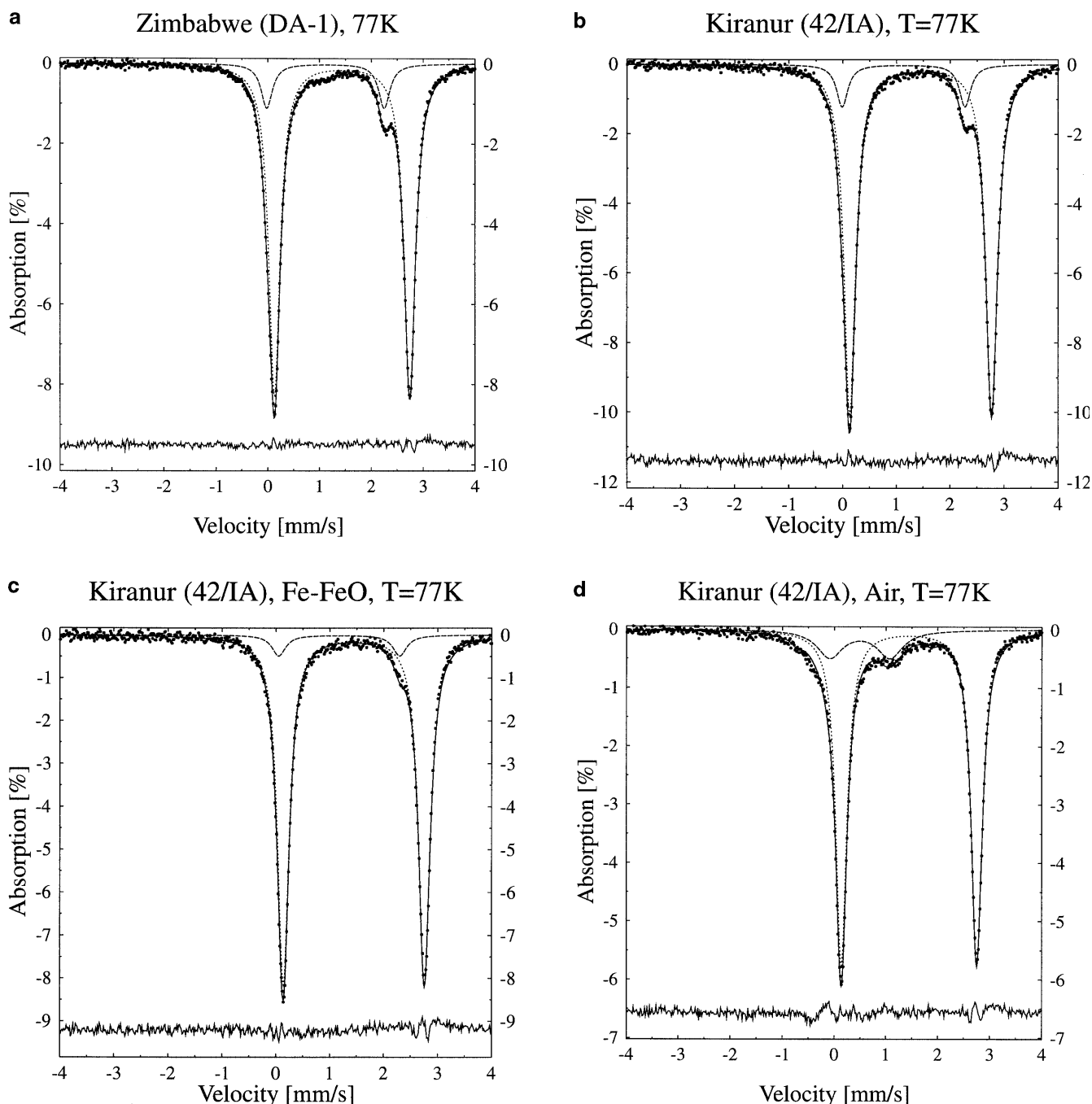


Fig. 1a–d Fitted ^{57}Fe Mössbauer spectra of the four cordierites at 77 K: **a** natural cordierite DA-1, **b** natural cordierite 42/IA, **c** sample 42/IA heated at the Fe–FeO buffer, and **d** sample 42/IA heated in air

Transmission electron microscopy

Both the natural and the in-air-heated Kiranur cordierite were examined. About 100 crystallites were examined in both cases. In the natural sample relatively few inclusions, most of which had a very small size (<300 Å), could be observed. The few particles enclosed in cordierite were too small to be identifiable by diffraction experiments and they are generally not found in dislocations and cracks. Qualitative EDS analysis

showed that they also did not appear to be exclusively iron rich. This was not the case for the sample heated at 1,000 °C in air. Here, in a few cases, domains, which look like pseudomorph twins, were detected. Moreover, two types of inclusions that occur in small amounts, but greater than the natural sample, were found. The first type is relatively large in size (up to 0.5 μm) and is heterogeneously intergrown with cordierite. In $[01\bar{1}]$ diffraction patterns these inclusions show satellite reflections (q forms an angle of about 5° with $g = 111$, that is, almost parallel with it) with a modulation length of about 23.5 Å. More work is required to identify this type of inclusion. The second inclusion type,

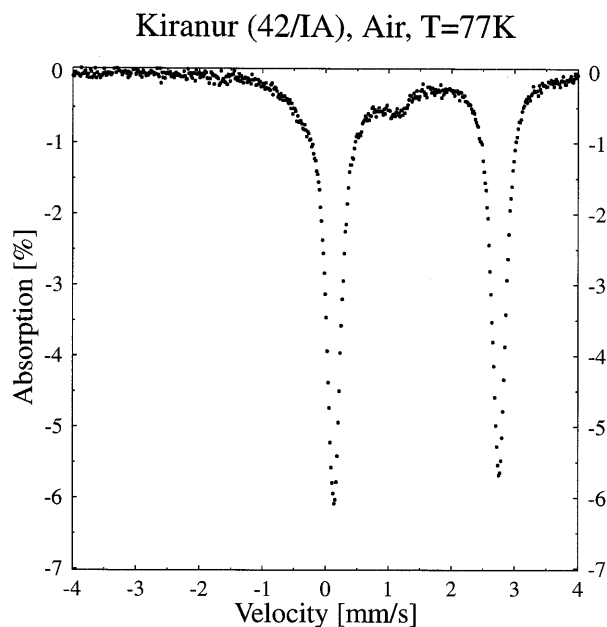


Fig. 2 Unfitted ^{57}Fe Mössbauer spectrum of the Kiranur (42/IA) cordierite heated in air

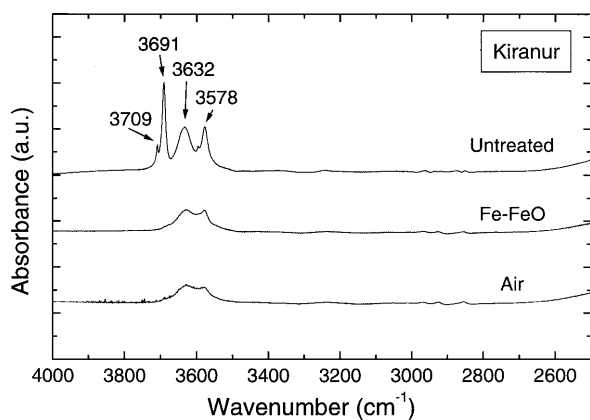


Fig. 3 Powder IR spectra of the natural and two heated Kiranur cordierites. The wavenumbers of the different H_2O stretching bands are given

with many having sizes between 200 and 800 Å, is found in or along cracks or displacements (Fig. 4). These inclusions are often somewhat elongated or platy and have different crystallographic orientations. Euhedral crystals having a probable octahedral habit are also present (Fig. 5). Qualitative EDS analyses show that this second inclusion type is iron rich. They have a spinel structure based on diffraction photographs and are therefore identified as magnetite.

EPR spectroscopy

The powder EPR spectrum of the Zimbabwe (DA-1) sample and the unheated powder spectrum of the Kiranur (42/IA) cordierite are shown in Fig. 6. The

Table 2 Chemical composition of the cordierites. Calculated on the basis of 18 oxygens per anhydrous formula unit and using Mössbauer results

Sample	42/IA	42/IA (air)	42/IA (Fe–FeO)	DA-1 ^a
SiO_2	48.91	49.72	49.83	49.66
TiO_2	0.01	0.01	0.01	0.01
Al_2O_3	33.16	33.63	33.78	33.34
MgO	12.40	12.70	12.62	12.73
FeO	2.44	2.47	2.47	2.21
MnO	0.03	0.02	0.03	0.02
CaO	0.02	0.00	0.00	0.01
K_2O	0.01	0.01	0.01	0.01
Na_2O	0.25	0.13	0.21	0.34
Total Cations	97.23	98.69	98.93	98.33
Si	4.97	4.97	4.97	4.98
Al	3.97	3.97	3.97	3.94
Fe^{2+}	0.02	–	0.01	0.02
IV_Σ	8.96	8.94	8.95	8.94
Mg	1.88	1.89	1.88	1.90
Fe^{2+}	0.19	0.20	0.21	0.17
Mn^{2+}	–	–	–	–
VI_Σ	2.07	2.09	2.09	2.07
Na	0.05	0.03	0.04	0.07
K	–	–	–	–
Ch_Σ	0.05	0.03	0.04	0.07

^a From Geiger et al. (2000)

powder spectra of the two samples heated at 1,000 °C are shown in Fig. 7. The Kiranur sample spectrum heated at 1,000 °C and an oxygen fugacity defined by the Fe–FeO buffer is similar to the spectra of the untreated cordierites. The EPR spectrum of the Kiranur sample heated at 1,000 °C in air exhibits, besides the typical Fe^{3+} signal at $g_{\text{eff}} = 9.0, 5.06, 3.68,$ and $3.23,$ a broad and asymmetric line around 0.37 T that is often observed in samples with high concentrations of paramagnetic ions. A signal for octahedral Mn^{2+} is seen in all the spectra except for the Kiranur sample heated in air. Figure 8 compares the EPR powder spectrum of the Zimbabwe cordierite with a calculated spectrum using the data in Hedgecock and Chakravarty (1966) as discussed below.

Discussion

Fe^{3+} in natural cordierite

Following upon the EPR study of Hedgecock and Chakravarty (1966), and the optical absorption spectroscopic study of Faye et al. (1968) and Smith and Strens (1976), Geiger et al. (2000) argued that very small concentrations of Fe^{3+} in cordierite should be located on the T_{11} site. The presence of Fe^{3+} on T_{11} enables a charge-transfer process between it and the bulk of Fe^{2+} located on the edge-shared octahedral M-site (Fig. 9). Geiger et al. (2000) showed that small amounts of Fe^{2+} , up to 0.02 cations pfu, could also be located on T_{11} in Mg-rich cordierites. Thus, this site is primarily occupied

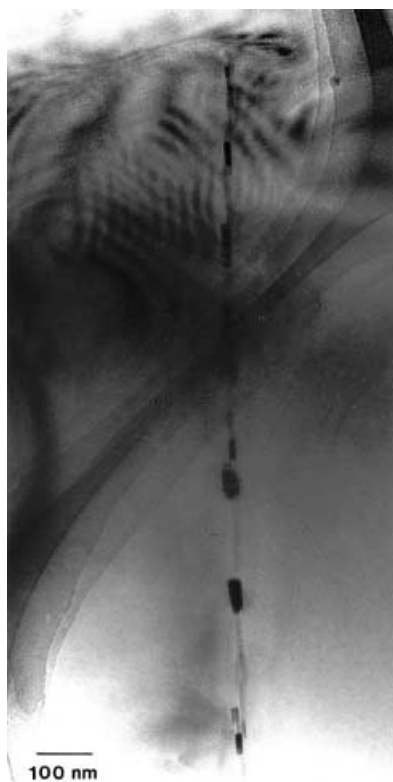


Fig. 4 Bright-field image of magnetite inclusions found along a crack or surface. The sample was tilted so that many inclusions display strong diffraction contrast. The surface is not completely parallel to the electron beam and so a narrow contrast band can be seen (scale 1 mm \cong 140 Å)

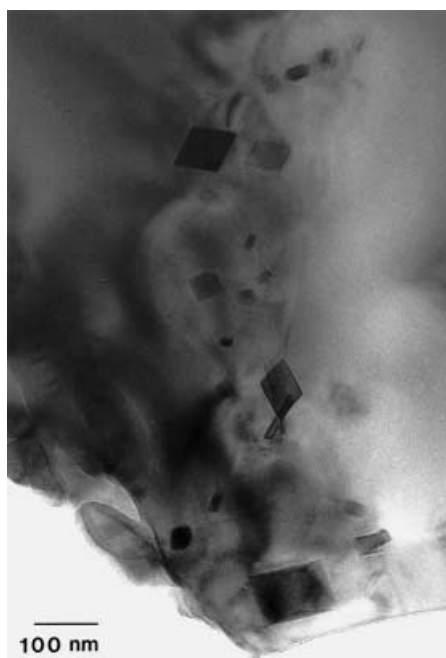


Fig. 5 Bright-field image of magnetite inclusions along a displacement. Note the euhedral crystals of octahedral shape and the irregular strain contrast near the displacement (scale 1 mm \cong 140 Å)

by Al^{3+} , but it can also contain measurable Fe^{2+} . However other proposals have been put forth for the site occupation of Fe^{3+} . Goldman et al. (1977) proposed, using primarily single-crystal optical absorption spectroscopy, that Fe^{3+} is located in the channel cavities, presumably near the walls as close as possible to the M-site. They argued further that heating cordierite in air caused an oxidation of small amounts of Fe^{2+} occurring in the six-membered rings and its migration into the channel cavity. Pollak (1976) proposed that Fe^{3+} occurs on the octahedral M-site.

Our EPR spectra allow a direct determination of where Fe^{3+} is located. In cordierite of space group Cccm Fe^{3+} should most likely occupy the Al sites T_{11} and/or T_{26} (Fig. 9), and so for the analysis of the EPR spectra we consider the 8k and 8l Wyckoff positions (International Tables of Crystallography 1983, vol. A). In magnetic resonance experiments like EPR both the 8k and 8l positions may be magnetically inequivalent depending on the symmetry operations of the space group and on the orientation of the magnetic field, \mathbf{B} , with respect to the crystal-axis system. In the case considered here, a fourfold EPR spectrum would occur for both Fe^{3+} at 8k and at 8l, if \mathbf{B} is arbitrarily oriented to the crystal axes. Each of these fourfold spectra degenerates to a twofold one with \mathbf{B} in (001) and, finally, to one spectrum with \mathbf{B} in (010), in (100), or with \mathbf{B} parallel to the a , b , or c axis. Thus, from the degree of the degen-

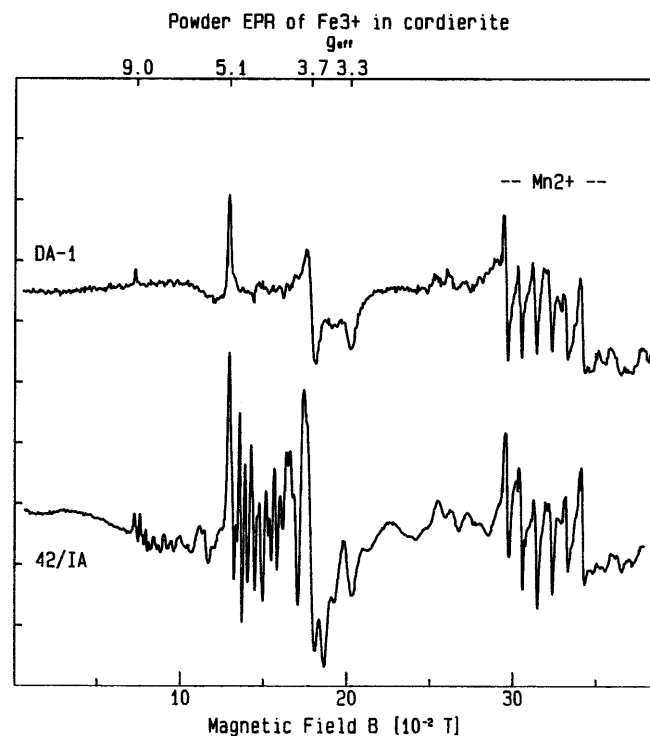


Fig. 6 Powder EPR spectrum of cordierite DA-1 (spectrometer setting: 9.24 GHz, gain 1,250, microwave power 1 mW, modulation amplitude 0.2 mT) and spectrum of unheated sample 42/IA (spectrometer setting: 9.24 GHz, gain 1,250, microwave power 2 mW, modulation amplitude 0.5 mT)

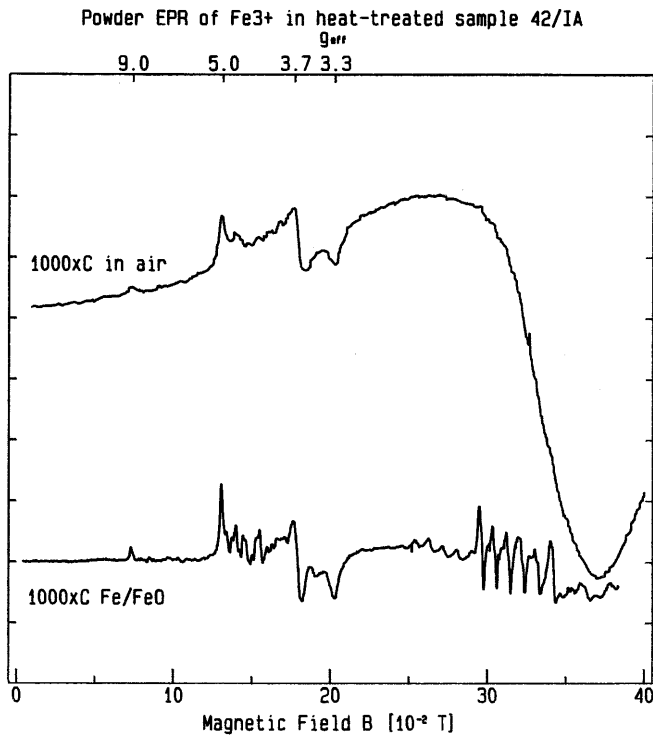


Fig. 7 Powder EPR spectra of the Kiranur cordierite (42/IA) heated at 1,000 °C in air (spectrometer setting: 9.24 GHz, gain 1,250, microwave power 1 mW, modulation amplitude 0.025 mT) and at the Fe-FeO buffer (spectrometer setting: 9.24 GHz, gain 1,250, microwave power 1 mW, modulation amplitude 0.2 mT)

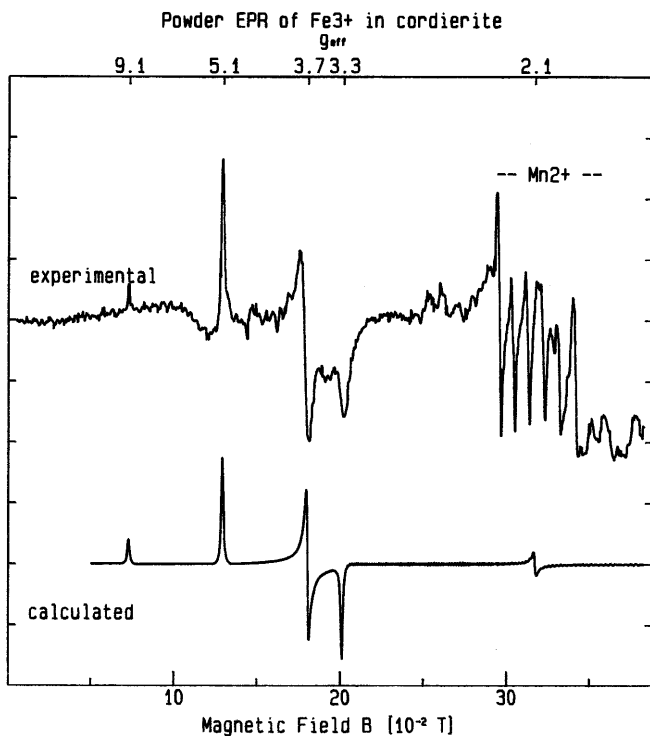


Fig. 8 Comparison of the powder EPR spectrum of cordierite DA-1 and a calculated EPR spectrum using the data of Hedgecock and Chakravarty (1966)

eration Fe^{3+} at 8k cannot be distinguished from Fe^{3+} at 8l. Therefore, the angular dependence of the Fe^{3+} EPR spectrum of sample DA-1 was measured in the planes (001) and (010). As expected, the EPR pattern splits into two spectra in (001), whereas in (010) no splitting occurs. Further, all experimental results are in excellent agreement with the data in Hedgecock and Chakravarty (1966; Table 1 and Fig. 2, upper part). Taking the spin Hamiltonian parameters listed there, a powder spectrum was calculated and is shown in Fig. 8 together with the experimental spectrum of the DA-1 sample. The agreement between them is excellent. Therefore, we follow the interpretation of Hedgecock and Chakravarty (1966) who proposed that Fe^{3+} substitutes for Al^{3+} on the distorted 8k (T_{11}) site, because the minimum and maximum in the angular variations in (001) coincide with the pseudo twofold axis of this site. None of the EPR spectra give any indication of Fe^{3+} on another site. These conclusions refer only to our natural Mg-rich cordierites and not necessarily to other Fe-rich samples. There is no reason to believe, however, that the latter are fundamentally different from the Mg-rich samples.

The amount of Fe^{3+} in natural cordierites is too low to be measured quantitatively by Mössbauer spectroscopy, but it can place an upper constraint (Geiger et al. 2000; Khomenko et al., unpublished). The intrinsic sensitivity of the Mössbauer measurements lies around 1–2% of Fe. We have not observed any Fe^{3+} doublet having an area greater than 2% of the octahedral Fe^{2+} doublet. The most Fe^{3+} -rich cordierite we have found in any of our cordierites studied to date (Geiger et al. 2000; Khomenko et al., unpublished) is that from Zimbabwe (DA-1), where a very weak Fe^{3+} absorption doublet in the Mössbauer spectrum is observed. We place an upper limit of about 0.004 Fe^{3+} cations pfu for Mg-rich cordierites.

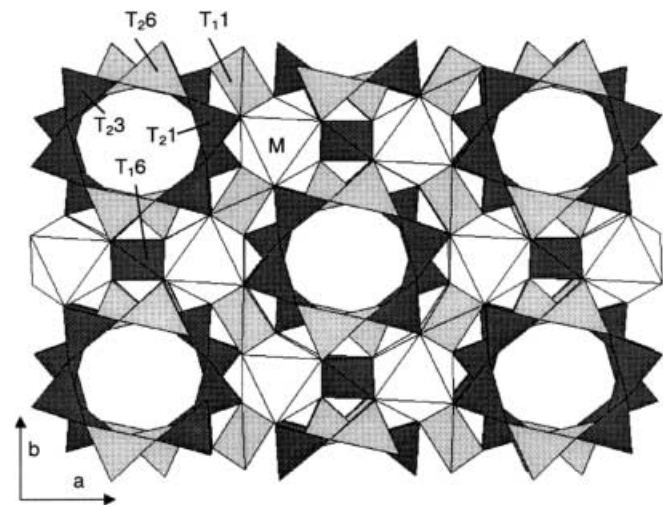


Fig. 9 Polyhedral model of the cordierite structure projected onto (001). The dark-shaded tetrahedra are occupied by Si and the lighter ones by Al

Fe³⁺ in heat-treated cordierite

The amount of Fe³⁺ can be increased by heating a cordierite with Fe²⁺ on T₁1 in air. The heating experiments and Mössbauer spectra show that Fe²⁺ can be oxidized or removed. The simplest interpretation is that much of it is oxidized to Fe³⁺ as shown by the broad weak absorption feature appearing around 1.0 mm/s (Fig. 1d). The spectrum does not show the presence of magnetite or hematite and the I.S. value of 0.35 mm/s for this doublet is more consistent with Fe³⁺ in tetrahedral than octahedral coordination. The reported isomer-shift values of Fe³⁺ in tetrahedral and octahedral coordination in other silicate structures overlap, but those of tetrahedral Fe³⁺ are somewhat lower in the range of about 0.45 to 0.65 mm/s at 298 K (Hawthorne 1988). The half width of the Fe³⁺ Mössbauer doublet is somewhat broad (i.e., ≈0.45 mm/s). The line broadening could result from the different number of local cation configurations that can occur around T₁1. Different cations can be located on the two different M-sites (Fe²⁺, Mg, small amounts of Mn²⁺), which are edge-shared with the T₁1 tetrahedron (Fig. 9). The EPR spectrum of the in-air-heated Kiranur sample shows that Fe³⁺ is located on T₁1 (cf. Figs. 6 and 7). Taking into account the experimental parameters and especially the modulation amplitude, it follows that the amount of Fe³⁺ is approximately ten times higher in the sample heated in air than in the unheated sample.

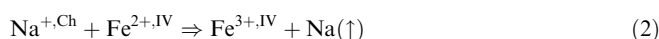
The Mössbauer spectrum of the Kiranur sample heated at the Fe–FeO buffer is different from that heated in air. The smaller Fe²⁺ doublet remains, although it is slightly less intense. No new Fe³⁺ doublet occurs. It is not clear why the amount of Fe²⁺ on T₁1 is somewhat less and where the rest went in the structure during heating. Very small amounts located on other structural sites would not be detected by our Mössbauer measurements and Fe²⁺ is not seen in the EPR spectra. Vance and Price (1984) made similar observations for a cordierite heated under vacuum. Hence, no or little oxidation of Fe²⁺ in cordierite takes place at low f_{O₂}'s. It follows that Fe²⁺ on T₁1 is oxidized only at relatively high f_{O₂}'s (e.g., 0.2 atm). It is not the effect of temperature primarily, but of f_{O₂} in destabilizing this Fe²⁺. Heating cordierite in air causes an increase in the broad Fe²⁺–Fe³⁺ charge-transfer band located at about 18,000 cm⁻¹ (Goldman et al. 1977; Vance and Price 1984; Khomenko et al., unpublished). This is best explained by the direct oxidation of Fe²⁺ to Fe³⁺ on T₁1, thus increasing substantially the number of Fe²⁺–Fe³⁺ pairs in the edge-shared M-site octahedron and T₁1 tetrahedron (Fig. 9). This possibility is more consistent with the data than that of migration of Fe³⁺ cations into the channel cavities of cordierite with dehydration (Goldman et al. 1977). Octahedral Fe²⁺ does not, in contrast, appear to be affected greatly by heating at 1,000 °C for 2 days. It remains relatively stable in air to about 1,150 °C, as documented by the optical absorption spectra measured on other samples heated for

hours to days (Goldman et al. 1977; Vance and Price 1984).

The IR measurements show that class I H₂O is lost completely by heating at 1,000 °C in air or at the Fe–FeO buffer, while some class II H₂O remains. This is consistent with the idea that class I H₂O has only very weak bonding with the cordierite framework, while class II H₂O is bonded to alkali cations (here Na⁺) residing in the six-membered rings (Goldman et al. 1977; Kolesov and Geiger 2000). However, much of the class II H₂O is lost, as is some Na, by heating and more strongly by heating in air. This agrees with the proposal (Geiger et al. 2000) that the following substitution occurs in natural cordierites:



and the oxidation reaction by heating can thus be written as:



whereby Fe²⁺ is oxidized to Fe³⁺ on T₁1 and Na is lost from the channels. The microprobe and Mössbauer results show that for each Fe²⁺ cation oxidized on T₁1 one Na cation pfu is lost from the channels in agreement with Eq. (2).

Hochella et al. (1979) undertook high-temperature single-crystal X-ray diffraction refinements on two natural cordierites at different temperatures. They identified hematite in samples heated above 600–700 °C. The brown-color description of their heated samples matches that of our Kiranur cordierite heated in air. The same color change upon heating was also noted by Goldman et al. (1977) and Vance and Price (1984). Our sample contains microscopic magnetite and we did not observe any hematite inclusions. We have no good explanation for the differences observed herein versus Hochella et al. (1979), except to state that their sample was enclosed in a small capillary tube. It is also not possible to determine precisely where the Fe in the magnetite originates, but we think the most probable source is from the T₁1 site, because the large Fe cation on this site should be relatively unstable. Vance and Price (1984) did not think the Fe³⁺ in hematite occurred from oxidation and expulsion of Fe²⁺ from T₁1. They proposed that hematite crystallizes in cracks and on surfaces, stating that “surface Fe³⁺ is associated with strain effects derived from the crushing of powders and localized cracking on dehydration of bulk samples.” However, the details behind this process were not specified. Hochella et al. (1979) proposed that the Fe in hematite could originate from the octahedral site in their Fe-rich Dolni Bory sample, but they were not aware that small amounts of Fe²⁺ can be located on T₁1. We propose that the formation of submicroscopic magnetite/hematite particles in heated cordierite on surfaces or in cracks/dislocations, requires the formation of site defects in the structure. This question is difficult to address because of uncertainties in the detailed chemistry of natural cordierites. The major element chemistry of cordierite is well understood, but the minor element chemistry has not

been investigated completely. The degree and types of nonstoichiometry are also unknown. Natural cordierites can incorporate measurable Li, Be, and Mn^{2+} on structural framework sites, and Na and K can be found in the channels in variable amounts (Schreyer 1985). The EPR results here show that Mn^{2+} substitutes on the octahedral site. It remains stable after heating. Because the light element concentrations are not known quantitatively, and because any possible defect structure of cordierite is unknown, it is not possible to analyze further the site occupancies of the minor cations and the problem of Fe loss from cordierite.

From this study it does appear though, that significant concentrations of Fe^{3+} (greater than 0.004 cations pfu) are very unlikely in cordierite under most petrologic P–T– f_{O_2} conditions. The amounts in Fe-rich cordierite are not as well known, but should be also small (Cerny et al. 1997; Geiger et al. 2000; Khomenko et al., unpublished). The degree of solid solution between $(\text{Mg,Fe})_2\text{Al}_2\text{Al}_2\text{Si}_5\text{O}_{18}$ and $(\text{Mg,Fe})_2\text{Fe}_2^{3+}\text{Al}_2\text{Si}_5\text{O}_{18}$, the latter of which is a hypothetical cordierite component with Fe^{3+} on T₁1, should be very small. The results herein are consistent with the low concentrations of Fe^{3+} measured with Mössbauer and optical absorption spectroscopy on a large number of natural cordierites (Geiger et al. 2000; Khomenko et al., unpublished). We have not observed more than 1–2 atomic% Fe^{3+} , in relation to the total Fe content, in any natural cordierite. No natural cordierite has shown nearly as much Fe^{3+} as that of the oxidized Kiranur sample herein. Therefore, we cannot confirm the larger Fe_2O_3 concentrations of 3–4 wt% in natural cordierites determined in older wet-chemical analyses (Leake 1960; Schreyer 1965; Smith and Strens 1976) or other Mössbauer analyses (Parkin et al. 1977). They should be viewed with caution. Low Fe_2O_3 concentrations are also found in synthetic Mg-cordierite even those synthesized at high temperatures and at high oxygen fugacities (Abs-Wurmbach et al. 1989).

From a crystal-chemical point of view, a large Fe cation in either oxidation state should be relatively unstable in tetrahedral coordination. The relative ease in oxidizing Fe^{2+} on T₁1 compared to octahedral Fe^{2+} in cordierite heated in air is evidence for this. The concentration of Fe^{3+} on T₁1 may even be lower than that of Fe^{2+} on the same site, because it does not obtain a crystal-field stabilization energy in the distorted tetrahedron.

Acknowledgements This work was supported by a grant, Ge 659/6-1, from the “Deutsche Forschungsgemeinschaft.” We thank M. Neumaier for making the buffered heating experiment.

References

- Abs-Wurmbach I, Boberski C, Hafner S (1989) Zum Problem des Einbaus von dreiwertigem Eisen in den Cordierit: Synthesen und Mößbauer-Spektroskopie. *Fort Mineral* 66: 1
- Cerny P, Chapman R, Schreyer W, Ottolini L, Bottazzi P, McCammon CA (1997) Lithium in sekaninaite from the type locality, Dolni Bory, Czech Republic. *Can Mineral* 35: 167–173
- Faye GH, Manning PG, Nickel EH (1968) An interpretation of the polarized optical absorption spectra of tourmaline, cordierite, chloritoid and vivianite. *Am Mineral* 53: 1174–1201
- Geiger CA, Armbruster T, Khomenko V, Quartieri S (2000) Cordierite I: the coordination of Fe^{2+} . *Am Mineral* 85: 1255–1264
- Goldman DS, Rossman GR, Dollase WA (1977) Channel constituents in cordierite. *Am Mineral* 62: 1144–1157
- Hawthorne FC (1988) Mössbauer spectroscopy. *Mineral Soc Am Rev Mineral* 18: 255–340
- Hedgecock NE, Chakravartty SC (1966) Electron spin resonance of Fe^{3+} in cordierite. *Can J Phys* 44: 2749–2755
- Hochella MF, Brown GE, Ross FK, Gibbs GV (1979) High-temperature crystal chemistry of hydrous Mg- and Fe-cordierites. *Am Mineral* 64: 337–351
- International tables for X-ray crystallography (1983) Volume A, D. Reidel, Boston
- Kolesov BA, Geiger CA (2000) Cordierite II: the role of CO_2 and H_2O . *Am Mineral* 85: 1265–1274
- Leake BE (1960) Compilation of chemical analyses and physical constants of natural cordierites. *Am Mineral* 45: 282–298
- Miyashiro A (1957) Cordierite–indialite relations. *Am J Sci* 255: 43–62
- Parkin KM, Loeffler BM, Burns RG (1977) Mössbauer spectra of kyanite, aquamarine, and cordierite showing intervalence charge transfer. *Phys Chem Miner* 1: 301–311
- Pollak H (1976) Charge transfer in cordierite. *Phys Status Solidi* (b) 74: K31–K34
- Schreyer W (1965) Synthetische und natürliche Cordierite II: die chemischen Zusammensetzungen natürlicher Cordierite und ihre Abhängigkeit von den PTX-Bedingungen bei der Gesteinsbildung. *Neues Jahrb Mineral Abh* 103: 35–79
- Schreyer W (1985) Experimental studies on cation substitutions and fluid incorporation in cordierite. *Bull Minéral* 108: 273–291
- Smith G, Strens RGJ (1976) Intervalence transfer absorption in some silicate, oxide and phosphate minerals. In: Strens RGJ (ed) *The physics and chemistry of minerals and rocks*. Wiley, New York, pp 583–612
- Vance ER, Price DC (1984) Heating and radiation effects on optical and Mössbauer spectra of Fe-bearing cordierites. *Phys Chem Miner* 10: 200–208