Semi-quantitative determination of the Fe/Mg ratio in synthetic cordierite using Raman spectroscopy

REVISION 1

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ABSTRACT

Investigations of H_2O-bearing synthetic well-ordered Mg-Fe-cordierites (X_{Fe} = 0-1) with micro-Raman spectroscopy revealed a linear correlation between the Fe/Mg ratio and the position of certain Raman peaks. In the range between 100 and 1250 cm^{-1} all peaks except for three peaks shift towards lower wavenumbers with increasing X_{Fe} as a consequence of the substitution of the lighter Mg by the heavier Fe atom on the octahedral sites and the associated structural changes. Selected medium and strong peaks show a shift of 5 to 13 cm^{-1}, respectively. Based on recent quantum-mechanical calculations (Kaindl et al. 2011) these shifts can be attributed to specific vibrational modes in the cordierite structure, thus showing that the Mg-Fe exchange affects the vibrational modes of tetrahedral, octahedral and mixed sites. The peaks (wavenumber Mg-/ Fe-cordierite) at 122/111 cm^{-1}, 262/257 cm^{-1}, 430/418 cm^{-1}, 579/571 cm^{-1}, 974/967 cm^{-1} and 1012/1007 cm^{-1} were selected for detailed deconvolution analysis. The shifts of these peaks were then plotted versus X_{Fe} and

regression of the data lead to the formulation of a set of linear equations. Assuming ideal Fe-Mg mixing of the end-members and using linear peak shifts then allows the development of calibration diagrams for the semi-quantitative determination of the Fe-Mg contents of cordierite samples with Raman spectroscopy. In addition the effect of different H_2O contents and the degree of Al-Si ordering on the Fe/Mg determination were also investigated. Testing the calibration against data from six well-characterized natural cordierite samples yielded excellent agreement.

Keywords

Raman spectroscopy, cordierite, Mg-Fe exchange, peak shift, Al-Si ordering.

INTRODUCTION

The Mg-Fe silicate cordierite with the idealized formula $(Mg,Fe)_2Al_4Si_5O_{18}$ x nH_2O occurs as hexagonal, high-temperature and orthorhombic, low-temperature polymorphs with disordered/ordered Al-Si distribution on the tetrahedral sites. Cordierite is an important petrogenetic mineral because when in equilibrium with other Mg-Fe-silicates the Mg/Fe ratio of cordierite can be used as a geothermobarometer (e.g., Lonker 1981; Bhattacharya 1986; Kalt et al. 1999; Kalt 2000). Various amounts of volatiles like H_2O and CO_2 can also be incorporated into the structural channels of cordierite, which allows paleofluid reconstructions (Harley et al. 2002, Bul´bak and Shvedenkov 2005; Rigby et al. 2008). Most of the natural cordierites are fully ordered and have the space group symmetry Cccm. Structurally, six-membered rings of $(Si,Al)O_4$ are stacked along the crystallographic c-axis and form channels, laterally and vertically linked by additional (Al, Si) tetrahedrons. The octahedral coordinated M-sites, two different tetrahedral coordinated T-sites (T_1, T_2) and the channel sites (Ch0, Ch1/4) are distinguished in the structure, according to the general formula: $(M)_2(T_11)_2(T_26)_2(T_23)_2(T_21)_2(T_16)O_{18}(Ch0,Ch1/4)$,

where Si occupies the $T_2$3, $T_2$1 and $T_1$6 sites and Al the remaining two $T_1$1 and $T_2$6 sites. Structural refinement and Al/Si-ordering was investigated by various authors (e.g., Gibbs 1966; Langer und Schreyer 1969; Meagher and Gibbs 1977; Cohen et al. 1977; Hochella et al. 1979; Putnis 1980; Wallace and Wenk 1980; Putnis 1983; Armbruster 1985; Malcherek et al. 2001; Bertoldi et al. 2004 and references therein; Miletich et al. 2010). The Mg and Fe^{2+} ions are located in the octahedral coordinated M-sites and their mixing is assumed to be ideal (e.g., Boberski and Schreyer 1990); 90 to 99% Fe^{2+} occupies the octahedral site (Khomenko et al. 2001). The amount of Fe^{3+} in natural cordierites is insignificantly low (Geiger et al. 2000). The incorporation of Fe^{2+} in exchange for Mg leads to multiple structural changes: 1) expansion of the mean M-O-distances within the octahedra leads to the elongation of the unit cell in a- and b-directions and 2) $T_1$1-O distances decrease slightly, leading to a contraction along the c-axis (e.g., Wallace and Wenk 1980; Armbruster 1985; Boberski and Schreyer 1990; Malcherek et al. 2001; Geiger and Grams 2003). Raman and FT-IR spectroscopic methods were already used by several authors to investigate and describe different properties of cordierite, like polymorphism (Langer and Schreyer 1969), volatile content (Vry et al. 1990; Kalt 2000; Kolesov and Geiger 2000; Yakubovich et al. 2004; Bul'bak and Shvedenkov 2005; Khomenko and Langer 2005; Kaindl et al. 2006; Kolesov 2006; Nasdala et al. 2006; Rigby et al. 2008; Weikusat et al. 2010), Al-Si ordering (McMillan et al. 1984; Güttler et al. 1989; Poon et al. 1990), structural heterogeneity and energetic and structural changes under high pressure (Geiger and Grams 2003; Likhacheva et al. 2011). Local structural heterogeneities in natural Fe-Mg-cordierites and their thermodynamic mixing properties have also been investigated with IR spectroscopy (Geiger and Grams 2003). Quantum-mechanical calculations of the Raman spectra of Mg- and Fe-cordierites have also been done for a detailed peak assignment and a theoretical description of the effects of the Mg-Fe

exchange and Al-Si ordering (Kaindl et al. 2011). Semi-quantitative techniques for the determination of chemical compositions, based on the shifts of vibrational modes within certain mineral solid solutions, have been presented for example for garnets, olivines and pyroxenes (Geiger and Grams 2003; Smith 2005; Kuebler et al. 2006; Bersani et al. 2009; Stalder et al. 2009). The aim of this work is the detailed Raman spectroscopic description of structural changes in H_2O-bearing synthetic cordierite as a consequence of Mg-Fe-exchange and the development of semi-quantitative calibrations for the determination of the Mg/Fe ratio in natural and synthetic cordierite samples.

EXPERIMENTAL METHODS

Synthesis of Mg-Fe-cordierites and sample preparation

Cordierites with the composition $(Mg,Fe)_2Al_4Si_5O_{18}$ x nH_2O were synthesized using annealing and hydrothermal techniques. SiO_2 nanopowder (99.5%, metals basis, Aldrich), Al_2O_3 (gamma, 99,997%, metals basis, Alfa Aesar), MgO (Art. 5865, Merck), FeO (Iron (II) oxide, 99.5%, metals basis, Alfa Aesar), Fe (Art. 3819, Merck) and graphite powder were used for the synthesis. The synthesis of the hydrous Fe- and the dry Mg-end-member has been described in detail by Kaindl et al. (2011). To obtain H_2O-bearing samples, orthorhombic Mg-cordierite was treated hydrothermally in a welded gold capsule together with H_2O at 700 °C and 0.2 GPa for 7 days. The full synthesis sequence was: stoichiometric glass → nucleation/formation of "beta-cordierite" → disordered hexagonal anhydrous cordierite → ordered orthorhombic anhydrous cordierite → ordered orthorhombic hydrous cordierite. The transition from hexagonal to orthorhombic Mg-cordierite caused the formation of a patchy "tweed" microstructure in the cordierite crystals (Putnis 1983; Armbruster 1985; Putnis et al. 1987; Blackburn and Salje 1999).

Powdered glass with Mg-cordierite stoichiometry and the oxides FeO, Al_2O_3 and SiO_2 in various fractions were used as starting material for the synthesis of hydrous cordierite crystals with X_{Fe} [= Fe/(Fe + Mg)] ranging from 0.1 to 0.4. Sealed buffered double capsules were then used, with IW (iron/wüstite)-buffer and H_2O in the outer gold-capsule and the starting material and H_2O in an inner $Ag_{70}Pd_{30}$ capsule. The experimental conditions were 700 °C and 0.2 GPa and the experimental duration was 7 days. For the synthesis of hydrous crystals with X_{Fe} = 0.5-0.8 cordierite glasses with X_{Fe} = 0.5-0.8 were produced. The glasses were then tempered in a welded gold capsule together with graphite powder for 16 to 24 hours at 900 °C to obtain the unordered hexagonal cordierite. This cordierite was then loaded together with H_2O in a hydrothermal apparatus at 700 °C and 0.25-0.3 GPa for 7 days to obtain well-ordered H_2O-bearing orthorhombic cordierite. The synthesis were done in buffered capsules with IW-buffer and H_2O in the outer gold capsules and the starting material and H_2O in the inner $Ag_{70}Pd_{30}$ capsules.

Electron microprobe analysis

For electron microprobe analysis all synthesis products were embedded in an epoxy mount, grinded and finally polished using a 1 µm diamond suspension. The orientation of the crystals from run products was random. The JEOL JXA 8100 SUPERPROBE at the Institute of Mineralogy and Petrography at the University of Innsbruck was used for the chemical analyses of the glasses, the intermediate run products and the final cordierite samples. Analytical conditions for the wavelength dispersive measurements were 15 kV acceleration voltage and a beam current of 10 nA. Counting times for all elements were 20 seconds for the peak and 10 seconds for the background. For the calibration synthetic (corundum) and natural (almandine, quartz, orthoclase and diopside) microprobe standards were used. Mineral formulae

were calculated on the anhydrous basis of 18 oxygens. Some measurements were performed in point mode due to the small grain size and inhomogeneities in the synthesis materials. Depending on the elements and their concentrations the standard deviation of the measurements of each element is between 0.34 and 1.79%. For precise correlation we used BSE imaging to be able to correlate the locations of the analyzed spots with the locations of the subsequent Raman spectroscopic investigations.

X-ray powder diffraction

Powder X-ray diffraction for the determination of the lattice parameters and the degree of Al-Si ordering in the Mg-cordierite samples was done with a Stoe STADI-MP diffractometer system in bisecting transmission geometry in a 2Θ range from 2 to 129.8° in steps of 0.009°. The system is equipped with a "Mythen" 1k detector and an asymmetric Ge(111)-monochromator yielding a strictly monochromatic CuKa1 radiation. For the Fe-end-member a Bruker D8 Discover system with Bragg-Brentano-geometry over a 2Θ range from 5° to 80.25° in steps of 0.009° was used. The system is equipped with a copper target and a silicon-strip-detector. Rietveld calculations and LeBail fits were done using the program FullProf. 2k (Rodriguez-Carvajal, 2011). The background was determined by linear interpolation between a set of breakpoints with refineable heights. Intensities within 10 times the full-width at half-maximum of a peak were considered to contribute to the central reflection. Thompson–Cox–Hastings pseudo-Voigt functions were chosen for the simulation of the peak shape, including an asymmetry correction following Finger et al. (1994). For the hydrous orthorhombic Mg-end-member the cell parameters a = 17.055, b = 9.724, c = 9.348 and a distortion index (Miyashiro, 1957) of ≈0.24 were obtained. The

cell dimensions of the hydrous orthorhombic Fe-end-member are a = 17.244, b = 9.828, c = 9.288 and the distortion index is ≈0.24.

Raman Spectroscopy

Due to small grain sizes and the patchy microstructure of synthetic cordierite all measurements were done on randomly oriented crystals. Unpolarized and polarized spectra of synthetic cordierite crystals were measured on a Labram HR-800 confocal Raman-spectrometer by HORIBA, using the 532 nm excitation wavelength of a 30 mW Nd:YAG laser through a 100× objective with a numerical aperture of 0.9. The size and power of the laser spot on the surface was approximately 1 μm and 5 mW, respectively. The confocal pinhole aperture was 1000 μm and the width of the entrance slit 100 μm. A grating with 1800 lines/mm was used to disperse the scattered Raman light, which was detected by an open-electrode charge-coupled device with 1024 × 256 pixels, each with a size of 43 μm. The spectral resolution of 1.4 cm^{-1} was determined by measuring the Rayleigh line. Accuracy of the Raman line shifts was checked by regular measurements of the emission lines of a Ne spectral calibration lamp and the deviation was ±0.24 cm^{-1}. Background and Raman peaks were fitted using the built-in spectrometer software LabSpec with the line-segments baseline correction and convoluted Gauss-Lorentz functions. The spectra were recorded for 2 x 200 seconds in the area of 100 – 1250 cm^{-1} using unpolarized (no additional polarizers used) and polarized laser light (polarizers were used for excitation and the scattered Raman light). Deconvolution is not trivial since the spectra of cordierite are characterized by a) complex peak overlaps forming band systems (envelopes) and by b) peak broadening in Fe-rich samples. In the unpolarized spectra most of the band systems are dominated by intense peaks and cordierite shows a strong spectroscopic anisotropy. While peak intensities strongly

depend on the orientation of the crystal to the polarisation plane of the laser light, there are no orientation effects of the peak positions though. The contribution of individual peaks to the band system varies with the overall orientation of the crystal thus influencing band shapes and positions. For the determination of individual peaks and their positions within the band systems each sample was measured twice using polarized laser light for excitation and a polarizer for the scattered light set perpendicular and parallel to the laser polarization. This filtering-procedure was necessary for a successful deconvolution process because removing specific peaks within complex band systems facilitates the identification of others. In addition, the area between 100 and 350 cm^{-1}, which shows a higher peak density, was measured for 2 x 200 sec in a high-resolution mode with an entrance slit set to 20 µm. The sub-pixel acquisition function was then used to increase the peak definition by providing five-times more data points. The information gained from the detailed measurements was used together with the calculated peak positions by Kaindl et al. (2011) thus providing the initial values for the deconvolution of the band systems. Multi-peak fitting with simultaneous and stepwise fitting of several narrow peaks was necessary for the more complex band systems (Bradley, 2007; Knorr, 2011). The errors of the deconvolution process were determined empirically by repeating the curve-fit routine for all six peaks of Fe-cordierite used in the calibration diagrams in an unpolarized spectrum for 10 times. The Fe-end-member was selected because the effect of peak-broadening and peak-overlapping is higher compared to Mg-bearing cordierites. For the calibration the peak position of the unpolarized and polarized measurements were used. Detailed chemical analyses and descriptions of the investigated natural cordierite samples can be found in Bertoldi et al. (2004).

RESULTS

208 **Mg-cordierite**

209 The Raman spectra of 16 randomly oriented cordierite samples with compositions
210 from X_{Fe} = 0 to 1 were investigated between 100 and 1250 cm^{-1}. Characteristic for
211 the Raman spectra of Mg-Fe-cordierites are regions with dominant peaks and band
212 systems containing various numbers of overlapping peaks, which show a diagnostic
213 shift towards lower wavenumbers with increasing Fe-contents. Exceptions are the
214 low-intensity bands around 330, 909 and 960 cm^{-1}. After a close investigation of the
215 Raman spectra of all available samples in different orientations we selected six
216 peaks, which seem to be most suitable for the development of a calibration curve
217 because of their accessibility in terms of intensities, orientation effects and peak shift
218 values (Fig. 1). In Mg-cordierite these are medium- to high-intensity peaks at 121 cm^{-1}
219 (A), 261.5 cm^{-1} (B), 430 cm^{-1} (C), 579 cm^{-1} (D), 974 cm^{-1} (E) and 1012.5 cm^{-1} (F).
220 The peak at 121 cm^{-1} is the dominant peak in the complex band system in the region
221 from 100 to 135 cm^{-1}. Towards lower wavenumbers we find medium- to low-intensity
222 peaks at 118 and 116 cm^{-1}. Adjacent to a small gap between 114 and 109 cm^{-1} a
223 low-intensity peak follows at 107 cm^{-1}. Towards higher wavenumbers the peak at 121
224 cm^{-1} is strongly overlapped by a second intense peak at 123 cm^{-1}, followed by
225 medium- to high-intensity peaks at 126 cm^{-1}, 129 cm^{-1} and 131 cm^{-1}.
226 The peak at 261.5 cm^{-1} is the most intense peak in the band system in the region 230
227 to 275 cm^{-1} containing 8 individual peaks. Towards lower wavenumbers this peak is
228 overlapped by a high-intensity peak at 260 cm^{-1} followed by a low-intensity peak at
229 256 cm^{-1}. A group of three medium- to low-intensity peaks follows at 243 cm^{-1}, 242
230 cm^{-1} and 241 cm^{-1}. Towards higher wavenumbers this peak is overlapped by
231 medium- to low-intensity peaks at 265 cm^{-1} and 269 cm^{-1}.
232 The medium-intensity peak at 430 cm^{-1} is flanked by a low-intensity peak at 436 cm^{-1}.

The high-intensity peak at 579 cm^{-1} is part of a band system with 5 individual peaks. Towards lower wavenumbers it is overlapped by the medium-intensity peak at 566 cm^{-1} and a high-intensity peak at 557 cm^{-1}, followed by a low-intensity peak at 546 cm^{-1}. Towards higher wavenumbers this peak is overlapped by a low-intensity peak at 592 cm^{-1}. The high-intensity peak at 974 cm^{-1} has a neighbouring peak at 952 cm^{-1} with medium intensity. The medium- to high-intensity peak follows at 1012.5 cm^{-1}. The experimental data are in good agreement with the calculated cordierite Raman spectra by Kaindl et al. (2011), which allow the unambiguous assignment of the peaks A – E. According to Kaindl et al. (2011) peak A results from the modes deforming and rotating mainly the $T_1$6 site. Peak B results from the bending modes of both the Si- and Al- tetrahedral and the M-octahedral sites. Peak C is a result from the bending of the $T_2$6 site. The split bands between 500 and 630 cm^{-1} including band (D) are related to the bending vibrations of the $T_2$6, $T_2$1 and $T_2$3 and the stretching of the M- and $T_2$6-sites. Peak E is caused by the stretching of the $T_2$1 and $T_1$6 sites. Peak F is caused by the stretching of the $T_2$1 and $T_2$3 ring-tetrahedra as well as the $T_1$6 tetrahedron, which connects two M-sites. A complete band assignment for both cordierite Fe- and Mg-end-members can be found in Kaindl et al. (2011).

Fe-cordierite and peak shifts

In the spectra of the Fe-end-member the equivalent peaks can be found at 110.5 cm^{-1} (A´), 256.5 cm^{-1} (B´), 418 cm^{-1} (C´), 571.5 cm^{-1} (D´), 967 cm^{-1} (E´) and 1007.5 cm^{-1} (F´). Figure 2A-F shows the peak shifts as a function of the Fe-content for the 16 samples listed in Table 1. Peaks A/A´ and C/C´ show the highest shifts with 11 and 12 cm^{-1}, while peaks B/B´ and E/E´ show the lowest shifts with 5 cm^{-1}.

Regressions of the data of peaks A – F lead to the following linear equations:

(A) $X_{Fe} = \frac{P_{(A)} - 121.67}{-10.814}$ (B) $X_{Fe} = \frac{P_{(B)} - 261.52}{-5.2198}$

(C) $X_{Fe} = \frac{P_{(C)} - 430.48}{-12.526}$ (D) $X_{Fe} = \frac{P_{(D)} - 579.02}{-6.5019}$

(E) $X_{Fe} = \frac{P_{(E)} - 973.8}{-6.7901}$ (F) $X_{Fe} = \frac{P_{(F)} - 1012.9}{-4.3776}$

The standard deviations $2\sigma_1$ (hardware uncertainties) and $2\sigma_2$ (fitting procedures) for the Raman positions were calculated with equation 1, the overall standard deviations $2\sigma_{overall}$ were calculated with equation 2:

1.) $\sigma_{1,2} = \sqrt{\frac{\sum (x - \bar{x})^2}{(n-1)}}$ 2.) $\sigma_{overall} = \sqrt{\sigma_1^{\,2} + \sigma_2^{\,2}}$

The 2σ standard deviations are given in figure 2A-F. The calculations based on a spectrum of Fe-cordierite yielded a significantly higher error in the peak position and thus in the prediction of X_{Fe} due to the uncertainties using spectral curve fitting procedures compared to Mg-cordierite.

DISCUSSION

Peak shifts and structural changes in Mg-Fe-cordierite

The general trend of downshift of peaks in Fe-cordierite compared to their equivalents in Mg-cordierite is probably caused by decreasing mean M-O and increasing $T_1$1-O bond distances (Malcherek et al. 2001). However, for individual peaks the interplay seems to be extremely complex: The equivalent peaks C/C´ for example result both from vibrations of Al in the $T_2$6 site. Peak A in contrast in Mg-cordierite is assigned to Si in the $T_1$6-, $T_2$1- and $T_2$3-site whereas peak A´ in Fe-cordierite to Al in the $T_1$1- and Fe in the M-site (Kaindl et al. 2011). This complexity is

reflected in the larger number of Gauss-Lorentz functions necessary to deconvolute peaks A/A´. Furthermore, one has to take into account the limited accuracy of peak assignments by quantum mechanical calculations (up to ±16 cm^{-1} for individual peaks), substitutions of Mg and Fe^{2+} for Al and compositional dependence of Al-Si ordering (Malcherek et al. 2001; Kaindl et al. 2011). Further discussions are therefore restricted to the practical aspects of the observed dependencies between peak shifts and Fe-contents.

Influences on the Raman measurements I: the effects of Al-Si ordering and H_2O contents

Natural Mg-Fe-cordierites are mainly orthorhombic with a fully ordered Al/Si distribution on the tetrahedral sites and distortion indices (Miyashiro 1957) between 0.21 and 0.27 (e.g., Hochella 1979; Armbruster and Bloss 1981). Since the disordered hexagonal polymorph (distortion index 0) occurs as an intermediate phase in the annealing experiments and was used as starting material for some of the hydrothermal experiments it was necessary to reinvestigate the effect of Al/Si ordering on the Raman peak positions, mainly because the distortion indices of our synthetically grown hydrous cordierites do not exceed values of ≈0.245. The hexagonal to orthorhombic transition and related changes in the Raman spectra (Fig. 1) can be described with an increase of the number of Raman active modes from 10 to 33, peak-sharpening accompanied by intensity increase and the simultaneous splitting of the strong band at 567 cm^{-1} into three bands at 557, 564 and 578 cm^{-1} (McMillan et al.1984; Poon et al. 1990). Kaindl et al. (2011) calculated five modes in this energy region for the ordered orthorhombic polymorph. Al-Si ordering in synthetic annealed cordierite is a function of temperature and time (Putnis and Bish 1983, McMillan et al. 1984). While longer annealing times at temperatures of 1200 °C

results in increasing distortion indices, the Raman spectra of cordierites do not change significantly after the transition from hexagonal to orthorhombic symmetry. The spectra of orthorhombic cordierite samples with annealing times of 3 h and 348 h at 1400 °C show no significant differences of the peak positions in the area between 100 and 1250 cm^{-1}, only the split band at ≈557 cm^{-1} shows a small shift of <1 cm^{-1} towards lower wavenumbers.

The hydrothermal experiments with glass or disordered cordierite as starting material have shown that 1. the ordering process depends of the amount of H_2O present in the capsule during the hydrothermal synthesis at relatively low temperatures of 700 °C . Experiments with no or very low amounts of H_2O available show no or only low degrees of Al-Si ordering. 2. The size of the starting material also has an effect on the ordering process. Figure 3A and 3B show Raman data at the rim of a hydrothermally-treated stoichiometric Fe-cordierite glass fragment with a size of several 100 µm. The split peak region between 500 and 650 cm^{-1} and the intensities of the H_2O peak around 3600 cm^{-1} are shown across a distance of 80 µm from the rim into the interior. The amount of H_2O incorporated and the peak-splitting distance decrease with increasing distance to the fluid contact zone at the outer rim. The profiles suggest a maximum penetration depth limit of water of about 20 µm. Investigations of anhydrous and hydrous orthorhombic Mg-cordierite confirm that H_2O incorporation does not affect the position of the Raman peaks except for one peak at ≈1180 cm^{-1}, which shifts towards lower wavenumbers with increasing H_2O contents. Therefore, this peak was excluded for Mg-Fe determination since the amount of H_2O in the channels of natural cordierites is variable (e.g., Bertoldi et al., 2004).

Influences on the Raman measurements II: the nature of the starting materials

Some of the electron microprobe analyses of Fe-rich samples gave low totals of 95.68 - 97.50 wt.%. All of the synthetic cordierites used in this study contain water but the amount of channel H_2O is insufficient to explain these deviations. A possible reason could be the presence of Fe^{3+} within the structure, which was not considered in mineral formula calculations. Attempts for Fe^{3+} determinations with Mössbauer-spectroscopy failed due to too little amounts of sample material.

Electron microprobe analyses showed that the synthesis products of our Mg-Fe-experiments are in some cases inhomogeneous with variations of $\pm X_{Fe} \leq 0.08$ within the same capsule. We assume that the short synthesis times prevented pervasive equilibration within the capsules. To avoid further uncertainties related to inhomogeneous compositions in the intermediate Fe-Mg range structural data with powder X-ray methods were only collected for the homogeneous Fe- and Mg-end-members.

High-resolution Raman investigations of the region 100-135 cm^{-1} of Mg-cordierite reveal a higher peak density than expected since quantum-mechanical calculations by Kaindl et al. (2011) predicted six peaks, but the experimental data show at least eight individual peaks in this area. This might result from an imperfect cordierite structure with defects and/or distortions, activating otherwise forbidden bands due to breaking of selection rules. Such theoretically not allowed bands were observed for example in halides, borosilicate feldspar, zeolites, silica glasses, dodecaborides and GeO_2 (Benedek and Nardelli 1967; Bäuerle 1973; Best et al. 1994; Mihailova et al. 2005; Nesterova et al. 2005; Werheit et al. 2011; Kaindl et al. 2012).

Application of the calibration to natural samples

All of the presented correlation diagrams (Fig. 2A-F) can be used for semi-quantitative determinations of X_{Fe} in natural samples. The main difficulty when

working with Raman spectra of cordierites are peak-overlaps and hence the precise determination of individual peak positions. For practical purposes and in order to reduce the errors introduced by the fitting procedures we recommend the use of calibration diagrams 2C, D, E and F, although the correlation coefficients of all six regression equations are close to 1. Band deconvolution of these peaks is less complex and time consuming, the other diagrams (2A, B) can be used when the results are inconsistent or higher precision is necessary. The complexity of the two band systems in the region 100 - 350 cm^{-1} is a potential source of error during the de-convolution process.

Figure 4 shows a calibration diagram based upon peak D at 575 cm^{-1}. The obtained peak positions of six natural well-characterized cordierite samples were added to the diagram and are in good agreement with the experimental data. The Fe-Mg composition of the samples TA-1 with X_{Fe} = 0.04, WYO-2 with X_{Fe} = 0.10, C005 with X_{Fe} = 0.19, VS3 with X_{Fe} = 0.24, HO6 with X_{Fe} = 0.54 and TUB-1 with X_{Fe} = 0.76 could be adequately reproduced by the developed Raman technique. The good reproducibility of these natural samples also shows that chemical deviations from the ideal stoichiometric composition have no effect on the measurements so far. The natural samples contain minor amounts of Mn, Be, Li and Zn as well as channel cations and volatiles (Na, K, CO_2).

CONCLUSIONS

This study confirmed that Mg-Fe exchange in cordierite causes linear and non-linear structural changes, which are manifested as shifts of Raman peaks. The six Raman peaks investigated in this study shift linearly with Mg-Fe exchange and were fitted to obtain calibration equations (equations A-F). The presented calibrations are based on a set of synthetic hydrous Mg-Fe-cordierites and allow fast and non-destructive

semi-quantitative X_{Fe} determinations of cordierite in thin sections, single crystals and hand specimen without additional sample preparation. Applicability of the method was checked on natural cordierite with minor amounts of Be, Li or Mn and various amounts of channel cations (Na, K) and volatiles (CO_2, N_2). The good agreement of X_{Fe} derived by independent methods and Raman spectroscopy confirms that incorporation of these components influences the cordierite structure to a much lesser extent than Fe-Mg exchange and Si-Al order-disorder.

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588 **Figure captions:**

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590 **FIGURE 1.** Unpolarized Raman spectra of disordered, hexagonal (bottom) and
591 ordered, orthorhombic modifications (top) of Mg-Fe-cordierite with X_{Fe} = 0, 0.49 and 1
592 over the range of 100 – 1250 cm^{-1}. The positions of the peaks A – F in Mg-cordierite
593 are indicated by vertical stippled lines. The position of C´ is indicated by a vertical
594 solid line.

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596 **FIGURE 2 A – F.** Resulting calibration diagrams. The diagrams show the peak shift of
597 the peaks A – F towards lower wavenumbers as a function of Fe/(Fe + Mg) based on
598 the samples listed in Table 1. The error bars show the maximum 2σ standard
599 deviations (calculated for the Fe-end-member).

600

601 **FIGURE 3 A and B.** The figures show the splitting of the peaks in the area of 575 cm^{-1}
602 as a consequence of Al-Si ordering in Fe-cordierite (A) and the intensities of the type-
603 1 water peak at 3597 cm^{-1} (B) over a distance of 80 µm from the rim towards the
604 interior of the crystal.

605

606 **FIGURE 4.** Raman shift of band D. The open circles represent the data as a function of
607 X_{Fe}. The black line is the linear regression to the data. Six natural cordierite samples
608 from Bertoldi et al. (2004) with X_{Fe} 0.04-0.76 (black diamonds) are also shown in the
609 diagram. The error bars show the maximum 2σ standard deviations (calculated for
610 the Fe-end-member).

611

612 **Tables:**

613 **TABLE 1.** Electron microprobe analysis of 16 synthetic hydrous cordierite samples

Sample	1	2	3	4	5	6	7	8
Name	12.5h#7	33.4#5	33.4#2	33.4#6	33.7.2#2.2	33.7.2#5	33.7.2#2.1	29.2#1
SiO_2	50.03(36)	48.61(33)	48.72(33)	48.43(33)	48.60(33)	47.73(32)	47.71(32)	48.92(34)
Al_2O_3	33.82(28)	32.94(26)	33.64(26)	33.36(26)	32.13(26)	32.84(26)	33.03(26)	31.96(26)
FeO	n.d.	3.48(12)	6.00(16)	6.40(16)	7.44(17)	7.62(18)	8.21(18)	11.34(22)
MgO	13.85(21)	11.67(17)	9.08(15)	8.98(15)	9.03(15)	8.72(15)	8.08(14)	6.64(14)
Total	97.70(50)	96.70(47)	97.44(47)	97.17(47)	97.20(48)	96.91(47)	97.03(47)	98.86(50)
Si	4.988(36)	4.978(34)	4.998(34)	4.993(34)	5.037(34)	4.969(34)	4.972(34)	5.069(36)
Al	3.975(33)	3.976(32)	4.068(32)	4.054(32)	3.924(31)	4.030(32)	4.057(32)	3.903(32)
Fe	n.d.	0.298(11)	0.515(13)	0.552(14)	0.645(15)	0.663(15)	0.715(16)	0.982(19)
Mg	2.058(31)	1.781(26)	1.389(23)	1.38(23)	1.395(24)	1.353(23)	1.255(23)	1.025(22)
X_{Fe}	0.00	0.14	0.27	0.29	0.32	0.33	0.36	0.49

Sample	9	10	11	12	13	14	15	16
Name	30.1B1_2	29.2#3	29.2#2	31.2#6r	31.2#5r	37#1_3	38	26.5#8
SiO_2	48.26(34)	47.9(34)	47.86(34)	45.16(32)	44.99(32)	47.45(25)	46.44(24)	45.96(32)
Al_2O_3	32.36(27)	31.73(26)	31.66(26)	32.53(26)	32.26(26)	32.25(20)	30.84(20)	30.64(25)
FeO	11.25(21)	12.47(22)	13.18(23)	14.23(24)	14.46(24)	16.65(36)	17.68(37)	21.09(29)
MgO	6.57(14)	5.33(13)	4.82(12)	4.05(11)	3.97(11)	3.04(08)	2.42(07)	n.d.
Total	98.44(50)	97.43(50)	97.52(50)	95.97(49)	95.68(49)	99.39(49)	97.38(49)	97.69(50)
Si	5.023(35)	5.063(35)	5.070(36)	4.904(34)	4.907(34)	5.011(26)	5.034(26)	5.053(35)
Al	3.97(33)	3.954(32)	3.953(32)	4.163(33)	4.147(33)	4.037(25)	3.95(25)	3.97(33)
Fe	0.979(19)	1.102(20)	1.168(21)	1.292(21)	1.319(22)	1.491(32)	1.613(34)	1.94(26)
Mg	1.019(21)	0.841(20)	0.762(19)	0.656(18)	0.645(17)	0.498(12)	0.402(11)	n.d.
X_{Fe}	0.49	0.57	0.61	0.66	0.67	0.75	0.80	1.00

Note: the chemical formulae are normalized to 18 oxygens; X_{Fe} = Fe/(Fe + Mg); n.d.: not detected.

The numbers in brackets are 2σ standard deviations in terms of the last two digits.

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