Improved calibrations for Raman-spectroscopic determinations of CO$_2$ in cordierite using three excitation wavelengths (488, 515 and 633 nm)

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Abstract: Ten natural cordierite single crystals with $X_{Fe}$ in the range 0.044–0.76 and 0.12 to 1.97 wt% CO$_2$ were investigated with Raman microspectroscopy using three different wavelengths. Improved calibration diagrams for CO$_2$ determinations in single crystals and thin sections for the 488, 515 and 633 nm laser excitation wavelengths show significantly lower standard deviations for CO$_2$ determinations ($\pm 0.04$ to 0.07 wt%) compared to an earlier study done solely at 633 nm. The diagrams are based on the linear relationship between CO$_2$ in wt.% and the ratios of the Raman peak of CO$_2$ to two Si-O-stretching vibrations. The consideration of orientation dependencies and the improvement of background corrections and spectra fitting procedures also contributed to the significantly higher precision. Because Fe-incorporation in cordierite leads to structural changes that result in Raman peak shifts and peak broadening, including peaks considered in this investigation, a correction was introduced for precise CO$_2$ determination on Fe-bearing samples. This improved CO$_2$ determination method was then applied on a 2D spatial scale to two cordierite grains in a thin section of a granulite-facies metapelite from Kösselsdorf in the Saurwald area (southern Bohemian Massif, Upper Austria), which yielded CO$_2$ contents of 0.27–0.31 ±0.07 wt%.

Key-words: Raman spectroscopy, cordierite, CO$_2$-determination, Raman map, calibration.

1. Introduction

Cordierite is a common mineral in medium- to high-grade metamorphic aluminous rocks and used as an important geothermobarometer, especially in rocks of the granulite facies where it is in equilibrium with other Fe-Mg-silicates (Lonker, 1981; Bhattacharya, 1986; Kalt et al., 1999; Kalt, 2000). Since cordierite has the ability to incorporate fluid molecules like H$_2$O and CO$_2$, it can also be used as a monitor of fluid composition during metamorphism (Carrington & Harley, 1996; Knop & Mirwald, 2000; Harley et al., 2002). The simultaneous incorporation of different fluid molecules allows an estimation of the amount of H$_2$O and CO$_2$ in the coexisting fluids or melts and hence calculation of their activities. This information can then be used for improved phase-diagram calculations. Different pressure ($P$) – temperature ($T$) conditions lead to significant variations in the partitioning of H$_2$O and CO$_2$ into cordierite (Harley, 1994; Stevens et al., 1995; Carrington & Harley, 1996; Harley & Carrington, 2001; Thompson et al., 2001; Harley et al., 2002). The dominant channel occupant in natural samples is H$_2$O but, especially in granulite-facies rocks, CO$_2$ and N$_2$ may also become important volatile components (Armbruster, 1985). For instance Rigby et al. (2008) analysed 34 samples from the Etive thermal aureole, Scotland, using Fourier-transform infrared spectroscopy (FTIR) and the measured volatile contents were then used to calculate peak metamorphic H$_2$O and CO$_2$ activities.

Cordierite has also received considerable attention as an electronic packaging material, one of the key technologies to meet a variety of microelectronic applications, because of its low dielectric constant and thermal expansion coefficient (Tummala, 1991; Shannon et al., 1992). In order to obtain more accurate results on dielectric constants and the dielectric loss of cordierite, the contributions of channel H$_2$O and CO$_2$ must be taken into account (Shannon et al., 1992). The thermal expansion coefficient, dielectric constant and Young’s modulus of cordierite ceramics may also vary due to the substitution of part of the oxygen atoms by nitrogen (Unuma et al., 1993). As it will be seen in the next section, CO$_2$ determination using micro-Raman spectroscopy has been done for quite a while (e.g., Kolesov & Geiger, 2000). After a review of the previous investigations, this paper presents new data for the improved CO$_2$ determination.
2. Overview of Raman-based CO\textsubscript{2} determination in cordierite

Confocal Raman micro-spectroscopy offers a good tool for quick and destruction-free determination of CO\textsubscript{2} in cordierite (Kolesov & Geiger, 2000). The in situ method can be applied to single crystals and to grains within thin sections. This method is based on linear relationships between the CO\textsubscript{2} content in wt% and the Raman intensity ratio of the CO\textsubscript{2}-stretching mode against two Si–O stretching modes of the cordierite structure in a certain orientation (Kolesov & Geiger, 2000; Kaindl et al., 2006). The incorporation and orientation of CO\textsubscript{2} molecules in the structural channels of cordierite were investigated using various methods including DTA and dehydration studies (Sugiura, 1959), X-ray and neutron diffraction (e.g., Cohen et al., 1977; Armbruster, 1985), IR spectroscopy (Farrell & Newnham, 1967; Goldman et al., 1977; Le Breton, 1989; Vry et al., 1990; Kalt, 2000), proton NMR spectroscopy (Carson et al., 1982), quasi-elastic neutron scattering (Winkler et al., 1994b), and quantum mechanical calculations (Winkler et al., 1994a). Most of the rod-shaped CO\textsubscript{2}-molecules within the channels are aligned perpendicular to the crystallographic c-axis (Farrell & Newnham, 1967); only a small part is aligned parallel to the c-axis (Farmer, 1974; Armbruster, 1985). Infrared spectroscopic studies confirm the position of the CO\textsubscript{2}-molecule parallel to the a-axis (Armbruster & Bloss, 1982; Armbruster & Bürgi, 1982; Aines & Rossman, 1984; Khomenko & Langer, 2005). According to the Raman- and IR-spectroscopic examinations of Kolesov & Geiger (2000) at least 90% of the CO\textsubscript{2}-molecules are aligned parallel to the a-axis, less than 10% parallel to b. The position parallel to the a-axis is energetically favoured, because the diameter of the channels is bigger in direction of the a-axis than in direction of the b-axis (Hochella et al., 1979).

To gain the maximum intensity of the Raman-active, symmetric 2\textsubscript{v1} vibrational mode of CO\textsubscript{2} at 1383 cm\textsuperscript{-1}, the Raman spectra have to be recorded in aa-geometry (abbreviated Porto notation, where the first symbol gives the polarization direction of the incident light and the second one the polarization direction of the scattered light, Damen et al., 1966; Nasdala et al., 2004). The vector component of the electric field of the incident laser beam must be parallel to the grains a-axis. Both the polarisation plane of the incident laser beam and the scattered Raman light are polarised parallel to a. Two symmetric stretching modes of the cordierite structure at 972 and 1182 cm\textsuperscript{-1} show similar angular dependency and maximum intensity in the aa-oriented Raman spectra. To avoid uncertainties in the measurement of absolute Raman mode intensities, the intensities of the CO\textsubscript{2} stretching mode can be normalized to the lattice vibration modes. The two ratios obtained are approximately constant in the angular range between ±30° and may, therefore, be used for this analytical measurement (Kolesov & Geiger, 2000; Kaindl et al., 2006).

Kolesov & Geiger (2000) investigated ten cordierite samples with varying chemical compositions using polarized single-crystal Raman spectroscopy at room temperature and 5 K and polarized infrared spectroscopy at room temperature. They found a linear trend between the CO\textsubscript{2} content in wt% and the intensity ratios of the Raman active CO\textsubscript{2}-stretching mode and the Si-O-stretching modes using the 514 and 488 nm lines of an Ar-laser for excitation. The CO\textsubscript{2} contents of seven samples were determined previously by bulk measurements (Vry et al., 1990).

Kaindl et al. (2006) presented a method for in situ determination of CO\textsubscript{2} content of natural cordierites in thin section using the 633 nm wavelength. Their investigation of nine synthetic and natural cordierite samples with different chemical compositions and CO\textsubscript{2}-contents led to an improvement of the calibration curve although, for samples with X\textsubscript{CO2} <0.1, the calibration curve was slightly shifted away from the origin. The results agree with those of Kolesov & Geiger (2000) and show a smaller scattering. The Raman measurements were performed on oriented cordierite single crystals. Linear least squares regression of the data showed correlation coefficients R\textsuperscript{2} of 0.912 and 0.883 for equations intersecting the origin of the diagram. The estimated error of about ±0.11 wt% is very similar to the error of the CO\textsubscript{2} determination by SIMS analysis (Harley et al., 2002).

A preliminary investigation was undertaken to expand applicability of the method to three different laser excitation wavelengths (Haefeker et al., 2006). Ten natural cordierite single crystals with different chemical compositions were used for the Raman measurements. Bulk CO\textsubscript{2} contents, determined by coloumetric titration, varied from 0.12 to 1.97 wt% CO\textsubscript{2}.

This work presents new data for the improved CO\textsubscript{2} determinations of cordierite in thin sections at three different laser excitation wavelengths (488, 515 and 633 nm). Sources of errors like orientation dependency, background correction and spectra fitting procedures have been thoroughly investigated, which leads to an increase in the precision of measurement and analysis. The influence of peak shifts and peak broadening due to Fe incorporation based on the investigation by Haefeker et al. (2012) has been corrected. In addition, 2D images of the spatial CO\textsubscript{2} and Fe distribution within natural cordierites, generated by Raman mapping techniques, are presented.

3. Experimental setup and data evaluation

The natural single crystals of cordierite used in this study were collected by Charles A. Geiger, University Kiel, DFG project Nr. Ge 659/6-1. Their CO\textsubscript{2} content was measured after thermal extraction by Bertoldi et al. (2004) using CO\textsubscript{2} coulometric titration. Sample designations, localities, rock types, mineral parageneses, pressure-temperature conditions and chemistry are given in the appendix of Bertoldi et al. (2004). The CO\textsubscript{2} content of the samples varies between 0.12 and 1.97 wt%, the molar
ratio $X_{Fe} = [Fe/(Fe + Mg + Mn + Zn)]$ is between 0.044 and 0.76. A description of the used synthetic cordierite samples can be found in Haefeker et al. (2012). The Raman spectra were recorded on a Labram HR-800 confocal Raman-spectrometer by HORIBA using a 100× objective with a numerical aperture of 0.9. The emission lines of a 17 mW He-Ne-laser at 633 nm and a 30 mW Ar-ion laser at 515 nm and 488 nm were used. The spectra were recorded in the range of 900 to 1400 cm$^{-1}$. The confocal pinhole aperture was 1000 μm and the width of the entrance slit was 100 μm. Light was dispersed by a static grating with 1800 lines/mm. The scattered Raman light was detected by an open-electrode charge-coupled device with 1024 × 256 pixels, each with a size of 43 μm. The spectral resolution, determined by measuring the Rayleigh line was 0.9 to 2 cm$^{-1}$. The system was calibrated with the 520 cm$^{-1}$ line of a Si-wafer. Background and Raman peaks were fitted using the built-in spectrometer software LabSpec with the line-segments baseline correction and convoluted Gauss-Lorentz functions (pseudo-Voigt profile). The replacement of the Ar-ion laser with a 30 mW Nd-YAG laser made it necessary to switch to the 532 nm emission line to record recent Raman profiles and maps.

In order to achieve highest intensities of 2$v_2$(CO$_2$) the $a$-axis of the crystals were oriented parallel to the electric field vector component of the incident laser. To facilitate orientation the untreated single crystals were fixed on a pin on a goniometer head. The details of the orientation procedure can be found in Kaindl et al. (2006). The selection of suitable cordierite grains in thin sections is also described there. The Raman spectra of a natural cordierite single crystal with a CO$_2$ content of 1.74 wt.% in the spectral range 900–1400 cm$^{-1}$ are shown in Fig. 1. In $aa$ scattering geometry, the two components of the Fermi doublet of structurally bonded CO$_2$ at 1383 and 1270 cm$^{-1}$ [2$v_2$, $v_1$(CO$_2$)] can clearly be distinguished (Kolesov & Geiger, 2000). The intensity ratio of the two components in the measured samples ranged between 2.56 and 3.03. In cordierites with very low CO$_2$ contents $v_1$(CO$_2$) intensity was very low. For this study we assumed constant intensity ratios and therefore only 2$v_2$(CO$_2$) was taken into account for the determinations. The two intense bands at 973 and 1183 and the weak band at 1009 cm$^{-1}$ can be assigned to symmetric stretching vibrations of the SiO$_4$ tetrahedra [1$v_1$, 1$v_3$, 2$v_2$(SiO$_4$)] (Kolesov & Geiger, 2000). Detailed band assignments based on quantum-mechanical calculations for both cordierite Fe- and Mg-end-members can be found in Kaindl et al. (2011). The band at 973 cm$^{-1}$ ($v_1$) is related to the stretching of the ring tetrahedra T$_2$1 and the T$_6$ tetrahedron, which connects two M-sites. The peak at 1183 cm$^{-1}$ ($v_3$) is related to the T$_2$1 and T$_3$3 tetrahedra, which stretch in counter-tact. The peak at 1009 cm$^{-1}$ ($v_2$) is caused by the T$_3$1 and T$_3$3 tetrahedral vibration. A low intensity peak can be found at 950 cm$^{-1}$, which is related with the T$_2$1 and the T$_6$ site. In $cc$ scattering geometry, the intensity of 2$v_2$(CO$_2$) strongly decreases and the intensities of $v_1$(CO$_2$) and $v_3$(SiO$_4$) almost disappear. In order to reduce the analytical errors and to yield highest intensities of 2$v_2$(CO$_2$), every grain was rotated into $aa$ geometry before measurement. For example, the 2$v_2$(CO$_2$) intensity of the polarized single-crystal Raman spectra of sample 129875, which contains 1.74 wt% CO$_2$, was approximately 86% higher when measured in $aa$ compared to $cc$ scattering geometry (Fig. 1). Figure 1 also illustrates the spectroscopic approach to find the appropriate orientation: $v_1$(SiO$_4$) can be detected in every scattering geometry (cf. Kolesov & Geiger (2000)) whereas the intensity of $v_3$(SiO$_4$) trends to a maximum in $aa$. Subsequently, in perfect $aa$ geometry the intensity ratio I $v_1$(SiO$_4$)/I $v_3$(SiO$_4$) must trend to a minimum. In contrast to the method presented in Kaindl et al. (2006), the minimum intensity ratio I $v_1$(SiO$_4$)/I $v_3$(SiO$_4$) in $aa$ may lie in the range 0.68–0.9, since it also depends on the Fe-Mg ratio of the cordierite. Considering (1) the experimental setup (static grating, small wavenumber region) and (2) the presented equations based on intensity ratios only, a calibration of the instrument response function (e.g., Ray & McCrecery, 1997) was not undertaken.

4. Results and discussion

4.1. Peak overlap and peak broadening as a result of Fe-incorporation

The incorporation of Fe$^{2+}$ (up to $X_{Fe}$~0.8 in natural crystals) leads to multiple changes in the structure of cordierite (e.g., Wallace & Wenk, 1980; Armbruster & Schreyer, 1990; Malcherek et al., 2001; Geiger & Grams, 2003). As a result most Raman peaks shift towards lower wavenumbers with increasing $X_{Fe}$. Exceptions are the low-intensity bands around 330, 909 and 950 cm$^{-1}$ (Kaindl et al., 2011; Haefeker et al., 2012). In Fe-rich
samples opposite peak shift directions lead to a peak overlap in the 970 cm\(^{-1}\) region. For precise determination of I
\(v_1(\text{SiO}_4)\) the band at 970 cm\(^{-1}\) has to be deconvoluted into two individual peaks. The deconvolution for samples with
\(X_{\text{Fe}} = 0, 0.49\) and 1 is given in Fig. 2a. In Mg-cordierite
\(v_1(\text{SiO}_4)\) can be found at 974 cm\(^{-1}\) and it shifts to 966 cm\(^{-1}\) in the Fe-end-member. A low-intensity peak in Mg-Cordierite at 952 cm\(^{-1}\) shows the opposite shift direction and can be found at 958 cm\(^{-1}\) in samples with
\(X_{\text{Fe}} = 1\). Figure 2b shows the Raman shift as a function of
\(X_{\text{Fe}}\) for natural and synthetic cordierite samples. In addition the intensity (integrated peak area) of the peak 952/962 cm\(^{-1}\) increases as a function of
\(X_{\text{Fe}}\). To determine the intensity increase, six theoretical Gauss-Lorentz functions (pseudo-Voigt profile) with equal function parameters except FWHM were modelled (Fig. 3a). FWHM were taken from the experimentally derived values. This procedure showed that I
\(v_1(\text{SiO}_4)\) of cordierite with
\(X_{\text{Fe}} = 1\) is \(\sim 2.8\) times higher than I
\(v_1(\text{SiO}_4)\) of cordierite with
\(X_{\text{Fe}} = 0\). Based upon this model, correction factors for I
\(v_1(\text{SiO}_4)\) at six different
\(X_{\text{Fe}}\) were calculated (Fig. 3b). Linear interpolation can be applied for compositions between two data points. These correction factors were also applied to I
\(v_3(\text{SiO}_4)\). The
\(X_{\text{Fe}}\) value can be estimated by the shifts of selected Raman peaks (Haefeker et al., 2012) or, when available, chemical data from electron microprobe analysis can be used.
4.2. The influence of background correction and peak fitting

For the precise determination of the integrated peak areas \( I_{n2}(CO_2) \), \( I_{n1}(SiO_4) \) and \( I_{n3}(SiO_4) \) the recorded spectra have to be corrected for their background. When an automatic software-based baseline determination and correction function is used, a revision is recommended to manually correct or subtract misplaced background points, especially when the signal-to-noise ratio of the spectra is low. In some cases additional background points are needed for proper background definition. Erroneously or over-corrected spectra can result in a reduction or increase of the integrated peak area and thus wrong intensity ratios. In addition, wrong background correction can cause peak distortions, influencing both peak-fit quality and intensities.

In Fe-rich samples two peaks between 950 and 970 cm\(^{-1}\) overlap. In samples with \( X_{Fe} > 0.5 \) the de-convolution of the band into two single peaks is error-prone and can lead to erroneous \( I_{v1}(SiO_4) \) peak intensities. Therefore, as starting parameters for the fit functions the position 956 should be fixed and for 965 cm\(^{-1}\) a FWHM of 15 cm\(^{-1}\) should be given and variability restricted to \( \pm 5 \) cm\(^{-1}\). Examples of peak fitting and related sources of errors are given e.g. in Bradley (2007) and Knorr (2011).

4.3. Calibration diagrams

The intensity ratios \( I_1 = 2v_2(CO_2)/I_{v1}(SiO_4) \) and \( I_2 = 2v_2(CO_2)/I_{v3}(SiO_4) \) for three different laser excitation wavelengths are shown in Fig. 4–6. Least square regressions yielded very good linear correlations between both intensity ratios and CO\(_2\) contents (wt%) as indicated by high correlation coefficients \( (R^2 > 0.98) \). One sample shows larger deviations (sample TA-1), which is most likely due to smaller CO\(_2\) contents than the bulk composition determined by Bertoldi et al. (2004). The standard errors of prediction of CO\(_2\) concentrations by using the regression equations range between \( \pm 0.04 \) to 0.07 wt\%, which is a significant reduction compared to the error of \( \pm 0.11 \) wt\% given by Kaindl et al. (2006). The correlation coefficients \( R^2 \) for all equations are between 0.986 and 0.995, the standard errors of prediction for the CO\(_2\) concentrations were calculated with the equation:
where \( n \) is the number of observations, \( \bar{c}_{1.2} \) the mean CO\(_2\) concentration determined by intensity ratios \( I_{1.2} \), and \( I_{1.2} \) the mean intensity ratios.

The regression equations may be used for the determination of the CO\(_2\) content of unknown cordierite samples.

1. 488 nm
   (a) \( c_1 (\text{wt}%) \pm 0.048 = 1.6874 \cdot I_1 \)  
   (b) \( c_2 (\text{wt}%) \pm 0.04 = 2.3071 \cdot I_2 \)

2. 514 nm
   (a) \( c_1 (\text{wt}%) \pm 0.047 = 1.6875 \cdot I_1 \)  
   (b) \( c_2 (\text{wt}%) \pm 0.072 = 2.2748 \cdot I_2 \)

3. 633 nm
   (a) \( c_1 (\text{wt}%) \pm 0.043 = 1.5579 \cdot I_1 \)  
   (b) \( c_2 (\text{wt}%) \pm 0.054 = 2.4374 \cdot I_2 \)

### 4.4. Application to natural cordierites in thin sections

A granulite-facies metapelite from Kösseldorf in the Sauwald area (southern Bohemian Massif, Upper Austria), containing the assemblage garnet + spinel + cordierite + sillimanite + biotite + plagioclase + K-feldspar + quartz (Tropper et al., 2006), was used for the measurements. Within an uncovered, polished thin section two cordierite porphyroblasts in suitable aa-scattering geometry were found and selected for the CO\(_2\) determinations. The \( X_{Fe} \) determinations were done with the calibration diagrams presented by Haefeker et al. (2012). Along a line profile across a grain, 27 measurement points over a distance of 60 µm were recorded and the CO\(_2\) contents calculated by inserting into Equation (2b) and a correction factor of 1.4 for \( X_{Fe} \sim 0.5 \) (Fig. 3b and 7a, b). The CO\(_2\) distribution is homogeneous with CO\(_2\) contents in the range of 0.27–0.31 (±0.07) wt%. The Raman signal of...
point 2 on the grain boundary was very weak, resulting in a higher error of the CO₂ content determination. The points 1 and 27 belong to the neighbouring grains (plagioclase, quartz); therefore the CO₂ content was set to zero.

A hyperspectral Raman image (112 × 263 μm, 50 × 50 data points) of a second porphyroblast also shows the 2D homogeneous distribution of CO₂ and constant X_{Fe} within the grain (Fig. 8a–c). Figure 8b displays X_{Fe} in grey-scales,

Fig. 6. a, b: CO₂-content in wt% vs. the intensity ratios, measured at an excitation wavelength of 633 nm.

Fig. 7. a, b: a. Microphotography of a cordierite prophyroblast in transmitted polarized light. The vertical line marks the profile containing 27 measurement points over a distance of 60 μm. The linear structures are fibrolite inclusions. b. CO₂ contents (wt%) from top to bottom across the cordierite prophyroblast, calculated by the I_{1383}/I_{1182} intensity ratios, Equation (2b) and a correction factor for X_{Fe} ~ 0.55. The stippled line interconnects the data points for clarity purposes only.
Fig. 8c displays the CO$_2$ contents in grey-scales, calculated by Equation (2b) and a correction factor of 1.4 for X$_{Fe}$/$C_{24}$0.5. Deviations from a homogeneous CO$_2$ content of 0.28/$C_{6}$0.07 wt% throughout the grain are caused by errors in automatic background correction and determination of the integrated peak areas as well as inclusions (black and white spots in Fig. 8c).

5. Conclusions

The presented correlation diagrams allow fast and non-destructive determinations of CO$_2$ at standard errors of prediction from ±0.04 to 0.07 wt%. A linear correlation between CO$_2$ contents in wt% and the intensity ratios of the CO$_2$ mode at 1383 cm$^{-1}$ and the two lattice vibration modes at 972 cm$^{-1}$ and 1185 cm$^{-1}$ was found. The diagrams in Kaindl et al. (2006) did not take into account peak broadening in Fe-bearing samples (Haefeker et al., 2012), which could lead to erroneous results for samples with low CO$_2$ contents. Hence a correction for the influence of Fe-incorporation on selected Raman peaks was introduced. Additionally the influence of two peaks at 955 and 1157 cm$^{-1}$ in Fe-rich samples have been considered. It could be confirmed by our investigations that most of the CO$_2$ in the channel cavities is preferentially aligned parallel to the a-axis.

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References


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