

# A semi-quantitative technique for determination of CO<sub>2</sub> in cordierite by Raman spectroscopy in thin sections

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**Abstract:** Confocal micro-Raman spectroscopic measurements at high spatial resolution of about 5 µm<sup>3</sup> were performed to determine the CO<sub>2</sub> contents of natural cordierite. Nine cordierite single-crystals with known CO<sub>2</sub> concentrations, previously determined by colorimetric titration, were studied to obtain a calibration curve for this method. Measurements were also performed to quantify the CO<sub>2</sub> content of cordierite porphyroblasts in a thin section of a granulite-facies metapelite from Kösseldorf, Sauwald Area, Southern Bohemian Massif, Upper Austria. Fifteen points along a traverse through a large (560 µm) single crystal revealed low CO<sub>2</sub> contents of 0.14 ± 0.11 wt. % CO<sub>2</sub>. These results provide some constraints on the activity of CO<sub>2</sub> [*a*(CO<sub>2</sub>)] during granulite-facies metamorphism, only if fluid-saturated conditions prevailed or independent H<sub>2</sub>O measurements were made.

**Key-words:** Raman spectroscopy, cordierite, CO<sub>2</sub>, thin section, Bohemian Massif, Sauwald.

## 1. Introduction

Cordierite is a common metamorphic mineral in many medium- to high-grade aluminous rocks of the crust. In equilibrium with other Fe-Mg-silicates, cordierite can be used as geothermobarometer in high-grade (granulite-facies) rocks (e.g. Lonker, 1981; Bhattacharya, 1986; Kalt *et al.*, 1999; Kalt, 2000). Molecular CO<sub>2</sub> and H<sub>2</sub>O can be incorporated in the channel-cavities of cordierite (Goldmann *et al.*, 1977; Armbruster & Bloss, 1982; Armbruster, 1985, 1986), influencing its pressure- and temperature-stability field and geothermobarometric calculations. Recently, several authors investigated cordierite as a petrogenetic indicator in high-grade metapelites (Mirwald & Knop, 1995; Knop & Mirwald, 2000; Harley & Carrington, 2001; Thompson *et al.*, 2001, 2002; Harley *et al.*, 2002). Due to the incorporation of fluid molecules (e.g. CO<sub>2</sub>, H<sub>2</sub>O), cordierite can be used as a monitor of fluid composition during metamorphism (Carrington & Harley, 1996; Knop & Mirwald, 2000; Harley *et al.*, 2002). Because cordierite can incorporate both H<sub>2</sub>O and CO<sub>2</sub>, it can be used to estimate the H<sub>2</sub>O and CO<sub>2</sub> contents of coexisting fluids or melts and thus provide information on *a*(H<sub>2</sub>O) and *a*(CO<sub>2</sub>). Partitioning of H<sub>2</sub>O and CO<sub>2</sub> into cordierite shows significant variations with changing *P-T* conditions (e.g. Harley *et al.*, 2002). Harley & Carrington (2001) and Thompson *et al.* (2001) showed that H<sub>2</sub>O and CO<sub>2</sub> contents increase with increasing pressures and decrease with increasing temperatures.

Several studies investigated the concentration of CO<sub>2</sub> and H<sub>2</sub>O in natural cordierite single crystals (see Bertoldi *et al.*,

2004), where the CO<sub>2</sub> and H<sub>2</sub>O contents of crystals were determined quantitatively by colorimetric titration (e.g. Bertoldi *et al.*, 2004; Behrens *et al.*, 2004). Spectroscopic investigations and semi-quantitative determinations of CO<sub>2</sub> and H<sub>2</sub>O in natural Mg- and Fe-rich cordierites have been performed by Raman and IR-spectroscopy (Kolesov & Geiger, 2000). Spatial variations of volatile content single crystals at a microscopic scale were shown in the investigation by Harley *et al.* (2002). They analyzed *in-situ* and simultaneously CO<sub>2</sub> and H<sub>2</sub>O in thin sections of granulitic and migmatitic rocks by secondary ion mass spectrometry (SIMS) down to spot sizes of 20 µm diameter and 2–3 µm depth. The errors of this method are low, typically ± 0.08 wt. % CO<sub>2</sub>. Kalt (2000) measured H<sub>2</sub>O and CO<sub>2</sub> concentrations of cordierite by IR spectroscopy in doubly-polished thick sections. She reports errors of about 10–12 % for the average total H<sub>2</sub>O content and up to 50 % for CO<sub>2</sub> at a spatial resolution of about 100 µm. Micro-Raman spectroscopy provides high areal resolution of about ± 2 µm and effective volume resolution of ≤ 5 µm<sup>3</sup> (Markwort *et al.*, 1995; Nasdala *et al.*, 1996). Directional dependency of the measurements due to the polarization behavior of the analyzed crystals (Loh, 1973; Tlili *et al.*, 1989; Nasdala *et al.*, 2004), can be overcome by selecting appropriate scattering geometries, which will be discussed.

This paper presents a method for the semi-quantitative determination of the CO<sub>2</sub> content of natural cordierites *in-situ* in thin sections. The potential of the semi-quantitative Raman spectroscopy is demonstrated by determining the CO<sub>2</sub> contents along a traverse across a natural microscopic

cordierite porphyroblast from a granulite-facies metapelite from Kösseldorf, Sauwald Area, Southern Bohemian Massif, Upper Austria.

## 2. Experimental procedures

### 2.1 Electron microprobe analyses

Electron microprobe analyses of minerals were performed with a JEOL 8100 Superprobe at the Institute of Mineralogy and Petrography at the University of Innsbruck. Analytical conditions were 10 kV and a sample current of 10 nA on brass. Counting times for most elements were 20 s for the peak and 10 s for the background except for Na and K, which were analyzed with longer counting times of 100 s for the peak. Mineral formulae were calculated on the anhydrous basis of 18 oxygen with the program NORM II (Ulmer, 2002, written comm.). The cordierites from Kösseldorf show optical zoning with cores, rich in sillimanite inclusions, and sillimanite-free rims, but no obvious chemical zoning in  $X_{Mg}$  as well as in Na has been detected. The  $X_{Mg}$  ratio,  $[Mg/(Mg + Fe)]$ , is very uniform and ranges from 0.513 to 0.534. The Na contents are low and range from 0.021 to 0.029 Na a.p.f.u. and K contents are extremely low with <0.01 a.p.f.u.

### 2.2 Raman micro-spectroscopy

All Raman spectra were recorded with a LabRAM-HR800 (HORIBA JOBIN-YVON™) confocal spectrometer equipped with an OLYMPUS™ light microscope, enabling transmitted polarized light microscopy. The emission line of a 5.9 mW He-Ne laser at 633 nm was used for excitation. Spectra were recorded in the range from 900 to 1400  $cm^{-1}$ . Measurements were obtained with the 100x objective. The Raman signal was detected with a CCD-camera and the spectra were recorded using the “SCM” technique (Knoll *et al.*, 1990). Beam diameter was about 2  $\mu m$  and the power on the sample surface was 1 mW. All spectra were baseline corrected by subtracting line segments and fitted by using the Gauss-Lorentz functions.

Nine natural cordierite single crystals from different localities were chosen to constraint a calibration curve for semi-quantitative  $CO_2$  determinations. Chemical analyses of each crystal are given in Bertoldi *et al.* (2004, Table 1). Bulk  $CO_2$  and  $H_2O$  contents of these samples were previously measured by colorimetric titration (Bertoldi *et al.*, 2004). Sample numbers, localities, rock type, mineral assemblage and  $P$ - $T$  estimates can be found in Bertoldi *et al.* (2004). The samples cover a wide range of  $CO_2$  and  $H_2O$  contents ranging from 0.12 to 1.74 wt. %  $CO_2$  and 0.37 to 1.67 wt. %  $H_2O$ .

In order to achieve the highest intensities of the  $\nu_1$  mode of structurally bound  $CO_2$ , which is preferentially aligned parallel to the  $a$ -axis of the cordierite crystal (Aines & Rossman, 1984; Armbruster, 1985; Kolesov & Geiger, 2000), the vector component of the electric field of the incident laser must be parallel to the grains  $a$ -axis. Both the polarization plane of the incident laser beam and the scattered Ra-

man light were polarized parallel to  $a$  ( $aa$  scattering geometry in “abbreviated Porto notation”, Damen *et al.*, 1966; Nasdala *et al.*, 2004). In  $aa$  geometry, the intensity ratio of the two modes at 973 and 1185  $cm^{-1}$   $I_{973}/I_{1185}$ , which can be assigned to internal  $SiO_4$  stretching modes, yields lowest values around 0.8 and remains approximately constant in the angular range  $\pm 30^\circ$  around the  $a$ -axis (Kolesov & Geiger, 2000; You *et al.*, 2005). At angles deviating more than  $30^\circ$  from  $aa$ ,  $I_{973}/I_{1185}$  increases due to reduced intensity of the 1185  $cm^{-1}$  mode. The nine cordierite single crystals were therefore oriented by maximizing the internal  $SiO_4$  stretching mode at 1185  $cm^{-1}$ .

A suitable cordierite grain in the thin section from the Sauwald granulite was chosen by combined light-optical polarizing microscopy and Raman spectroscopy. Highest intensities at best signal-to-noise ratios of the  $\nu_1$  mode of  $CO_2$  are achieved, as described above, in  $aa$  scattering geometry. Subsequently, both internal  $SiO_4$  stretching modes at 973 and 1185  $cm^{-1}$  occur in the spectrum with the latter one at maximum intensity. Several grains within a standard, uncovered, polished thin-section, used for electron microprobe analysis, were examined by rotating the microscope stage at crossed polar conditions into the two extinction positions and acquiring the spectra. The carbon coating was removed before Raman spectroscopy to prevent any interference with the laser beam. A grain where both modes could be detected and the  $I_{973}/I_{1185}$  was approximately 0.8 was chosen for the semi-quantitative  $CO_2$  determinations. The  $a$ -axis of this particular grain was parallel to the polarization plane of the laser and the angle between  $a$  and the thin section plane was lower than  $30^\circ$ . Fifteen Raman spectra were recorded across the grain. Each spectrum was baseline-corrected and fitted applying the same procedures as for the spectra of the nine cordierite reference crystals.

## 3. Results

### 3.1 Calibration curve for semi-quantitative $CO_2$ determinations

The Raman spectrum in  $aa$ -geometry of a natural cordierite macro-crystal is shown in Fig. 1. The band at 1383  $cm^{-1}$  is the symmetric stretching mode  $\nu_1$  of the structurally bound  $CO_2$  molecule within the cordierite structure. Previous results showed that more than 90% of  $CO_2$  is preferentially aligned parallel to the  $a$ -axis (Aines & Rossman, 1984; Armbruster, 1985; Kolesov & Geiger, 2000). Possible small fractions of  $CO_2$  deviating from this preferential alignment were not investigated in this study but may introduce significant errors at higher  $CO_2$  contents (see below).

The intensity ratios  $I_1 = I_{1383}/I_{973}$  and  $I_2 = I_{1383}/I_{1185}$  vs. known  $CO_2$  content in wt. % for nine oriented cordierite single crystals are given in Fig. 2. In order to avoid the difficulties in obtaining absolute Raman mode intensities, the integrated peak area of the symmetric stretching mode,  $\nu_1$  at 1383  $cm^{-1}$ , was normalized against the two internal  $SiO_4$  stretching modes located at 973 and 1185  $cm^{-1}$ . For comparison the data of Kolesov & Geiger (2000) are also shown. Apart from a slightly higher scatter within the data set of

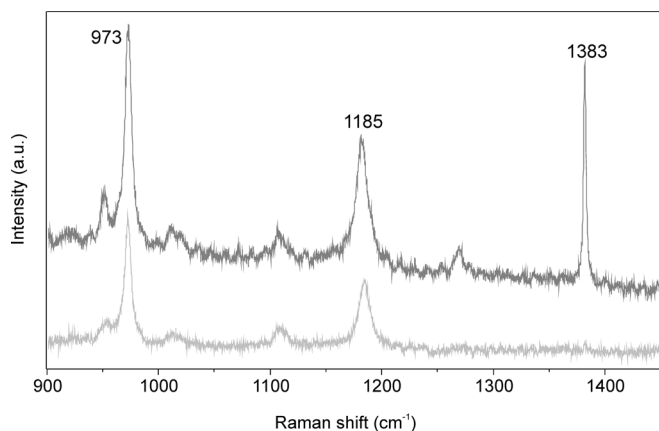


Fig. 1. Polarized Raman spectrum of two natural cordierite single-crystals, recorded in *aa*-geometry, in the region between 900 and 1500 cm<sup>-1</sup>. The two peaks at 973 and 1185 cm<sup>-1</sup> can be assigned to the internal SiO<sub>4</sub> stretching vibrations of the cordierite structure (You *et al.*, 2005). The CO<sub>2</sub> content of the two measured crystals is clearly distinguishable by amplitude and peak area of the  $\nu_1$  symmetric stretching vibration of structurally bound CO<sub>2</sub> in the cordierite channels at 1383 cm<sup>-1</sup>. The upper, dark-grey spectrum was taken from sample CtsiMm, which contains 0.90 wt.% CO<sub>2</sub>, the lower, light-grey spectrum from sample C005 with 0.12 wt.% CO<sub>2</sub>. Detailed petrographic and chemical descriptions of the samples are given in Bertoldi *et al.* (2004).

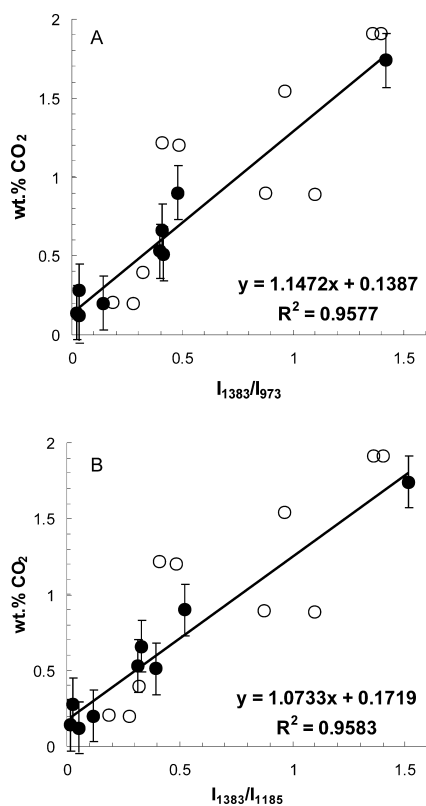


Fig. 2. CO<sub>2</sub> content in wt.% versus the  $I_{1383}/I_{973}$  (A) and  $I_{1383}/I_{1185}$  (B) intensity ratios of nine cordierite crystals (black circles), measured with a laser with an excitation wavelength of 633 nm. All measurements were performed in *aa*-geometry. The open circles indicate the data from the data set of Kolesov & Geiger (2000), which is shown for comparison. The solid lines indicate the least-squares regression to our data set. The regression equations and the R<sup>2</sup> coefficients are also shown. The estimated error is 0.11 wt.% CO<sub>2</sub> for both intensity ratios.

Kolesov & Geiger (2000) both data sets are in good agreement, although the latter was recorded at different excitation wavelengths (488 and 514 nm). Linear least squares estimation of our data yields two regression equations  $c_1$  and  $c_2$ , which can be used for the calculation of CO<sub>2</sub> concentrations out of the two intensity ratios  $I_1$  and  $I_2$ :

$$c_1 = 0.139 + 1.147 \cdot I_1 \text{ (wt. \%)} \quad (1)$$

and

$$c_2 = 0.178 + 1.073 \cdot I_2 \text{ (wt. \%)} \quad (2)$$

The correlation coefficient R<sup>2</sup> is 0.958 for both equations. The following equation was used to estimate the standard error of prediction of CO<sub>2</sub> concentrations:

$$\sigma(c_1, I_1) = \sqrt{\frac{1}{n-2} \left[ \sum (\bar{c}_1 - c_1)^2 - \frac{[\sum (\bar{I}_1 - I_1)(\bar{c}_1 - c_1)]^2}{\sum (\bar{I}_1 - I_1)^2} \right]} \quad (3)$$

$n$  is the number of observations, in our case nine,  $\bar{c}_1$  and  $\bar{I}_1$  are the mean values of  $c_1$  and  $I_1$ , respectively. The error of  $c_2$  was estimated analogously. Both intensity ratios deliver an error of about  $\pm 0.11$  wt.%, which is very similar to the error of CO<sub>2</sub> determination by SIMS analysis (Harley *et al.*, 2002).

Theoretically, for cordierite lacking CO<sub>2</sub>, the regression equations (1) and (2) should start in the origin of the diagram. Linear least square fitting using this boundary condition resulted in the following regression equations:

$$c_1 = 1.3146 \cdot I_1 \text{ (wt. \%)} \quad (4)$$

and

$$c_2 = 1.2651 \cdot I_2 \text{ (wt. \%)} \quad (5)$$

The correlation coefficients R<sup>2</sup> for equations (4) and (5) are lower (0.912 and 0.883) due to a slightly worse fit. Kolesov & Geiger (2000) attributed the scatter in the intensity ratios to uncertainties either in the bulk CO<sub>2</sub> determination or to local differences in the CO<sub>2</sub> contents of the natural cordierite single crystals used for their calibration. Simple error propagation shows that the total error increases above 0.05 wt.% CO<sub>2</sub> not preferentially aligned parallel to the *a*-axis. Subsequently, especially at high CO<sub>2</sub> contents, the estimated concentrations are slightly too low.

### 3.2 The CO<sub>2</sub> content of granulite-facies cordierite from the Southern Bohemian Massif: implications for $a(\text{CO}_2)$

Following the procedure outlined above, a cordierite porphyroblast in a granulite-facies metapelite with the assemblage garnet + spinel + cordierite + sillimanite + biotite + plagioclase + K-feldspar + quartz from Kösseldorf from the Sauwald Area (Southern Bohemian Massif, Upper Austria) was investigated. Mineral chemical and textural data indicate three stages of mineral growth in the metapelites: 1) the metamorphic peak phase assemblage is garnet + cordierite + green spinel + sillimanite + plagioclase (An<sub>35-65</sub>) and occurs as inclusions in garnet porphyroblasts; 2) the post-peak assemblage in the matrix is comprised of cordierite + spinel

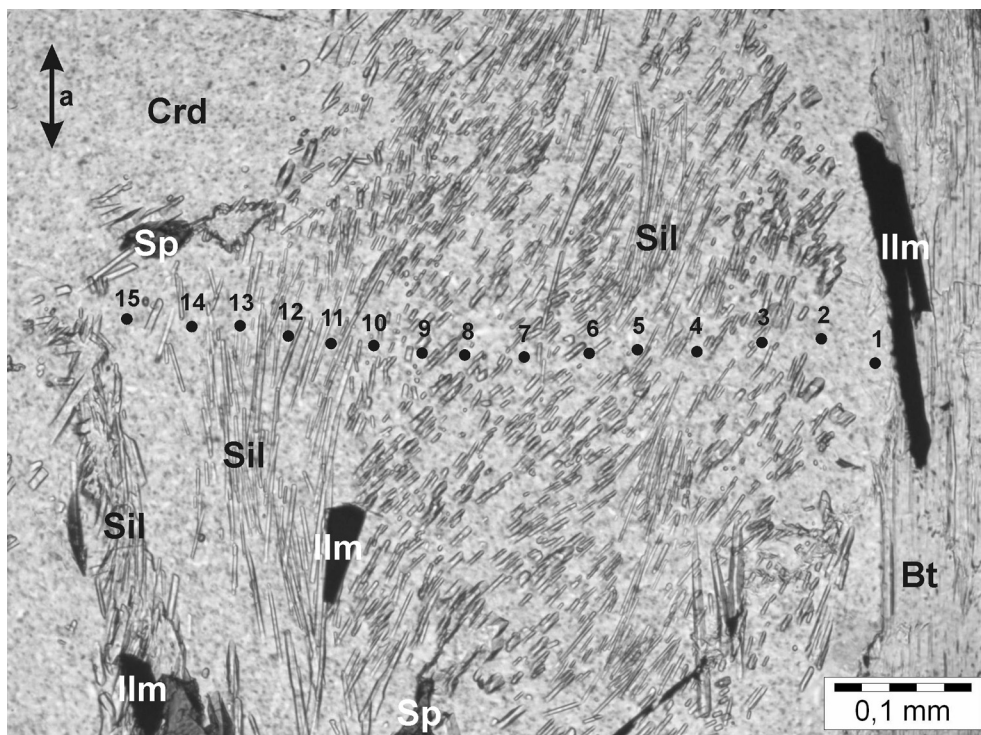


Fig. 3. Microphotograph of the cordierite porphyroblast investigated in this study in transmitted polarized light. Spectra were recorded in the inclusion free areas between the sillimanite inclusions. The black circles indicate the measuring spots across the grain, numbered consecutively from 1 to 15. The distance between point 1 and 15 is approximately 560  $\mu\text{m}$ . The crystallographic  $a$ -axis of the grain was N-S oriented (arrow), parallel to the polarization direction of the excitation laser, and lies approximately within the thin section plane. Abbreviations: Bt – biotite; Crd – cordierite; Ilm – ilmenite; Sil – sillimanite; Sp – spinel.

(brown-green and brown)  $\pm$  sillimanite  $\pm$  garnet + plagioclase ( $\text{An}_{10-45}$ ); and 3) at a late stage fibrolite, muscovite and albite-rich plagioclase ( $\text{An}_{0-15}$ ) grew. The clockwise  $P$ - $T$  evolution of this rock ranges from 750–840  $^{\circ}\text{C}$  and 0.29–0.53 GPa for the peak assemblage to 620–730  $^{\circ}\text{C}$  and 0.27–0.36 GPa for the post-peak assemblage to 530–570  $^{\circ}\text{C}$  below 0.38 GPa (Deibl *et al.*, 2003a, b).

We used equations (4) and (5) and the determined intensity ratios  $I_1$  and  $I_2$  to calculate an average  $\text{CO}_2$  content at each point along the line across the cordierite grain shown in Fig. 3. The average  $\text{CO}_2$  contents range from 0.06 to 0.26 wt. % (Fig. 4). Both equations yielded identical results within the estimated error of individual measurements of  $\pm 0.11$  wt. %. At point 5 and 9 a high background prevented detection of the  $\nu_1$  mode of  $\text{CO}_2$ .

The measured  $\text{CO}_2$  contents from this study are in accordance with cordierite data from high-grade metamorphic rocks (Vry *et al.*, 1990; Kalt, 2000; Harley *et al.*, 2002). Taking into account the relatively large errors of  $\pm 0.11$  wt. %, the spatial variation of the  $\text{CO}_2$  content from core to rim is insignificant in this particular grain. However, the bulk  $\text{CO}_2$  content 0.14 wt. % is at the lower end of the  $\text{CO}_2$  contents of the natural cordierites, which were used for this calibration and reach up to 2 wt. %  $\text{CO}_2$  (Bertoldi *et al.*, 2004). At higher concentrations, the proof of  $\text{CO}_2$  variations on a grain-scale should thus be possible.

Harley *et al.* (2002) investigated the use of cordierite as a sensor of fluid conditions during high-grade metamorphism. Their study is based upon the experiments in the systems cordierite- $\text{H}_2\text{O}$  and cordierite- $\text{CO}_2$  by Harley & Carington (2001) and Thompson *et al.* (2001). Harley *et al.* (2002) showed calculated  $\text{H}_2\text{O}$ - $\text{CO}_2$  saturation surfaces of fluids in equilibrium with cordierites at similar  $P$ - $T$  conditions (800  $^{\circ}\text{C}$ , 0.5 GPa), compared to our study. Our mea-

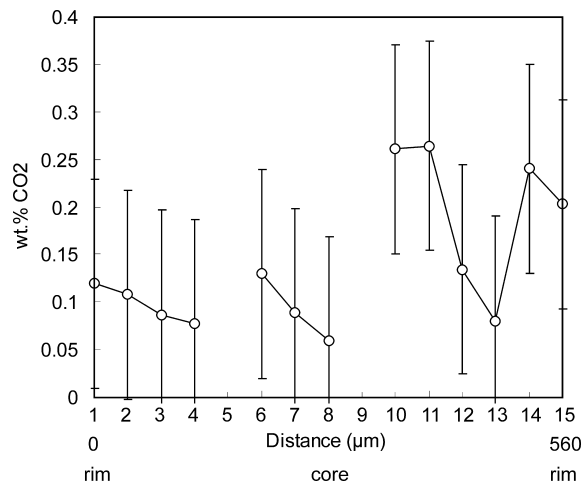


Fig. 4. The variation of the measured  $\text{CO}_2$  content (wt. %) across the cordierite porphyroblast. Open circles represent the average of the calculated  $\text{CO}_2$  values by using the  $I_{1383}/I_{973}$  and  $I_{1383}/I_{1185}$  intensity ratios and the linear regression equations (4) and (5) obtained in this study. Estimated error bars of  $\pm 0.11$  wt. %  $\text{CO}_2$  are also added to the data. The black line represents the interpolation between the points and is only shown for clarity. Both equations (4, 5) yield consistent  $\text{CO}_2$  contents. At points 5 and 9 a strong increase in background prevented detection of the  $\text{CO}_2$  modes.

sured  $\text{CO}_2$  contents indicate low molar concentration of  $\text{CO}_2$ , namely below 0.04. Thus  $X_{\text{CO}_2}$  values would be  $< 0.05$ . This corresponds to calculated  $a(\text{CO}_2)$  values ranging from 0 to 0.27. If fluid-saturated conditions would have prevailed, the number of moles of  $\text{H}_2\text{O}$  should be high, around 0.8, thus yielding a high  $a(\text{H}_2\text{O})$  of ca. 0.78. This would be an unusual high  $a(\text{H}_2\text{O})$  value for these high-grade granulite-facies rocks, and thus would lead to a very high

degree of melting which is not compatible with the observed textures. These calculations indicate that H<sub>2</sub>O-undersaturated conditions must have therefore prevailed during granulite-facies metamorphism, which has been proposed in previous studies of this area (e.g. Kalt *et al.*, 1999, 2000). Therefore calculations of  $a(\text{CO}_2)$  at H<sub>2</sub>O-undersaturated conditions are only possible if independent measurements of the H<sub>2</sub>O contents (e.g. IR, SIMS) are performed.

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