A crystal-chemical study of cordierite, synthesis and stability at variable $\text{H}_2\text{O}$ and $\text{CO}_2$ concentration: geological and technological applications

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“Though we cannot SEE angles, we can INFER them, and this with great precision. Our sense of touch, stimulated by necessity, and developed by long training, enables us to distinguish angles far more accurately than your sense of sight, when unaided by a rule or measure of angles.”

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...ad maiora!
ABSTRACT

Cordierite is a relatively widespread mineral, having a peculiar ability to trap H\textsubscript{2}O and CO\textsubscript{2} up to very high pressure and temperature. This is a unique property for a rock forming silicate, and has a significant role in the mineralogical equilibria in HT and UHT metamorphism (Harley and Thompson, 2004). In this work, great attention was paid to the study of the diffusion mechanisms of carbon dioxide inside these channel-like structures. Considering that carbon dioxide is probably one of the major responsible for long-term climate change on Earth (IPCC, 2005), the ability of these minerals to entrap CO\textsubscript{2} could provide insights for future research for the permanent CO\textsubscript{2} storage in minerals.

The aim of this Thesis was to investigate the diffusion of CO\textsubscript{2} across cordierite, and address possible implications from both a geological and a technological point of view. The work was completed by the parallel study of beryl, which is structurally correlated to cordierite.

The text is divided into four major sections:

1) In the first section (Chapter 1 and 2) I introduce the issues related to the qualitative and quantitative analysis of H\textsubscript{2}O and CO\textsubscript{2} in cordierite by means of Fourier-Transform Infrared Spectroscopy (hereafter FTIR). In detail I show the crystal-chemical and spectroscopic study of chemically different samples, from an almost Mg-cordierite end-member to its Fe-analogue sekaninaite. Additionally I will discuss the calibration of the molar absorption coefficient $\varepsilon$, an indispensable coefficient for quantitative measurement in FTIR micro-spectroscopy. Both these chapters have been published in first-rank mineralogical and petrological journals and are thus reported here as they are published.

2) In the second section (Chapter 3 and 4) I'll focus in mechanism of outward CO\textsubscript{2} diffusion: to this purpose, oriented single-crystal cordierite slabs were heated by using a
heating-stage under the FTIR microscope and investigated using in situ FTIR µ-spectroscopy. Part of this study was done using a synchrotron-light source (SR-FTIR) to improve the signal-to-noise ratio and attain higher spatial resolution in the data. In this section I studied in particular the absorbance variation at constant temperature as a function of time, and evaluated the kinetic and diffusion parameters for CO₂ expulsion from the matrix.

3) In the third section (Chapter 5) I discuss the mechanism of inward diffusion of CO₂ within the structural channel of cordierite and beryl under different pressure, temperature and time conditions. The experimental work was done using a piston cylinder apparatus. In this section I’ll make extensive use of high resolution single-crystal FTIR Focal Planar Array (FTIR-FPA) imaging to characterize possible inhomogeneity in the CO₂/H₂O across the samples, and identify the possible pathways for CO₂ diffusion. As it will be shown, the spectroscopic imaging was also necessary to locate the analytical spots for CO₂ measurements in the sample.

4) The last part (Chapter 6, 7 and 8) covers additional features observed during the work. In particular, chapter 6 deals with a multidisciplinary study of a peculiar diffusion pattern of CO₂ across an hourglass zoned beryl. This chapter relates on advances in techniques such as Time Of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) chemical imaging, polarized light FPA imaging and High Resolution SR-FTIR mapping. Chapter 7 deals with changes in coordination environment and physical state of H₂O in low-water beryl and cordierite. Chapter 8 eventually presents a summary of the work and illustrates the technological applications of CO₂ diffusion in beryl.
RIASSUNTO

La cordierite è un minerale abbastanza diffuso che ha la capacità di intrappolare H₂O and CO₂ anche ad altissime pressioni e temperature. Questa è una proprietà unica per un silicato diffuso nelle rocce che gioca un ruolo fondamentale negli equilibri mineralogici nel metamorfismo di alta o altissima temperatura (Harley and Thompson, 2004). In questo lavoro ci siamo dedicati allo studio approfondito dei meccanismi di diffusione nell’anidride carbonica all’interno di strutture cristalline a “canale”. Inoltre, considerando che l’anidride carbonica è uno delle principali cause dei cambiamenti climatici terrestri a lungo termine (IPCC, 2005), la capacità di questi minerali di intrappolare la CO₂ potrebbe fornire spunti per future ricerche sullo stoccaggio permanente della CO₂ nei minerali.

Lo scopo di questa tesi è quindi quello di studiare la diffusione della CO₂ nella cordierite, e individuare le possibili implicazioni da un punto di vista geologico e tecnologico. Il lavoro è stato arricchito con lo studio in parallelo della diffusione della CO₂ nel berillo, che è strutturalmente correlato alla cordierite.

Il lavoro di tesi è suddiviso in quattro sezioni principali:

1) Nella prima sezione (Capitoli 1 e 2) introduco le problematiche relative all’analisi qualitativa e quantitativa di H₂O e CO₂ nella cordierite attraverso la Spettroscopia Infrarosso a Trasformata di Fourier (più comunemente FTIR). In particolare illustro lo studio cristallochimico e spettroscopico di campioni di variegata composizione chimica, a partire da cordieriti di Mg fino all’analogo estremo ferrifero sekanaïte. Inoltre illustrerò la messa a punto della calibrazione del coefficiente di assorbimento molare ε, un parametro indispensabile per misure quantitative in micro-spettroscopia FTIR. Entrambi i capitolo sono
stati pubblicati su riviste di mineralogia e petrologia di alto impatto e qui riportati come da pubblicazione.

2) La seconda sezione (Capitoli 3 e 4) è focalizzata sui meccanismi di espulsione della CO$_2$: a questo proposito sono state riscaldate delle lamelle orientate provenienti da cristalli singoli di cordierite attraverso un tavolino riscaldante installato direttamente su di un microscopio FTIR ed analizzati tramite micro-spettroscopia FTIR in situ. Parte dello studio è stato condotto utilizzando una sorgente di luce di sincrotrone (SR-FTIR) in modo da aumentare il rapporto segnale-rumore e raggiungere una migliore risoluzione spaziale. In questa sezione ho studiato in dettaglio la variazione degli assorbimenti in funzione del tempo a temperatura costante, e ho ricavato i parametri cinetici e di diffusione per l’estrazione della CO$_2$ dai canali strutturali della cordierite.

3) Nella terza sezione (Capitolo 5) discuto il meccanismo di diffusione della CO$_2$ attraverso i canali strutturali di cordierite e berillo riequilibrati a varie condizioni di pressione, temperatura e tempo. La procedura sperimentale è stata condotta usando un apparato di tipo piston-cylinder. In questa sezione farò uso intensivo di imaging FTIR bidimensionale (FTIR-FPA) ad alta risoluzione su cristallo singolo per individuare possibili inomogeneità nella distribuzione di H$_2$O/CO$_2$ nei campioni trattati, ed identificare i possibili percorsi di diffusione della CO$_2$. Inoltre l’imaging FTIR è indispensabile per localizzare i punti analitici per la misura quantitativa della CO$_2$.

4) Nell’ultima parte del manoscritto (Capitoli 6, 7 e 8) discuterò ulteriori problematiche incontrate durante il lavoro di tesi. In particolare, il capitolo 6 illustrerà uno studio multidisciplinare su di un peculiare percorso di diffusione della CO$_2$ osservato in un berillo zonato a clessidra. Questo capitolo illustra alcune tra le tecniche più innovative nell’analisi mineralogica come le mappe composizionali in Time Of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS), imaging FTIR-FPA in luce polarizzata e mappatura SR-FTIR and altissima risoluzione. Il capitolo 7 è focalizzato sulle variazioni di coordinazione e speciazione dell’H$_2$O in berilli e cordieriti con poca acqua. Infine il capitolo 8 riporta un riassunto dell’intero lavoro svolto e illustra le implicazioni tecnologiche della diffusione della CO$_2$ nel berillo.
1. Structural details of cordierite and beryl and their relevance on technology

Carbon dioxide (CO$_2$) generated by the combustion of fossil fuels is by far the most abundant greenhouse gas; its reduction in the atmosphere is therefore a primary environmental concern. Due to several reasons, it can be easily understood that fossil fuels will continue to play a significant role in the world’s economy at least in the following decades, thus emphasis must be placed on improving methods to decrease the amount of CO$_2$ dispersed in the environment. The reduction of CO$_2$ from the atmosphere can be achieved by efficiency improvements in power plants, use of alternative energy technologies, sequestration of CO$_2$, or some combination of these methods. Up to the present, several techniques have been considered, and these include: 1) forestation, where CO$_2$ is removed from the atmosphere by biological activity; 2) aquifer storage, in which CO$_2$ is injected into terrestrial aquifers where it is trapped hydro-dynamically; 3) deep sea storage, where CO$_2$ is injected into the ocean at approximately 3,000 meter depths, where it is believed to remain stable; and 4) mineral carbonation, in which CO$_2$ is reacted with minerals to form solid carbonates. This final form of sequestration is the most efficient method, because the carbonates are stable over geologic time periods (millions of years), rather than the hundreds to thousands of years of stability expected for the first three forms of sequestration. This process is however highly expensive and energy consuming, therefore research in material science has focused in the last decade at developing technically feasible processes for mineral sequestration of carbon dioxide alternative to carbonation.

Actually, many minerals contain carbon as a major to trace constituent, however the carbon content analysed in naturally occurring silicates is traditionally assigned to CO$_3^{2-}$.
groups in the structure, whereas the possible presence of molecular CO$_2$ in these phases is almost completely ignored. Up to the present, the only accepted CO$_2$-bearing minerals are beryl (Wood and Nassau, 1967) and cordierite (Armbruster and Bloss, 1980, Della Ventura et al., 2009, 2012). Indeed these two isostructural minerals are able to trap CO$_2$ because of their peculiar structural channels.

Cordierite is a framework alumino silicate with the ideal formula $(\Box, \text{Na})(\text{Mg,Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}(\Box, \text{H}_2\text{O}, \text{CO}_2)$ and a continuous solid solution between the Mg$^{2+}$ end-member and the Fe$^{3+}$ end-member (sekaninaite) exists (e.g. Černý et al., 1997, Radica et al., 2013). The cordierite framework can be described as a stacking of pseudo-hexagonal Si/Al layers of tetrahedra and mixed layers of tetrahedra and octahedra (Fig. 1a). Alkali cations such as Na, K, Ca, and molecules such as H$_2$O and CO$_2$ may be allotted within the resulting pseudo-hexagonal channel, occupying sites on the c axis at the height of the narrow “bottle necks” for Na, and of the large cavities for H$_2$O and CO$_2$ (Gibbs, 1966, Hochella et al., 1979; Malcherek et al., 2001; Yakubovich et al., 2004).

Beryl (ideal formula $(\Box, \text{Na})\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}(\Box, \text{H}_2\text{O}, \text{CO}_2)$) is isostructural with cordierite (Fig. 1b). Its framework is constituted by 6-fold Si-centered tetrahedral rings stacked along
the c axis. The hexagonal rings are interconnected parallel to [001] by distorted Be-centered tetrahedra. Al occupies the octahedral sites (Gibbs et al., 1968). Beryl also has structural channels running along the c axis that can contain alkali cations and volatile molecules (Wood and Nassau, 1968).

Extra-framework H$_2$O groups occur in the structural channels with the molecular plane parallel to (100). In both cordierite and beryl H$_2$O can be oriented in two different ways: type I H$_2$O (hereafter H$_2$O$^{[I]}$) has its H–H vector oriented parallel to the c axis, and type II H$_2$O (H$_2$O$^{[II]}$) has its H–H vector normal to the c axis (parallel to the b axis in cordierite). H$_2$O groups of the latter type are locally associated with channel cations (Goldmann et al., 1977; Hawthorne and Černý, 1977). Winkler et al. (1994) proposed that H$_2$O$^{[I]}$ in synthetic Mg-cordierite is rotationally disordered about [001] and that a purely static description is inappropriate to describe its behavior in the channel cavity. They proposed a model whereby the H...H vector remains parallel to [001] and the H$_2$O molecule rotates in two different positions about its center of mass with an estimated hopping time of about 6 picoseconds at room temperature; this feature however cannot be observed by using FTIR spectroscopy. The linear CO$_2$ molecules are systematically oriented normal to the c axis and parallel to the crystallographic $a$ axis for cordierite (Aines and Rossman, 1984; Kolesov and Geiger, 2000; Khomenko and Langer, 2005).

The molecular dimension of H$_2$O is 2.8 X 3.2 X 3.7 Å and CO$_2$ is 2.8 X 2.8 X 5.0 Å (Wood and Nassau, 1968). However the CO$_2$ molecule barely fits inside the cage, so once inside it tends to be wedged to the structure behaving as a “plug” (Aines and Rosmann, 1984; Vry et al., 1990). On the opposite, the smaller H$_2$O polar molecules are bonded to the structure mainly by electrostatic interactions with the structural oxygens (H$_2$O$^{[I]}$) and alkali cations (H$_2$O$^{[II]}$).

Additionally, because of its thermal and mechanical properties, cordierite is used in industrial applications such as high-tech ceramics or as a catalyst in petroleum industry. Beryl is a pegmatitic mineral and has a lower thermal and baric stability; it is well known for providing some of the most notable gemstones, such as the varieties emerald (green), aquamarine (light-blue), heliodor (yellow) or bixbite (red).
2. The petrological relevance of cordierite

This PhD Thesis work has been mainly focused on cordierite because it represents the only case of a widespread microporous mineral (pore size under 2 nm, Rouquérol et al., 1994; McCusker et al., 2001) that is able to trap significant amounts of molecular H$_2$O and CO$_2$ (Schreyer and Yoder 1964; Mirwald et al., 1979; Newton and Wood, 1979; Armbruster and Bloss 1982; Kurepin 1985) under extreme geological (P, T) conditions. Cordierite stability extends from the amphibolite facies to ultra-high temperature metamorphism to crustal anatexis conditions (Mirwald and Schreyer, 1977; Vry et al., 1990; Carrington and Harley, 1996; Smith 1996; Kalt 2000; Harley et al., 2002; Bertoldi et al., 2004; Sarkar et al., 2010). The analysis of the volatile constituents of cordierite can used to determine the composition of the fluid phase during crystallization (Vry et al., 1990; Carrington and Harley, 1996; Harley et al., 2002; Kurepin, 2010). H$_2$O and CO$_2$ contents affect the stability of cordierite (Schreyer 1985; Carey 1995; Harley et al., 2002). Therefore, a quantitative determination of its channel constituents is crucial in petrologic studies.

Among the wide range of cordierite occurrences, the most investigated is the ultra-high temperature metamorphism of pelitic rocks. Dehydration melting of biotite-bearing pelites with moderate to high $X_{Mg}$ variations ($X_{Mg}/X_{Mg+Fe}>0.5$) is often controlled by cordierite-forming reactions in migmatites and leuco-granites at 200–700 MPa and 700–900°C (Fitzsimons, 1996; Harley et al., 2002). Thus understanding the role of cordierite as an H$_2$O and CO$_2$ bearing phase is essential for understanding melting processes and for thermodynamic calculation of fluid activities during these events (Harley and Thompson, 2004). Kurepin (2010) made calculations of the dependence of H$_2$O and CO$_2$ contents in cordierite as a function of P, T and fluid composition for the aforementioned P-T conditions, and his thermodynamic model showed a non-ideality of thermodynamic behavior of H$_2$O and CO$_2$ mixing. In addition evaluation of the H$_2$O and CO$_2$ activities showed that cordierites in high temperature and pressure assemblages were formed under fluid-saturated conditions over a wide range of H$_2$O/CO$_2$ ratios (Vry et al., 1990; Kurepin, 2010).

In order to understand these mechanisms, several experimental studies on the solubility of volatile components in cordierite have been performed, in particular H$_2$O (Schreyer and Yoder 1964; Mirwald et al., 1979, Harley and Carrington, 2001 among the
others), CO₂ (Armbruster and Bloss, 1982, Armbruster, 1985; Le Breton and Schreyer, 1993), and mixed H₂O – CO₂ (Johannes and Schreyer 1981; Thompson et al., 2001).

As a result of these studies, there is agreement that pressure exerts a stronger influence on the solubility of both H₂O and CO₂ than does temperature. Both H₂O and CO₂ contents slightly decrease with increasing temperature, while increasing pressure favors higher concentrations (e.g. Fig. 2, modified after Harley and Thompson, 2004). It is important to note that the maximum H₂O content obtained at 700 MPa is about 2.4 wt.%, which is close to the maximum theoretical value of 2.9 wt.% or 1 molecule per formula unit in the channel (Deer et al., 2004). The maximum calculated value for CO₂ is about 2.2 wt.% (Deer et al., 2004) corresponding to about 0.3 molecules per formula unit.

Figure 2 – (a) Pressure – temperature phase diagram of the isopleths of H₂O (expressed in wt.%) for Xₘ₆ = 0.75 cordierite coexisting with pure H₂O fluid, as calculated by Harley and Carrington (2001); (b) isopleths of CO₂ (expressed in wt.%) for Xₘ₆ = 0.80 cordierite in a pure fluid after Thompson et al., (2001) and Harley et al., (2002).

Studies on X₇⁵, where X₇⁵ = CO₂/(CO₂+H₂O), partitioning between melt and cordierite have shown that H₂O tends to be incorporated preferentially into the cordierite structure, while CO₂ preferentially remains in the melt (Fig. 3b and Johannes and Schreyer, 1981). This behavior is only slightly changed at higher temperatures (Harley and Carrington, 2001), while X₇⁵ increases with increasing pressure, facilitating CO₂ uptake (Johannes and Schreyer, 1981). Moreover, increasing X₇⁵ decreases significantly the amount of H₂O+CO₂ diffused into the mineral. In particular, there is a decrease of H₂O (Fig. 3a) probably because the presence of CO₂ obstructs its diffusion to the channel ways. This behavior, which is observed also in natural samples (Vry et al., 1990), can be explained by the configuration of
the CO₂ molecule inside the channels. Another factor that decreases the total amount of diffused fluids is the alkali content within the structural channels (Johannes and Schreyer, 1981; Vry et al., 1990). There is evidence suggesting that CO₂ (and possibly alkali cations) may act as plugs in the channel ways obstructing inward and outward molecule diffusion, drastically slowing down the time of degassing and re-equilibration in case of pressure drop (Johannes and Schreyer, 1981; Kalt, 2000). This behavior complicates the possibility to predict the diffused molecules coexisting with mixed H₂O and CO₂ fluids, although a theoretical approach has been attempted by Kurepin (2010).

Figure 3 (a) variation of the volatile composition in cordierite ($X_{Mg} = 0.68$) channels with fluid-saturated, intermediate H₂O - CO₂ fluid composition. The lines show the calculated values at Thompson et al. (2001). Squares = H₂O, triangles = CO₂, circles = total number of molecules per formula unit (modified after Thompson et al., 2001). (b) partition curves showing $X_{CO2}$ fractioning between cordierite and coexisting fluid at 500 MPa and 600°C for two different synthetic cordierites A and B (modified after Johannes and Schreyer, 1981).

The experiments were performed with small cordierite grains as starting materials (about 200 µm in Armbruster and Bloss, 1982 and Armbruster, 1985; 125-250 µm in Thompson et al., 2001) in order to maximize the surface-to-volume ratio, and were carried out for a long duration (up to a few weeks) in order to achieve fluid/mineral equilibration. However there is still no agreement on the results, among the different authors. For instance, Johannes and Schreyer (1981) obtained different results as a function of different starting material (Fig. 2b) or grain size of cordierite, and Le Breton and Schreyer (1993) observed a nonlinear behavior of the CO₂ contents between 15 minutes to 3 weeks experimental runs. Major problems arise with CO₂ diffusion, because its “sluggish” nature delays or even prevents sample saturation. Thus, the study of the run products cannot be addressed by conventional bulk methods, such as coulometric tritation (Armbruster and
Bloss, 1982; Johannes and Schreyer, 1981) or powder FTIR spectroscopy (Vry et al., 1990) or single spot micro-analytical techniques, such as SIMS (secondary ion mass spectrometry) (Thompson et al., 2001), which do not allow characterizing the inhomogeneous distribution of the target element. For this reason, we have predominantly used, in this Thesis, single-crystal FTIR spectroscopy to examine the run products, and have developed in particular novel FTIR procedures to characterize the sample inhomogeneities.

3. Advances in FTIR micro-spectroscopy

Several times during this introduction we mentioned that FTIR micro-spectroscopy was chosen as a principal probing tool, and the reason is that FTIR is one of the main tool in Earth Science able to deal with light and crucial elements like H (both as H$_2$O and OH$^-$) and C (both as CO$_2$ and CO$_3^{2-}$ groups). Several complementary techniques were developed in the last decades to overcome some of the most common issues occurring in Earth Science.

1) Focal Plane Array (FPA) FTIR imaging and FTIR mapping are extremely important imaging techniques capable of detecting and quantify the distribution of an absorber across a sample. In Earth Science materials these techniques are useful to examine the possible inhomogeneity of natural samples, such as chemical zoning, but also melt/fluid inclusions, structural defect of the occurrence of included micro-phases. Several works have been devoted to this topic, in particular Della Ventura et al. (2010, 2014) revised the data in literature and illustrated the possibilities offered by imaging techniques in Earth Science. During the present Thesis I made extensive use of this technique, in particular each experimental sample was preliminary analyzed through 2D FTIR FPA imaging in order to locate the most suitable spots for CO$_2$ quantitative measurement.

Polarized-light FTIR single spot analysis (Libowitzky and Rossman, 1996) was used for quantitative measurements and to define the orientation of the absorbers in the samples. In addition in Chapter 6 I describe the results of FPA imaging done on oriented single crystals using polarized radiation (Fig. 4a); this is the first time that polarized imaging is applied in Earth Science and the data show that this technique opens interesting scenarios: for instance the work presented in chapter 6 shows how it is possible to map in detail the distribution of absorbers with different orientation in the same section.
In this work I also illustrate the possibilities offered by synchrotron-light FTIR mapping. In FTIR spectroscopy the increased brilliance of a synchrotron source translates into improved signal to noise ratio in 2D FPA imaging and thus in a higher spatial resolution for spot measurements and mapping (Della Ventura et al., 2014). In Figure 4 I reported for comparison the contour map of CO₂ distribution in the same area of a thermally-treated beryl sample obtained using a conventional Globar source (Fig. 4b) and a synchrotron source (Fig. 4c).

Figure 4 – (a) FTIR-FPA contour map of CO₂ distribution collected for E⊥c in a beryl sample treated at 800 °C and 500 MPa, 4 days. (b) Enlargement of (a) showing the CO₂ distribution obtained with conventional light, spot size 20 x 20 µm, sampling step 10 µm, and (c) obtained with synchrotron light with spot size 10 x 10 µm, sampling step 5 µm. Chromatic scale is proportional to the CO₂ content, units are arbitrary. See Chapter 6.

2) In-situ FTIR techniques were developed to study phase equilibria and kinetic process at extreme pressures and temperatures using diamond anvil cells (DAC) and heating stages (Koch-Müller et al., 2003, Iezzi et al., 2006, 2009, Keppler and Smyth, 2006; Hawthorne et al., 2007, Welch et al., 2007, Della Ventura et al., 2010, 2014). In Chapter 3 and 4 of this Thesis I will describe the CO₂ absorbance variations in cordierite up to 1200 °C and the kinetic of CO₂ expulsion from the structural channels. In-situ high temperature measurements up to 1200 °C could be performed for the first time using a modified heating stage capable to operate at extreme temperatures directly under the IR microscope (Fig. 5a).
The kinetic of CO$_2$ expulsion was studies using two different sections with different thickness; to collect the spectra for the thinner 19 µm slice with enough S/R we used a synchrotron light source, because the reduced thickness of the samples coupled with the strong beam absorbance caused by the stage windows, sample holder and polarizers (Fig. 5b) affected significantly the transmitted signal.
Introduction

SUMMARY

Section I: Structural and spectroscopic characterization of cordierite (Chapters 1 and 2).

Eight different cordierite samples (Chapter 1) from different localities and geological occurrences were chosen to cover a wide range in H\textsubscript{2}O/CO\textsubscript{2} ratio.

Single-crystal X-ray diffraction data were collected on optically clean grains free from inclusions and alteration products at CNR Istituto di Cristallografia (Bari) with a Nonius Kappa CCD area detector diffractometer, revealing all samples to be orthorhombic Cccm. Major oxides were analysed by EMPA while H and C were quantified by SIMS (secondary ion mass spectrometry). Accordingly, the Si:Al ratio is close to 5:4; X\textsubscript{Mg} ranges from 76.31 to 96.63; extraframework K and Ca are negligible, with Na up to 0.84 apfu. SIMS shows H\textsubscript{2}O up to 1.52 and CO\textsubscript{2} up to 1.11 wt%.

Figure 1 - Selected single-crystal polarized-light FTIR spectra of cordierite along the principal optical directions, peak identification after Della Ventura et al., (2009).
Introduction

Optically transparent single-crystals were oriented using the spindle-stage and examined by FTIR micro-spectroscopy under polarized light. The observed bands were assigned to water molecules in two different orientations H$_2$O$^{[I]}$ and H$_2$O$^{[II]}$, and to CO$_2$ molecules in the structural channels (Fig. 1). Prior to the quantitative analyses, the samples were examined for their water and carbon dioxide distribution using a focal-plane-array (FPA) of detectors. The evidence was that at the µm-scale the distribution of H and C in cordierite were significantly inhomogeneous, particularly for H$_2$O, whose zoning within the crystal can be strongly affected by the geological history of the mineral after its formation.

The core of this work was the quantitative calibration of H$_2$O and CO$_2$ in cordierite based on single-crystal FTIR micro-spectroscopy (Fig. 1), based on the Beer-Lambert relationship.

![Figure 2 - Relationship between the analysed (SIMS) CO$_2$ content and the integrated absorption coefficient ($a_i$=A/t) for the studied cordierites. The calibration curve provides the specific absorption coefficient ($\varepsilon$) to be used in the Beer-Lambert equation for the spectroscopic quantitative analysis of CO$_2$ in cordierite.](image)

For H$_2$O the integrated molar coefficients for type I and type II water molecules were calculated separately and turned out to be [I] $\varepsilon = 5000 \pm 1000$ l·mol$^{-1}$·cm$^{-2}$ and [II] $\varepsilon = 13200 \pm 500$ l·mol$^{-1}$·cm$^{-2}$, respectively. For CO$_2$ the integrated coefficient is $\varepsilon_{CO2} = 19000 \pm 1000$ l·mol$^{-1}$·cm$^{-2}$. The same procedure just illustrated was then applied to the Fe end-member of the cordierite group, sekaninaite (Chapter 2). Additionally single crystal X-ray refinement, laser ablation mass-spectroscopy for Li$^+$ and Raman spectroscopy characterization were performed.
Electron-micro-probe analysis shows the sample to be close to the Fe end-member \( X_{Fe} = Fe/(Fe+Mg) = 94\% \) with significant Mn (1.48 wt.%); laser ablation mass-spectrometry showed the presence of 0.42 wt.% Li\( _2 \)O. H\( _2 \)O and CO\( _2 \) contents (1.48 and 0.17 wt.\%, respectively) were determined via secondary-ion mass-spectrometry (SIMS). X-ray site occupancy refinement suggested that the lack of monovalent charge at the octahedral site due to the presence of Li\(^+\), is counter-balanced by the presence of Na\(^+\) in the channel.

Sample homogeneity was confirmed by FPA imaging (Fig. 3) and single-crystal FTIR spectroscopy confirmed the presence of two types of H\( _2 \)O groups in different orientations (with prevalence of the type II orientation).

Using the Beer-Lambert relation, integrated molar coefficients \( \varepsilon \) were calculated for both types of H\( _2 \)O (\( \varepsilon_{H_2O^{[I]}} = 6000\pm2000; \varepsilon_{H_2O^{[II]}} = 13000\pm1000 \)) and for CO\( _2 \) (\( \varepsilon_{CO_2} = 2000\pm1000 \)).

![Fig. 6. FTIR FPA image of the (100) section, 47 µm thick slab of sekaninaite. Integration of the H\( _2 \)O stretching bands in the range 3500-3700 cm\(^{-1}\). The chromatic scale is proportional to volatile contents, units are arbitrary.](image)

The integrated molar absorption coefficients \( \varepsilon \) for H\( _2 \)O are very close to those reported for Mg-rich cordierite in Chapter 1. On the other hand, the value of \( \varepsilon_{CO_2} \) obtained here cannot be considered reliable because of the uncertainty of the SIMS data, which is > 50\%. However, it is close to the one calibrated by Della Ventura et al. (2006) from a CO\( _2 \)-poor cordierite.
Section II: *In-situ* HT-IR spectroscopy and kinetic study of CO\textsubscript{2} expulsion from cordierite (Chapters 3 and 4).

In this section I will describe the *in situ* HT-FTIR micro-spectroscopy of cordierite and will evaluate the kinetic and diffusion parameters of CO\textsubscript{2} expulsion as a function of increasing $T$. Experiments were performed using a Linkam TS 1400 XY heating stage at LNF-INFN and at beamline B22, Diamond Light Source laboratory Oxford (UK). Fragments of two natural cordierites, BM 96512 from Cabo de Gata (Almaria region, Spain) and Rp 3237 from Kragero (Arendal region, Norway) were used.

In a first series of step-heating experiments, the (001) section of cordierite Rp 3237 was heated up to 1000 °C with a rate of 20 °C/min and FTIR spectra were collected for every step. At the end of the run, the sample was allowed to cool down to $RT$ and a spectrum was measured, than was heated up at 1100 °C (rate 100 °C/min) and then cooled down again at $RT$; spectra were collected at 1100 °C and at $RT$. A second series of experiments was performed heating up the (010) section with a rate of 100 °C/min up to 600 °C; measurements were performed every 100°C during the ramp. Then the sample was cooled down to RT and heated up again up to 600 °C with a rate of 100 °C/min. The same procedure was repeated at 800, 900, 1000, 1100 and 1200 °C. FTIR spectra were collected at $RT$ and at any target temperature every 50 °C. After each experiment FPA-FTIR images were collected to check for the homogeneity of residual CO\textsubscript{2}.

*In-situ* measurements on (001) oriented sections that up to $T > 800$ °C there is a significant intensity increase of the CO\textsubscript{2} stretching mode at 2348 cm\textsuperscript{-1}, followed by a sudden decrease for $T > 900$°C; the absorbance is virtually zero at 1000°C (Fig. 7a). On the opposite, the integrated absorbance ($A$) of the CO\textsubscript{2} ($\nu_3 + \nu_1$) combination mode at 3708 cm\textsuperscript{-1} (Fig. 7a) is almost constant up to about 450 °C, then decrease up to 850 °C. For higher $T$ the intensity decreases with a much faster rate; the band disappears at 950°C. Similar trends for the (010) section cut out from the same cordierite crystal (Fig. 7c).

The evolution of the H\textsubscript{2}O absorbance as a function of increasing $T$ is extremely different to that of CO\textsubscript{2} (Fig. 7a and b, in purple), and shows a linear and constant decrease of ~50% of the intensity up to 800°C; in the 800°-900°C range there is a sudden drop and at 950°C the sample is completely anhydrous. Similarly to what observed for CO\textsubscript{2}, the data collected on quenched samples show a different scenario: the integrated H\textsubscript{2}O absorbance is
constant up to 800°C and suddenly drops in the 800-900°C range. At 1000° the sample is completely anhydrous.

![Figure 7 - (a) Sample Rp 3237 (001) section: integrated absorbance variation ($A_{RT_0}$ in %) of H$_2$O (purple triangles), CO$_2$ stretching mode (filled orange squares) and CO$_2$ combination mode (open orange squares). Sample Rp 3237_14 (010) section: integrated absorbance variation ($A_{RT_0}$ in %) of H$_2$O (b) and CO$_2$ (c) absorptions. In (b) and (c) the intensities measured after quenching the sample are given for comparison (dashed black lines). The shaded areas represent the estimated error on $A_{RT_0}$. Several authors (e.g. Keppler and Bagdassorov, 1993; Yamagishi et al., 1997; Zhang et al., 2007; Tokiwai and Nakashima, 2010b) revised recently the absorbance in minerals and glasses in HT-FTIR spectroscopy and showed that the intensity measured during in situ data collection is not related to the concentration of the target absorber via the same Beer-Lambert relationship calibrated at room-$T$. This feature is shown in Figure 7, where it is evident that in situ FTIR data collection does not provide a real estimate of the CO$_2$ and H$_2$O behavior in cordierite as a function of increasing $T$. In particular, based on the Beer-Lambert relationship, assuming no or negligible change in the sample thickness across the studied $T$ range, the trends of Figure 7 suggest a significant change in the molar absorption coefficients $\varepsilon$ for both volatile species at varying $T$.

Interestingly, as already observed for H$_2$O/OH in several mineral species (Zhang et al., 2007) the temperature dependence of the principal modes is different from that of multi-phonon bands (Fig. 7a and c open squares).

Continuous heating experiments were performed on (001) oriented BM 96512 cordierite slabs. Two fragments were double-polished at 60 µm and 19 µm, respectively and broke up into four pieces each. Four fragments of the same 60 µm thick section were heated to 850, 900, 950 and 1000 °C (heating rate 100°C/min) and kept at the target $T$ for two hours. Polarized spectra were collected using conventional light with both E//a and E//b at $RT$ before the experiment, and at the target $T$, every 5 minutes for the first hour and every 10 minutes for the second hour of isothermal heating. Additional four fragments of the same
19 µm thick BM 96512 slab were heated to 825, 850, 900 and 1000 °C (heating rate 100°C/min) at different annealing times. For this second set of samples, spectra were collected using synchrotron light exclusively along the $a$ crystallographic direction at RT and at the target $T$ every 5 minutes. This experimental layout was necessary to get a better S/N because the reduced thickness of the samples coupled with the strong beam absorbance caused by the stage windows, sample holder and polarizers affected significantly the transmitted signal.

Figure 8 shows the CO$_2$ loss curves expressed as $A_t^\% = 100 \cdot A_t/A_0$ where $A_t$ is the $A_i$ at time $= t$ and $A_0$ is $A_i$ at time $= 0$, i.e. just after the sample reached the target temperature; data obtained with E$/a$ for the $v_3$ mode at 2348 cm$^{-1}$ for the 60 µm thick BM96512 and the 19 µm thick BM96512 (001) sections are displayed.

Figure 8 – Isothermal plots of residual CO$_2$ within the cordierite channels ($A_t^\% = 100 \cdot A_t/A_0$ of the 2348 cm$^{-1}$ band) as a function of time; sample BM96512, (001) section for E$/a$. Shaded areas represent the estimated error on the absorption. (a) 60 µm thick section, (b) 19 µm thick section.

The curves in Figure 8 were fitted using three different approaches: the Avrami JMAK rate equation (Hancock and Sharp, 1972), the Avrami Putnis rate equation (Putnis, 1992) and the mono-dimensional plane sheet diffusion (Ingrin, 1995).

Activation energies calculated using the Avrami approaches yield four different results on the basis of the used formula and the sample thickness. However, based on different assumptions, it is possible to conclude that the most reliable activation energy for CO$_2$ expulsion from cordierite provided by the Avrami formalism is $E_a = 138 \pm 12$ kJ/mol, i.e. the value obtained using the Avrami Putnis equation on the thinner sample data set. This
value is very close to those obtained by previous authors for the dehydration of cordierite (Giampaolo and Putnis, 1989).

Using the mono-dimensional plane sheet diffusion approach it was possible to evaluate both the diffusion coefficient $D$ and the activation energy $E_a$ for CO$_2$ in cordierite. Results confirmed that this approach is not influenced by sample thickness variation and fitted data for both sample set yield a value of $-\log D_0 = 4.4\pm0.7$ m$^2$/sec and $E_a = 204\pm15$ kJ/mol.
Section III: Experimental diffusion of CO$_2$ in cordierite and beryl at different $PTt$ conditions (Chapter 5).

In this section I examined the interaction of cordier with a CO$_2$–rich fluid under different experimental $P$, $T$, $t$ conditions and evaluated the diffusion coefficients within the crystals. Experiments were performed using a non-end loaded piston cylinder apparatus (QUICKpress™ design by Depths of the Earth Co. Fig. 9a). FTIR spectra were acquired using a Bruker™ Hyperion 3000 microscope (Fig. 9b) at Laboratori Nazionali di Frascati- Istituto Nazionale di Fisica Nucleare (LNF-INFN,) Frascati (Rome).

Several cordierite fragments (Mg-cordierite sample RP 7344 from Karur, Tamil Nadu, Chapter 1) were separated from a large single crystal (Fig. 9c). Before the experiments, the grains were pre-treated at 1250 °C for 24 hour in order to remove all H$_2$O and CO$_2$ from the sample (Chapter 5). Grains were optically clean, however cracking of larger grains occurred
during the heat-treatment. Beryl samples are from the very first flux-grown synthetic emeralds made by P.G. Hautefueille and A. Perrey in 1888 in Paris (Bellatreccia et al., 2008); samples show a perfect prismatic hexagonal habitus with a maximum length of 1 mm and width of 0.5 mm (Fig. 9d).

The experiments were carried in 3 x 9 mm Pt capsules; silver carbonate was used as a CO\(_2\) source. Al\(_2\)O\(_3\) powder was mixed in 1 to 1 ratio by wt. with Ag\(_2\)CO\(_3\), and added to the charge. The aluminum oxide powder was used to prevent the contact between the crystals and the capsule walls after the silver carbonate disappearance due to its decomposition. Layers of Ag\(_2\)CO\(_3\)/Al\(_2\)O\(_3\) mix were alternated to layers of starting crystals (Fig. 10a). Each capsule contained from 4 to 7 grains of cordierite/beryl, for a total crystal weight of 2 to 10 mg. All components used to prepare the tubes were dried up at 110 °C.

Piston cylinder experiments were conducted using two different set-ups (Fig. 10b): using a standard 19 mm assembly (Moore et al., 2008), operating at P from 300 to 800 MPa and a 19-25 or 25 mm assembly (P from 150 to 300 MPa). The 25 mm assembly may accommodate up to 4 samples in a single run (Masotta et al., 2012b). We used a NaCl-Pyrex-Graphite-crushable-MgO–pyrex assembly with capsule surrounded by pyrex powder instead of pyrophyllite to avoid water infiltration. Temperature was controlled using a C-type (W\(_{95}\)Re\(_5\) – W\(_{75}\)Re\(_{25}\)) thermocouple with a ±5 °C uncertainty (Holtz et al., 2001). Heating rates were set to 100 °C/min; the isobaric quenching rate ranged from 50 °C/s (25 mm assembly) to 100 °C/s (19 mm and 19-25 mm assembly) in the first 5 seconds (Masotta et al., 2012b). Experiments were performed in the pressure range 200 – 700 MPa, temperature range 700 – 900 °C; run duration varied from 1 to 72 hours.
Preliminary FTIR single spot measurements confirmed that H$_2$O and CO$_2$ had been diffused in the samples (Fig. 11), however an evident heterogeneity in carbon dioxide absorbance was observed. Therefore all samples were carefully examined by FPA to locate the area suitable for analytical spots. In particular FPA imaging revealed that the CO$_2$ diffusion in both cordierite and beryl proceeds exclusively along the structural channels (Fig. 12). FPA images also showed a strong enhancement of the CO$_2$ diffusion along cracks.

On the basis of these results we located the most suitable area for the analytical spots avoided measurements close to fractures; the beam size was kept as small as possible, usually at 20x20 µm$^2$ and the highest absorbance values were selected as representative of the CO$_2$ content of the sample.

The CO$_2$ contents were calculated from polarized FTIR spectra using the Beer-Lambert relationship using the procedure described in Della Ventura et al. (2010).

Final data shows that $T$ plays only a minor role on the CO$_2$ diffusion for both cordierite and beryl, while pressure has a significant effect. In particular, beryl shows a steep increase in CO$_2$ content from 200 MPa to 500 MPa and from 500 MPa to 700 MPa. The CO$_2$ contents in cordierite, on the other side, show only a minor increase from 200 MPa to 500 MPa, with a significant jump from 500 MPa to 700 MPa.
The diffusion coefficient ($D$) for beryl was obtained by fitting the concentration profiles (Fig. 12) using a simple mono dimensional equation (Crank, 1975, Zhang and Cherniak, 2010):

$$C = C_0 \cdot \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right)$$

where $C$ is the concentration at depth $x$ (m) from the sample rim, $C_0$ is the maximum concentration, $D$ is the diffusion coefficient (m$^2$/s), $t$ is the time duration (s), and $\text{erfc}$ is the complementary error function. Obtained $D$ values range from 7.6E-13 to 6.3E-14 for cordierite, and 1.1E-14 to 9.5E-14 for beryl.

Activation energy ($E_a$) and pre-exponential factor (-log$D_0$) were determined fitting the data on the basis of the Arrhenius equation.

$$\log(D) = \log(D_0) - \frac{E_a}{R} \cdot \ln(10) \cdot \frac{1}{T}$$

Mean activation energy ($E_a$) for beryl data is 122±15 kJ/mol with a pre-exponential (-log$D_0$) factor of 7.2±0.7.
Section IV: The diffusion of volatiles in hourglass zoned beryl, the coordination environment of H$_2$O in low-water samples and comments on the geological storage of CO$_2$ in beryl (Chapters 6, 7 and 8).

Chapters 6 and 7 deal with some particular features observed during the present Thesis, i.e. the role of chemical inhomogeneity in the diffusion of CO$_2$ in beryl, and the coordination environment of H$_2$O in the channels.

Some synthetic samples used for the diffusion experiments had a typical hourglass structure due to the distribution of Cr during the crystal growth (e.g. Bellatreccia et al., 2008). After the experimental run, the FTIR-FPA imaging of these sample showed an unexpected distribution of the diffused molecules within the channels (Fig. 14): CO$_2$ apparently diffuses following the hourglass boundaries, while H$_2$O$_{[II]}$ is homogeneously distributed except along the hourglass traces.

Figure 14 – Polarized light FPA images of the beryl sample treated for four days at 800°C, 500 MPa. Optical image of the grain (a), E//c FTIR-FPA map of H$_2$O$_{[I]}$ (b) and H$_2$O$_{[II]}$ (c) distribution, and (d) E⊥c FPA map of CO$_2$. Chromatic scale is proportional to CO$_2$ content.

Considering that the carbon dioxide diffusion in beryl and cordierite is significantly enhanced by the presence of fractures (chapter 5) we performed high-resolution FESEM imaging (Fig. 15) to check for the possible presence of physical discontinuities across the hourglass boundary. The results showed that indeed the hourglass structure was exclusively due to a chemical zoning, thus suggesting that the diffusion pattern of CO$_2$ observed in
Figure 14 must be related to a kind of defect fast-path diffusion mechanism (Zhang et al., 2006).

Figure 15 – Field Emission SEM pictures of the treated beryl sample in correspondence of the “hourglass” structure in a fracture free area. (a) EDS chemical mapping of Cr$^{3+}$ zoning. (b) topological Secondary Electron (SE) images of the highlighted area. The red dashed line indicates the limit of the “hourglass” sector zoning.

TOF-SIMS chemical maps showed K is enriched along the hourglass boundary, while Na is depleted. Considering that H$_2$O$^{[II]}$ is preferentially associated Na$^+$ cations inside the channels it is reasonable to infer that H$_2$O$^{[II]}$ depletion along the hourglass discontinuity is the result of the increased K$^+$ content at the expense of Na occurring along these chemical boundary.

As explained in chapter 5, the HT/HP experiments aimed at the CO$_2$ diffusion across cordierite and beryl were done using a piston-cylinder apparatus, where the pressure was mechanically and not hydrothermally increased. The infrared spectra of the run products, as expected, showed the presence of significant CO$_2$ but also of minor H$_2$O; due to the experimental conditions, this water content must be related to moisture present in the starting products used for the synthesis, thus its bulk amount is very low. Single-spot spectra collected along profiles parallel to the c crystallographic axis show subtle changes as a function of the distance from the crystal edge; these changes can be correlated to a progressive change in the H$_2$O coordination environment in the channel (Fig. 16), as a response to the varying H$_2$O/alkali content. In particular, the data show that when 2·H$_2$O > Na$^+$ apfu, H$_2$O can assume both type I and type II orientation; in the latter case, each Na cation coordinates two H$_2$O$^{[III]}$ molecules (doubly coordinated H$_2$O). If 2·H$_2$O < Na$^+$ apfu, than
H$_2$O$^{[II]}$ molecules are singly coordinated to each Na cation. The same type of feature is observed and commented for the structurally related cordierite.

The implication of this finding is that H$_2$O in beryl and in cordierite is trapped in the structural channel following very different bonding environments, and this has a significant consequence on the diffusion rates (both inward and outward) obtained in experiments and hence on the calculation of thermodynamic properties from the observed data. For cordierite in particular, considering it is widely used in metamorphic petrology as an
indicator of the fluid system in equilibrium with the rock, the different diffusion mechanisms of water and CO$_2$ could affect the closing temperatures modeled on the basis of field studies.

Chapter 8 reports a short paper in press on the *Rendiconti Online della Società Geologica Italiana* discussing problems related to the permanent storage of carbon dioxide in microporous minerals.
Chapter 1: Quantitative analysis of H$_2$O and CO$_2$ in cordierite using polarized FTIR spectroscopy

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CHAPTER 1

QUANTITATIVE ANALYSIS OF H$_2$O AND CO$_2$ IN CORDIERITE USING POLARIZED FTIR SPECTROSCOPY

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Abstract

We report a FTIR (Fourier-transform infrared) study of a set of cordierite samples from different occurrence and with different H$_2$O/CO$_2$ content. The specimens were fully characterized by a combination of techniques including optical microscopy, single-crystal X-
ray diffraction, EMPA (electron micro probe analysis), SIMS (secondary ion mass spectrometry), and FTIR spectroscopy. All cordierites are orthorhombic Ccmm. According to the EMPA data, the Si:Al ratio is always close to 5:4; $X_{Mg}$ ranges from 76.31 to 96.63 and additional octahedral constituents occur in very small amounts. Extraframework K and Ca are negligible, while Na reach values up to 0.84 apfu. SIMS shows $H_2O$ up to 1.52 and $CO_2$ up to 1.11 wt%.

Optically transparent single-crystals were oriented using the spindle-stage and examined by FTIR micro-spectroscopy under polarized light. On the basis of the polarizing behaviour, the observed bands were assigned to water molecules in two different orientations and to $CO_2$ molecules in the structural channels. The IR spectra also show the presence of small amounts of CO in the samples. Refined integrated molar absorption coefficients were calibrated for the quantitative microanalysis of both $H_2O$ and $CO_2$ in cordierite based on single-crystal polarized-light FTIR spectroscopy. For $H_2O$ the integrated molar coefficients for type I and type II water molecules ($\tilde{\nu}_3$ modes) were calculated separately and are $[I] = 5200 \pm 700$ l·mol$^{-1}$·cm$^{-2}$ and $[II] = 13000 \pm 3000$ l·mol$^{-1}$·cm$^{-2}$, respectively. For $CO_2$ the integrated coefficient is $[CO_2] = 19000 \pm 2000$ l·mol$^{-1}$·cm$^{-2}$.

Key words: cordierite, EMPA and SIMS, polarised FTIR spectroscopy, quantitative $H_2O$ and $CO_2$ analysis.

1. Introduction

Cordierite, ideally $(Mg,Fe)_2Al_4Si_5O_{18}$, is a unique case of a microporous mineral stable under geological conditions spanning from the amphibolite facies to UHT metamorphism to crustal anatexis (Vry et al. 1990; Carrington and Harley 1995, 1996; Smith 1996; Kalt 2000; Harley et al. 2002; Bertoldi et al. 2004). Because of its structural channels, cordierite is able to trap $H_2O$ and $CO_2$ (Schreyer and Yoder 1964; Armbruster and Bloss 1980; Kurepin 1985; Schreyer 1985; Carey 1995), but also hydrocarbons (Zimmermann 1981; Mottana et al. 1983; Khomenko and Langer 1999), CO (Khomenko and Langer 2005; Della Ventura et al. 2009), Ar (Armbruster 1985; Schreyer 1985) and $N_2$ (Armbruster 1985; Cesare et al. 2007). For this reason, the
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Analysis of the volatile constituents of cordierite can be a very useful tool to define the composition of coexisting fluids during its formation (e.g. Vry et al. 1990; Visser et al. 1994; Carrington and Harley 1996; Kalt 2000; Harley et al. 2002). Moreover, H₂O and CO₂ contents may significantly affect the stability of cordierite (e.g. Schreyer 1985; Carey 1995; Harley et al. 2002), therefore the quantitative evaluation of the channel constituents is crucial in petrologic studies.

The microanalysis of light elements like hydrogen and carbon is still extremely complex (e.g. Rossman, 2006); due to their low atomic number these elements cannot be easily studied by electron microprobe; moreover H and C are very poor X-rays scatterers hence they cannot be studied with conventional X-rays diffraction methods.

On the other hand, infrared spectroscopy is an efficient technique to detect the volatile components within the structural pores of cordierite (Farrell and Newnham 1967; Goldman et al. 1977; Aines and Rossman 1984; Le Breton 1989; Kolesov and Geiger 2000; Khomenko and Langer 2005; Rigby et al. 2008, Della Ventura et al. 2009); coupled with well-tested methods for volatile quantification like secondary ion mass spectroscopy (e.g. Thompson et al. 2001), it can be a simple yet powerful tool for sample volatile quantification (Della Ventura et al. 2009). In addition, IR has the distinguishing advantage of providing information on the closest structural environment of the target element, its molecular arrangement (for example OH vs H₂O, CO₂ vs CO₃) and the orientation of the molecules within the structure. Moreover, by using the modern techniques of FTIR imaging with the bidimensional focal plane array of detectors (FPA), enables detection of the zoning of volatile species across the studied sample.

Despite the large number of studies, a calibration for unambiguous infrared quantitative analysis of H₂O and CO₂ in cordierite is still lacking. The quantitative determination of an absorber (c, concentration) in a mineral is based on the Beer-Lambert law: 
\[ c = \frac{A_i}{(t \mu_i)} \]
where \( A_i \) (cm⁻¹) = integrated absorbance, \( t \) (cm) = sample thickness and \( \mu_i \) (cm⁻² per mol H₂O/L) = integrated molar absorption coefficient. \( A_i \) and \( t \) are measured, but the \( \mu \) coefficient must be calibrated for any mineral matrix by combining an independent method. Libowitzky and Rossman (1996) definitively showed that for quantitative purposes the measurement of the absorbance in anisotropic minerals must be obtained summing-up the integrated absorbance along the three principal optical directions. For orthorhombic cordierite thus \( A_i = A_x + A_y + A_z \).
Chapter 1: Quantitative analysis of H$_2$O and CO$_2$ in cordierite using polarized FTIR spectroscopy

For H$_2$O, the only molar absorption coefficient available for cordierite has been calibrated by Goldman et al. (1977) using linear (peak height) intensity data, while the only coefficient available for CO$_2$ has been recently calibrated by Della Ventura et al. (2009) on one cordierite crystal from a partially melted graphite-bearing granulitic enclave within the dacitic lava dome of El Hoyazo (SE Spain). According to Della Ventura et al. (2009) several problems are involved in the analysis of cordierite, primarily the possible zoning of H$_2$O/CO$_2$ in the sample and the widespread presence of inclusions or alteration products even in apparently gemmy crystals.

We address in this paper the calibration for a reliable analysis in cordierite by studying a set of samples from different occurrences.

2. Samples and analytical methods

Eight different cordierite samples (Table 1) from different localities and geological occurrences were chosen for this work such as to cover a wide range in the H$_2$O/CO$_2$ ratio. The crystals used for the spectroscopic data collection were previously fully characterized using a multidisciplinary approach.

Table 1- Sample labels and occurrence of the studied samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM 96512</td>
<td>Cabo de Gata, Almaria Region, Spain</td>
</tr>
<tr>
<td>8/90</td>
<td>Serre Massiff, Calabria, Italy</td>
</tr>
<tr>
<td>RIG</td>
<td>Unknown</td>
</tr>
<tr>
<td>BB3a</td>
<td>Brattstrand Bluffs, Prydz Bay, Antarctica</td>
</tr>
<tr>
<td>Rp 7344</td>
<td>Karur, Tamil Nadu, India</td>
</tr>
<tr>
<td>Rp 5578</td>
<td>Tsihombe, Madagascar</td>
</tr>
<tr>
<td>Rp 3237</td>
<td>Kragero, Arendal, Norway</td>
</tr>
<tr>
<td>Rp 7045</td>
<td>Region de Bekily, Madagascar</td>
</tr>
</tbody>
</table>

Single-crystal X-ray diffraction data were collected on optically clean grains free from inclusions and alteration products at CNR Istituto di Cristallografia (Bari) with a Nonius Kappa CCD area detector diffractometer, using Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). Cell refinement and data reduction was performed via EvalCCD (Duisenberg et al. 2003) and absorption correction via
Chapter 1: Quantitative analysis of H$_2$O and CO$_2$ in cordierite using polarized FTIR spectroscopy

SADABS (Sheldrick 1996).

The structures were solved through the Direct Methods procedure of SIR2008 (Burla et al. 2007), within the orthorhombic space group Cccm, and refined by a full-matrix least-square techniques based on F$^2$ using SHELX-97 (Sheldrick 1997).

The electron microprobe analyses (EMPA) were done using a Joel JXA 8200 WD-ED at the Istituto Nazionale di Geofisica e Vulcanologia (INGV), Roma. Working conditions were 15 kV accelerating voltage, 7 nA sample current, 5 µm beam diameter, counting times: 10 seconds on the peak and 5 seconds on the background on both sides of the peak. The standards, spectral lines and crystals used were: albite (NaK$\alpha$, TAP), pargasite (CaK$\alpha$, PET), wollastonite (SiK$\alpha$, PET), k-feldspar (KK$\alpha$, PET), kyanite (AlK$\alpha$, TAP), pargasite (MgK$\alpha$, TAP), augite (FeK$\alpha$, LIF), titan oxide (TiK$\alpha$, LIF) and spessartine (MnK$\alpha$, LIF). Data correction was performed using the ZAF method. Sample homogeneity was verified collecting several spots per crystal.

The H$_2$O and CO$_2$ contents were quantified by SIMS (secondary-ion-mass-spectrometry) using a Cameca IMS4f ion microprobe at EMMAC, the University of Edinburgh. Procedures follow those described in previous cordierite studies from the Edinburgh laboratory (Harley and Carrington 2001; Thompson et al. 2001; Harley et al. 2002). A 2.58 cm diameter analysis block incorporating the studied samples, and two standard cordierite grains (ANMH with $X$Mg = 0.89; H$_2$O = 1.54 wt%; and CO$_2$ = 0.7 wt% and 8/90 with $X$Mg = 0.75; H$_2$O = 0.81 %; and CO$_2$ = 1.31 wt%; Thompson et al. 2001) was prepared, coated with gold, and inserted into the IMS4f sample change chamber for overnight pump-down prior to in-situ SIMS analysis. Negative secondary ions $^1$H, $^{12}$C and $^{28}$Si were measured at an energy offset of 75 V and energy window of 19 eV, under operating conditions of 4500 V secondary beam voltage and 8 nA and 10 kV for the primary beam of O$^-$ ions. Under these conditions the primary ion beam sputters an elliptical analysis pit with long diameter 25-30 µm and maximum depth of 3 µm. All analyses involved a 3 minute burn-in time followed by 20 cycles of 5 second counts for each isotope. The mean isotope ratios of $^1$H/$^{28}$Si and $^{12}$C/$^{28}$Si for the last 10 cycles in each analysis has been taken as the final results, thereby avoiding surface contamination. Analyses expressed as isotopic ratios of $^1$H/$^{28}$Si and $^{12}$C/$^{28}$Si were converted to wt% H$_2$O or CO$_2$ by comparison with the calibration lines produced from fitting two standards analysed several times throughout the same analytical session.
Chapter 1: Quantitative analysis of H\textsubscript{2}O and CO\textsubscript{2} in cordierite using polarized FTIR spectroscopy

FTIR spectra were acquired with a Nicolet Magna 760 spectrophotometer, equipped with a NicPlan Microscope, a KBr beamsplitter and a liquid nitrogen-cooled MCT detector at University Roma Tre. Polarized spectra were collected using a gold-wire grid polarizer on a ZnSe substrate. The nominal resolution was 4 cm\textsuperscript{-1} and 128 scans were averaged for both spectrum and background. Several fragments from each specimen were oriented using a spindle stage (Bloss 1981) fitted on a polarizing microscope following the procedure of Gunter et al. (2004). The fragments were transferred on glass slides and doubly polished to thickness variable from 20 to 190 µm. Sample thickness was measured with a Leica DCM 3D optical profilometer, at LIME (Laboratorio Interdipartimentale di Microscopia Elettronica), Università Roma Tre; vertical resolution was < 15 nm in confocal mode (20X lens, NA = 0.50) and < 4 nm in interferometric mode (50X lens, NA = 0.50); final thickness was averaged for the whole surface of the sample. FTIR maps were collected at INFN (Istituto Nazionale di Fisica Nucleare) of Frascati (Roma) using a Bruker® Hyperion 3000 IR microscope equipped with a computer-controlled, motorized sample stage and an MCT detector. Single spot spectra were collected using a beam size varying from 50 to 200 µm, on a grid up to several mm\textsuperscript{2}. FTIR images for some selected areas were acquired using a 64×64 pixel focal plane array (FPA) of detectors. By using a 15X objective each image covers an area of 170 × 170 µm\textsuperscript{2} with a spatial resolution of ∼ 5 µm (Della Ventura et al. 2010). For both maps and images the nominal resolution was set at 8 cm\textsuperscript{-1}, and 128 scans were averaged for each spectrum and background.

3. X-ray diffraction, optical properties and microchemistry

Single-crystal X-ray diffraction showed all samples to be orthorhombic Cccm; refined cell parameters are listed in Table 2. Table 2 also give selected microchemical data, where all oxides are from EMPA, except H\textsubscript{2}O and CO\textsubscript{2} which are from SIMS; the resulting crystal-chemical formulae were calculated on the basis of 18 oxygen atoms. For all samples the Si:Al ratio is always close to the stoichiometric 5:4 value (Table 2) thus excluding additional cations, such as Be and Li (Schreyer et al. 1979, Sokol et al. 2010) at the four-fold coordinated sites. Fe has been considered as Fe\textsuperscript{2+} (Goldman et al. 1977, Geiger et al. 2000); Mg and Fe are the main
octahedral occupants, with the $X_{Mg} (= \text{Mg/Mg+Fe})$ ranging from 76.31 to 96.63. Additional elements occur in very low amounts; Ti and Mn are always < 0.01 apfu, except in sample BM96512 where Mn ≈ 0.03 apfu. K and Ca occur in very minor amounts (< 0.01 apfu) while Na may reach values as high as 0.84 apfu (sample Rp7344, Table 2). SIMS shows that the studied samples contain variable $H_2O$ and $CO_2$. $H_2O$, in particular, is extremely low in sample BB3a from Antarctica (Fitzsimons 1996; Thompson et al. 2001) and is > 0.50 apfu in sample RP7344 from Tamil Nadu (Bertoldi et al. 2004; Lal et al. 1984) (Table 2). This latter sample shows also the lowest content in carbon dioxide, while the highest $CO_2$ content is recorded in specimen 8/90 from the high-grade metamorphic rocks of Calabria (Italy). As expected, no relationship between $H_2O$ and $CO_2$ contents is observed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BM 96512</th>
<th>8/90</th>
<th>RIG</th>
<th>BB3a</th>
<th>RP 7344</th>
<th>RP 5578</th>
<th>RP 3237</th>
<th>RP 7045</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>49.10</td>
<td>48.33</td>
<td>49.61</td>
<td>48.27</td>
<td>49.65</td>
<td>49.43</td>
<td>49.55</td>
<td>49.19</td>
</tr>
<tr>
<td>Al</td>
<td>33.10</td>
<td>32.83</td>
<td>33.50</td>
<td>32.91</td>
<td>33.11</td>
<td>32.78</td>
<td>33.01</td>
<td>33.33</td>
</tr>
<tr>
<td>Mg</td>
<td>10.04</td>
<td>9.48</td>
<td>12.94</td>
<td>8.45</td>
<td>13.20</td>
<td>11.94</td>
<td>12.49</td>
<td>10.79</td>
</tr>
<tr>
<td>Fe</td>
<td>5.21</td>
<td>6.35</td>
<td>0.75</td>
<td>8.33</td>
<td>1.06</td>
<td>2.52</td>
<td>1.86</td>
<td>4.49</td>
</tr>
<tr>
<td>Ti</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
<td>0.04</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.06</td>
</tr>
<tr>
<td>Mn</td>
<td>0.34</td>
<td>0.05</td>
<td>0.03</td>
<td>0.06</td>
<td>0.01</td>
<td>0.05</td>
<td>0.02</td>
<td>0.12</td>
</tr>
<tr>
<td>Ca</td>
<td>0.04</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>Na</td>
<td>0.15</td>
<td>0.10</td>
<td>0.19</td>
<td>0.33</td>
<td>0.43</td>
<td>0.17</td>
<td>0.24</td>
<td>0.05</td>
</tr>
<tr>
<td>K</td>
<td>0.03</td>
<td>0.00</td>
<td>0.02</td>
<td>0.12</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>0.62</td>
<td>0.81*</td>
<td>n.a.</td>
<td>0.175</td>
<td>1.52</td>
<td>0.91</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>$CO_2$</td>
<td>0.51</td>
<td>1.3*</td>
<td>n.a.</td>
<td>0.74</td>
<td>0.22</td>
<td>1.11</td>
<td>1.01</td>
<td>0.69</td>
</tr>
<tr>
<td>Total</td>
<td>99.16</td>
<td>99.31</td>
<td>97.10</td>
<td>99.14</td>
<td>99.25</td>
<td>98.94</td>
<td>99.06</td>
<td>99.11</td>
</tr>
</tbody>
</table>

**Table 2 - Microchemical analysis, crystal-chemical formula, cell parameters, density and optical properties for the studied cordierites.**
Chapter 1: Quantitative analysis of H$_2$O and CO$_2$ in cordierite using polarized FTIR spectroscopy

Cell parameters (Å)

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>17.135(7)</td>
<td>17.118(1)</td>
<td>17.103(1)</td>
<td>2.602(4)</td>
</tr>
<tr>
<td></td>
<td>17.170(1)</td>
<td>9.764(3)</td>
<td>9.759(1)</td>
<td>2.612(6)</td>
</tr>
<tr>
<td></td>
<td>17.020(1)</td>
<td>9.766(2)</td>
<td>9.751(1)</td>
<td>2.5752(4)</td>
</tr>
<tr>
<td></td>
<td>17.085(2)</td>
<td>9.339(1)</td>
<td>9.380(1)</td>
<td>2.630(8)</td>
</tr>
<tr>
<td></td>
<td>17.132(2)</td>
<td>9.380(1)</td>
<td>9.368(1)</td>
<td>2.58(3)</td>
</tr>
<tr>
<td></td>
<td>9.020(1)</td>
<td>9.451(4)</td>
<td>9.353(1)</td>
<td>2.578(1)</td>
</tr>
<tr>
<td></td>
<td>9.343(7)</td>
<td>9.408(1)</td>
<td>9.380(1)</td>
<td>2.597(2)</td>
</tr>
</tbody>
</table>

Optic sign

<table>
<thead>
<tr>
<th></th>
<th>Positive</th>
<th>Positive</th>
<th>Positive</th>
<th>Negative</th>
<th>Positive</th>
<th>Positive</th>
<th>Positive</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Vx (°)</td>
<td>90(3)</td>
<td>102.9(9)</td>
<td>103.4(4)</td>
<td>91(1)</td>
<td>63.15(8)</td>
<td>96(1)</td>
<td>90.3(9)</td>
</tr>
</tbody>
</table>

Note: H$_2$O and CO$_2$ from SIMS, all other elements from EMPA; crystal-chemical formulae in atoms per formula unit (apfu) calculated on the basis of 18 oxygen pfu. For cell parameters, densities and optical 2Vx angle estimated standard errors on the last digit are given in brackets.

Table 2 also gives the 2V$_x$ optic axis angles measured using the spindle stage (e.g. Gunter et al. 2004); all samples are optically positive, except cordierite RP7344 which, having the lowest CO$_2$ content, is negative (Table 2a). The relationship between the 2V$_x$ optical axis angle and the CO$_2$ content in the cordierite channel has been investigated experimentally by Armbruster and Bloss (1982) who found a linear trend between all optical parameters and the gas (both CO$_2$ and H$_2$O) content in the channels. The data reported in Table 2a are in agreement with these results of Armbruster and Bloss (1982) and show that the CO$_2$ content indeed has a strong effect of the physical properties of cordierite.

Table 3 - Site populations (apfu) on the basis of the X-ray single-crystal refined site scattering for selected atoms. Errors in brackets. Thermal parameters for H$_2$O and CO$_2$ were considered all isotropic ($U_{iso}$) and fixed at values known from the literature (e.g. Malcherek et al. 2001) to avoid refinement instability. $\Delta$ = Difference between the microchemical and X-ray derived apfu

<table>
<thead>
<tr>
<th>Sample</th>
<th>BM96512</th>
<th>8/90</th>
<th>RIG</th>
<th>BB3a</th>
<th>RP 7344</th>
<th>RP 5578</th>
<th>RP 3237</th>
<th>RP 7045</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>1.564(8)</td>
<td>1.504(8)</td>
<td>2</td>
<td>1.328(8)</td>
<td>1.984(10)</td>
<td>1.858(10)</td>
<td>1.92(2)</td>
<td>1.660(8)</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.436(8)</td>
<td>0.496(8)</td>
<td>-</td>
<td>0.672(8)</td>
<td>0.016(10)</td>
<td>0.142(10)</td>
<td>0.08(2)</td>
<td>0.340(8)</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.042(8)</td>
<td>0.03(1)</td>
<td>0.04(1)</td>
<td>0.05(1)</td>
<td>0.15(1)</td>
<td>0.05(1)</td>
<td>0.05(2)</td>
<td>0.014(9)</td>
</tr>
<tr>
<td>O$_{H2O}$</td>
<td>0.048(8)</td>
<td>0.08(3)</td>
<td>0.09(3)</td>
<td>-</td>
<td>0.10(1)</td>
<td>0.06(6)</td>
<td>-</td>
<td>0.057(5)</td>
</tr>
<tr>
<td>C$_{CO2}$</td>
<td>0.09(2)</td>
<td>0.23(2)</td>
<td>0.29(2)</td>
<td>0.16(2)</td>
<td>0.11(1)</td>
<td>0.25(2)</td>
<td>0.25(3)</td>
<td>0.10(1)</td>
</tr>
</tbody>
</table>

$\Delta$ = apfu$_{EPMA+SIMS}$ - apfu$_{XR,SCR}$

Site occupancy refinements (Table 3) were performed from X-ray single-crystal data considering Mg and Fe at the same crystallographic site 8g (total site occupancy factor, s.o.f = 1), O$_w$ (the water oxygens) at the 4a site, C at the 4a site with the carbon-dioxide oxygens at the 8g site (constraining their s.o.f. to be equal), and channel Na at the 4c site (Armbruster 1985;
Malcherek et al. (2001). Comparison of EMP+SIMS values with site occupancies refined from XRD shows an excellent agreement between the two sets of data: Mg$^{2+}$ contents obtained from XRD are slightly overestimated by 0.056 apfu, while Fe$^{2+}$ is underestimated by roughly the same amount and Na$^+$ contents are similar within esds. Interestingly, the XRD-refined CO$_2$ contents are slightly overestimated (Table 3) but still in excellent agreement with SIMS data. On the other side, the agreement for water is rather poor, with H$_2$O underestimated by as much as 0.41 molecules pfu (Table 3).

4. Single-crystal FTIR spectroscopy

![Figure 1](image_url)

**Figure 1** - Non-polarized single-crystal FTIR spectra of samples 8/90 (top) and RP7344 (bottom). Regions 1 and 2 (see text) are highlighted; bending and combination modes at 1635 and 5270 cm$^{-1}$, respectively, are arrowed. The linear absorption coefficient is defined as linear absorbance / thickness (A/t).

Figure 1 shows two typical unpolarized-light spectra collected on a doubly-polished fragment. The pattern consists of several bands which have been grouped for simplicity in
two regions, from 3900-3300 cm\(^{-1}\) (region 1) and 2600-2000 cm\(^{-1}\) (region 2), respectively. In both regions intense and relatively sharp peaks are present. Additional peaks relevant to the present discussion occur around 1635 cm\(^{-1}\) and in the 4000-6000 cm\(^{-1}\) range. As it will be discussed below, these bands are related, respectively, to the bending mode and to the combination of the stretching and the bending modes of the H\(_2\)O molecule(s). Furthermore a cursory examination of the unpolarized spectra of Figure 1 shows that the single-crystal FTIR spectrum provides an immediate picture of the relative volatile content for samples with different H\(_2\)O/CO\(_2\) contents (RP7344, bottom: high-water and low CO\(_2\); 8/90, top: rich in both H\(_2\)O and CO\(_2\)).

The polarized-light spectra collected for cordierite RP5578 are displayed in Figure 2. In region 1 (Fig. 2a, left) the most intense peaks are observed for \(E//c\), centred at 3689 and 3575 cm\(^{-1}\). A broad and relatively intense band is present at 3630 cm\(^{-1}\) in the \(E//b\) spectrum, while the main features present in the \(E//a\) spectrum are the very sharp peak at 3708 cm\(^{-1}\) and a sharp and weak band at 3595 cm\(^{-1}\).

![Figure 2a](image_url) - Single-crystal polarized-light FTIR spectra of cordierite RP 5578 collected on oriented (010), 33 μm thick and (100), 34 μm thick, sections; left = region 1 and right = region 2. Spectra scaled to thickness and vertically displaced for clarity. The weak band at 2134 cm\(^{-1}\) (inset) is from sample RP 7045, 72 μm thick section; the linear absorption coefficient of the band is 2 cm\(^{-1}\).
Chapter 1: Quantitative analysis of H₂O and CO₂ in cordierite using polarized FTIR spectroscopy

Figure 2a - Left: single-crystal polarized-light FTIR spectra of cordierite RP 3237 collected in the combination region on oriented (010), 20 μm thick and (100), 88 μm thick sections. Right: single-crystal polarized-light FTIR spectra of cordierite RP 5578 in the H₂O bending region, same sections as in Figure 2a. Spectra scaled to thickness and vertically displaced for clarity.

In region 2 (Figure 2a, right) the E // a spectrum shows a very sharp and intense absorption at 2348 cm⁻¹, with a weak shoulder at 2332 cm⁻¹ on the low-frequency side (arrowed; see also Fig. 1 of Della Ventura et al. 2009). A minor band is observed at 2282 cm⁻¹, while a very weak peak is resolved, for some samples, at 2134 cm⁻¹ (see inset in Fig. 2a and Fig. 1 of Della Ventura et al. 2009). The E // c spectrum is featureless, while the E // b spectrum shows a minor band at 2348 cm⁻¹ with two side bands at 2390 and 2306 cm⁻¹, respectively.

In the NIR (near infrared) 4500-5500 cm⁻¹ region (Figure 2b, left) the E // c spectrum shows a sharp and relatively intense (note that the absorption coefficients in this range are one order of magnitude lower than those in Figure 2a) absorption at 5270 cm⁻¹; the E // b spectrum shows a broad and minor band centred at 5245 cm⁻¹, while the E // a spectrum is featureless. In the H₂O bending region (1500-1800 cm⁻¹, Figure 2b, right) there is a very sharp peak at 1635 cm⁻¹ for E // c; this peak disappears for both E // b and E // a.
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5. Interpretation of polarized FTIR spectra

The correct assignment of the bands observed in the spectra of cordierite is a critical point when attempting to use the absorbance data for quantitative purposes. This issue has been addressed by Della Ventura et al. (2009) who critically revised the existing literature on the interpretation of the IR spectra of cordierite. Their conclusions will be used as a guide in the following text, and will be augmented with the analysis of the entire wavenumber range extending from 6000 cm$^{-1}$ (NIR) to 1500 cm$^{-1}$ (MIR).

The structural environment of the H$_2$O and CO$_2$ molecules in cordierite is shown in Figure 3. Based on all previous spectroscopic and crystal-structural studies (see Della Ventura et al. 2009 for a list of references) the H$_2$O molecules may be oriented in two different ways within the structural channels: (I) with their H-H direction parallel to the c-axis (Figure 3 left); these are termed “type I” (nomenclature introduced by Goldman and Rossman 1977) water molecules (hereafter H$_2$O$^{(I)}$). (II) with their H-H direction perpendicular to the c-axis; these are termed “type II” water molecules (hereafter H$_2$O$^{(II)}$). This second type is invariably associated with alkali cations (e.g. Goldman and Rossman 1977; Vry et al. 1990) in the channel (Figure 3 center). The carbon dioxide molecule is oriented perpendicular to the c-axis (Figure 3 right), dominantly parallel to the a-axis (Armbruster and Bloss 1982).

Figure 3 - The structural environment of the channel constituents in cordierite: (left) type I water, (center) type II water, (right) CO$_2$. 

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The polarization behaviour of the fundamental modes of the water molecules in cordierite is a function of the orientation of the molecule with respect the crystallographic axis. As shown by Goldman et al. (1977), the $v_3$ antisymmetric stretching is polarized along the H...H direction, while $v_2$ and $v_1$ (symmetric stretching and bending, respectively) are polarized along the molecular two-fold axis; combining both information we may obtain the orientation of the molecular plane. The reference point for the interpretation of the spectra of Figure 2 is the powder spectrum of CO$_2$ and alkali-free synthetic Mg-cordierite (Paukov et al. 2007), which consists of two bands: a very intense peak at 3689 cm$^{-1}$, and a minor peak at 3595 cm$^{-1}$. Given the controlled chemistry of the sample, the former can be unambiguously assigned to the $v_3$ mode of H$_2$O$^{[I]}$, while the latter can be assigned to the $v_1$ mode of the same H$_2$O$^{[I]}$ molecule. The splitting between these two components [$\Delta(v_3 - v_1) = 94 \text{ cm}^{-1}$] suggests that H$_2$O$^{[I]}$ occurs in cordierite as a relatively free, unbound molecule (Geiger and Kolesov 2002). In Figure 2a, the intense peak at 3689 cm$^{-1}$ for E // c is thus assigned to the $v_3$ vibration of H$_2$O$^{[I]}$. The $v_1$ mode of the same H$_2$O$^{[I]}$ molecule at 3595 cm$^{-1}$ is observed as a very weak absorption in the E // b spectrum. A weak component at $\sim$ 3595 cm$^{-1}$ is also present in the E // a spectrum (Figure 2). Following Della Ventura et al. (2009) this is assigned to a combination mode of CO$_2$.

Based on the data available in the literature (e.g. Goldman et al. 1977; Kolesov and Geiger 2000), H$_2$O$^{[II]}$ is characterized by a $v_3$ antisymmetric stretching at $\sim$ 3630 cm$^{-1}$ associated with a $v_1$ symmetric stretching at $\sim$ 3575 cm$^{-1}$. Hence, the broad absorption at 3630 cm$^{-1}$ for E // b (Figure 2a) is assigned to the $v_3$ mode of H$_2$O$^{[II]}$, while the well defined peak at 3575 cm$^{-1}$ for E // c is assigned to the $v_1$ mode of the same H$_2$O$^{[II]}$ molecule. The splitting between these two bands [$\Delta(v_3 - v_1) = 55 \text{ cm}^{-1}$] is lower than that observed for H$_2$O$^{[I]}$ suggesting that H$_2$O$^{[II]}$ is involved in some sort of bonding with the closest atoms.

In the combination region, the most intense peak at 5270 cm$^{-1}$ is polarized for E // c hence it is assigned to the ($v_3 + v_2$) combination mode of H$_2$O$^{[I]}$, while the minor but resolvable band centred at 5245 cm$^{-1}$, polarized for E // b, is assigned to the ($v_3 + v_2$) combination mode of H$_2$O$^{[II]}$ (see also Goldman et al. 1977). In accordance with this interpretation, the integrated intensity of the 3689 cm$^{-1}$ is linearly correlated with the intensity of the 5270 cm$^{-1}$ band (Figure 4a), while the integrated intensity of the 3630 cm$^{-1}$ is linearly correlated with the intensity of the 5245 cm$^{-1}$ band (Figure 4b).
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Figure 4 - Relationship between the integrated absorbance of the 5250 cm$^{-1}$ band versus the 3630 cm$^{-1}$ band (bottom), and the integrated absorbance of the 5266 cm$^{-1}$ band versus the 3690 cm$^{-1}$ band (top).

One important conclusion of the above discussion is that the very sharp and relatively intense peak at 3708 cm$^{-1}$ is not related to water molecules, but, as suggested by Geiger and Kolesov (2002) and later established by Della Ventura et al. (2009), must be instead assigned to a combination ($\nu_3 + \nu_1$) mode of CO$_2$. In addition, Della Ventura et al. (2009) in their study of a CO$_2$-bearing, but H$_2$O-free cordierite from El Hoyazo (Spain) showed that the weak component at 3595 cm$^{-1}$ in the $E//a$ spectrum must also be related to a combination ($\nu_3 + 2\nu_2$) mode of CO$_2$. This band occurs at a frequency coincident with the frequency of the $\nu_1$ mode of type I water (see above). This observation is particularly important in this context,
because all studies dealing with the spectroscopic H₂O/CO₂ determination in cordierite, particularly those done using powder data (e.g. Vry et al. 1990; Kalt 2000; Rigby et al. 2008 and references therein), have been based on the Goldman et al. (1977) model, whereby all bands in the 3900-3300 cm⁻¹ range were assigned to H₂O.

In the 2600-2000 cm⁻¹ region (Figure 2a, right), the most intense band at 2348 cm⁻¹ is assigned to the ν₃ antisymmetric stretching mode of the ¹²C₁₆O₂ molecule (Khomenko and Langer 2005). The minor bands at 2282 and 2134 cm⁻¹, which are observed in single-crystal and powder spectra of CO₂-rich cordierites (e.g. Le Breton 1989), have the same polarisation behaviour as the main band at 2348 cm⁻¹. Their interpretation has been discussed recently by Khomenko and Langer (2005) who concluded that the former band can be assigned to the vibration of a ¹³C₁₆O₂ carbon dioxide molecule, while the latter can be assigned to the vibration of a ¹²C₁₆O carbon monoxide molecule, also aligned along the a crystallographic axis. Thus the IR spectrum of cordierite potentially provides information on both the composition and the isotopic signature of molecular carbon entrapped into the structural channels. Assignment of the two side bands at 2390 and 2306 cm⁻¹ observed in the \(E // b\) spectrum is still unclear; according to Aines and Rossman (1984), these bands may be related to librational, sum and difference motions of the CO₂ molecule on the (001) plane. Final band assignments are summarized in Table 4.

**Table 4 - Position, assignment and polarization for various peaks in the cordierite spectra.**

<table>
<thead>
<tr>
<th>Wavelength (cm⁻¹)</th>
<th>Molecule</th>
<th>Mode</th>
<th>Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1635</td>
<td>H₂O[ll]</td>
<td>bending ν₂</td>
<td>c</td>
</tr>
<tr>
<td>2134</td>
<td>¹²C₁₆O</td>
<td>stretch ν₃</td>
<td>a</td>
</tr>
<tr>
<td>2282</td>
<td>¹³C₁₆O₂</td>
<td>antisym stretch ν₃</td>
<td>a</td>
</tr>
<tr>
<td>2348</td>
<td>¹²C₁₆O₂</td>
<td>antisym stretch ν₃</td>
<td>a</td>
</tr>
<tr>
<td>3575</td>
<td>H₂O[ll]</td>
<td>sym stretch ν₁</td>
<td>c</td>
</tr>
<tr>
<td>3595</td>
<td>H₂O[ll]</td>
<td>sym stretch ν₁</td>
<td>b</td>
</tr>
<tr>
<td>3595</td>
<td>¹²C₁₆O₂</td>
<td>combination ν₃ + 2ν₂</td>
<td>a</td>
</tr>
<tr>
<td>3630</td>
<td>H₂O[ll]</td>
<td>antisym stretch ν₃</td>
<td>b</td>
</tr>
<tr>
<td>3689</td>
<td>H₂O[ll]</td>
<td>antisym stretch ν₃</td>
<td>c</td>
</tr>
<tr>
<td>3708</td>
<td>¹²C₁₆O₂</td>
<td>combination ν₃ + ν₁</td>
<td>a</td>
</tr>
<tr>
<td>5245</td>
<td>H₂O[ll]</td>
<td>combination ν₃ + ν₂</td>
<td>b</td>
</tr>
<tr>
<td>5270</td>
<td>H₂O[ll]</td>
<td>combination ν₃ + ν₂</td>
<td>c</td>
</tr>
</tbody>
</table>
6. The distribution of H$_2$O and CO$_2$ in the studied samples

Recent work done on several microporous materials such as leucite (Della Ventura et al. 2008) or minerals of the haüyine-sodalite group (Bellatreccia et al. 2009) has shown that water, but also carbon dioxide, can be zoned across the crystal. For cordierite in particular Della Ventura et al. (2009) have shown that the distribution of water may be complicated by the diffuse presence of alteration products or by fractures and cracks due to the geological history after the mineral formation, even in samples which are apparently optically clean. The possible inhomogeneous distribution of H$_2$O and CO$_2$ across the samples is obviously an important issue in quantitative micro-analytical work, therefore as a preliminary step we collected several FTIR maps and FPA images to test for the homogeneity of the crystals used for single-spot quantitative analyses. As discussed by Della Ventura et al. (2010), there are essentially two experimental set-ups in spectroscopic imaging: (1) FTIR mapping which is performed by integrating the signal from successive locations of the specimen surface; in this case a large number of single-spot spectra are collected by displacing the sample step-by-step using a motorized stage. The final resolution of the map depends on the single-spot size, which cannot be reduced below few tenths of µm$^2$ in conventional (globar) light (typically 20-50 µm$^2$), and on the grid-size. The advantage of this technique is that one can obtain maps of large areas (several mm$^2$) with a very good signal/noise ratio. The major disadvantage, besides the relatively poor lateral resolution (the single-spot size), is the large time needed to collect a map (up to hours for mm-sized maps). (2) FTIR imaging. In this case the whole image is obtained in a single data collection by using a bi-dimensional array of detectors (FPA). The number of pixels (the detectors) and their effective size will depend on the FPA type and the microscope objective. Typical arrays range from the 64×64 channels, providing 4096 individual spectra to 256×256 or 1024×1024 formats. Such arrays are coupled with 15X or 36X objectives, thus the physical dimensions of a single pixel is in the range 2.5 to 5 µm$^2$. The area covered in each data collection is in the order of 200-400 µm$^2$. Using this technique a resolution close to the diffraction limit can be attained, and the time needed to collect an image may scale down to few minutes (Della Ventura et al. 2010).
Prior to the quantitative analyses, we studied all samples by FTIR mapping; when needed, some key locations were examined using the FPA detector for higher resolution. Some crystals, for example cordierite BM96512 appeared homogeneous, while other specimens displayed an evident zoning. Cordierite RP5578 (Figure 5), for example, while being homogeneous with respect to CO$_2$, shows areas with different H$_2$O contents. A peculiar example is that of cordierite BB3a from Antarctica. Optically, the crystals show a weak chromatic zoning, consisting of light-blue to yellowish zones. The FTIR maps obtained by integrating the 3700-3400 cm$^{-1}$ region show that the yellowish part (top in Figure 6) is extremely enriched in H$_2$O with respect the light-blue, lower side of the grain. Interestingly, the opposite is observed for CO$_2$, which is extremely enriched in the top side of the grain. Single FTIR spectra, collected with a reduced beam size in the yellowish, water-richer side, show a very broad convolute band extending from 3700-3100 cm$^{-1}$ suggesting that this area contains dispersed very fine crystals of alteration products (Della Ventura et al. 2009) which account for the increased absorbance in the H$_2$O region.

Figure 5 - Sample RP 5578: (a) Optical image of the analyzed sample area, (b) FPA image of CO$_2$ distribution, (c) image of the total signal from 3800 to 2800 cm$^{-1}$ and (d) image of the 3689 cm$^{-1}$ band (H$_2$O$^{(i)}$) intensity.
To define with a better resolution the transition between the yellowish and the light-blue zones, we collected for the same section some FTIR images using a multi-channel FPA detector, under the conditions explained above. Figure 6d shows that there is a sharp transition between the region where secondary alteration products are present and account for the extremely intense absorption in the water-stretching region; in addition, strong intensity of the H$_2$O signal is also associated with micro-fractions (arrowed) within the sample.

**Figure 6** - Sample BB3a: (a) Optical image of the section with location of the single spots. The black box indicates the location of the FPA image in (d); (b) and (c) distribution of the CO$_2$ and H$_2$O band intensity, respectively. (d) FPA image of H$_2$O distribution on a 170x170 μm$^2$ area.

**7. Calibration of a molar absorption coefficient to quantify H$_2$O and CO$_2$ in cordierite using FTIR spectroscopy**

As explained above, the main problem in the quantitative spectroscopic analysis of H and C in cordierite is the lack of reliable integrated absorption coefficients to be used in the Beer-Lambert relationship $c$ (wt.%) = $A_i / (t \cdot \varepsilon_i)$. Rearranging this equation as $\varepsilon = A \cdot m / c \cdot t \cdot D$, we can calibrate both $\varepsilon_{H2O}$ and $\varepsilon_{CO2}$ substituting the concentrations obtained from SIMS. The
m factor in this formula is needed for the conversion of the concentration from wt% to mol l⁻¹; for H₂O m = 1.8 (Beran et al. 1993), for CO₂ m = 4.401 (Della Ventura et al. 2009). The density D (in g/cm³, Table 2a) was calculated as 0.0036X² + 0.00394X + 2.573 (Goldman et al. 1977) where X = (total Fe in wt% from Table 2a), while Aᵢ was obtained by summing up the single absorbances measured along the three optical directions (Libowitzky and Rossman, 1996).

For H₂O, one difficulty arises from the fact that SIMS provides the total water content in the sample, while FTIR (see above) provides two different H₂O signals due to the two water types, which are resolved at different frequency (3689 vs 3630 cm⁻¹). According to Libowitzky and Rossman (1997), εₜₕ₂ₒ is a function of the wavenumber, thus two εₜₕ₂ₒ are expected for the two water types. To solve this problem, we calculated for each sample the relative amounts of H₂Ot[I] and H₂Ot[II] assuming that each alkali cation located within the structural channels is locally associated with two H₂Ot[II] molecules. This relationship has been proposed by several authors (e.g. Goldman and Rossman 1977; Vry et al. 1990) and is also verified in this study, as it is apparent in Figure 7, where there is a well-defined linear trend connecting the total alkali content (Na+K+Ca) from EMPA, and the integrated absorbance of the 3630 cm⁻¹ band assigned to H₂Ot[II]. Therefore, H₂Ot[II] was set to be H₂Ot[II] = 2·(Na,K,Ca)ch and H₂Ot[I] = H₂Ot tot - H₂Ot[II] (Table 2a). εₜₕ₂ₒ coefficients were finally calculated for both water types, independently (Table 5).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Integrated (l·mol⁻¹·cm⁻²)</th>
<th>Linear (l·mol⁻¹·cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₃ (H₂Ot[I])</td>
<td>5200</td>
<td>400</td>
</tr>
<tr>
<td>ν₃ (H₂Ot[II])</td>
<td>13000</td>
<td>240</td>
</tr>
<tr>
<td>ν₃ (H₂Ot[II] + H₂Ot[I])</td>
<td>6700</td>
<td>260</td>
</tr>
<tr>
<td>ν₃ + ν₂ (H₂Ot[I])</td>
<td>420</td>
<td>22</td>
</tr>
<tr>
<td>ν₃ + ν₂ (H₂Ot[II])</td>
<td>340</td>
<td>8</td>
</tr>
<tr>
<td>ν₃ (CO₂)</td>
<td>19000</td>
<td>1000</td>
</tr>
</tbody>
</table>

For CO₂, again SIMS provides the total carbon content only, while FTIR spectra show (Figure 2a) that some of the examined cordierites contain also some carbon monoxide; from the intensity of the CO band (2134 cm⁻¹), its amount can, however, be estimated to be so small that the error introduced in the calculation of the molar absorption coefficient can be
considered as negligible. One point which is worth to be mentioned here is that for samples with higher CO$_2$ contents, the main band at 2348 cm$^{-1}$ is extremely intense, and when this is the case there is the need to reduce the thickness of the analysed slab. This feature is evident, for instance, for sample RP 5578 which has the highest CO$_2$ content within the studied specimens (CO$_2$ = 1.11 wt%, Table 2), and its CO$_2$ peak is at the limits of detector saturation, even for a thickness as low as 34 µm (Fig. 2a). We faced similar problems with other CO$_2$-rich samples, and the only way to handle it was to reduce the sample thickness in such a way to keep the main peak absorbance below 2.0. It is obvious that, given the sharpness of the 2348 cm$^{-1}$ band, the problem of peak truncation is relatively minor when using integrated intensities, while being much more significant if linear intensities are used for quantification purposes. An alternative way to handle this problem is by using the combination or overtone bands which have intensities much lower compared to the principal stretching bands. For CO$_2$ we tested the feasibility of using the 3595 cm$^{-1}$ band assigned to the $(\nu_3 + 2 \nu_2)$ combination (Table 4) and obtained an excellent linear relationship as a function of the SIMS measured CO$_2$ content in the sample (not shown). However, this band, as well as the 3708 cm$^{-1}$ peak assigned to the $(\nu_3 + \nu_1)$ combination of CO$_2$ (Table 4), overlap strongly with the water bands and thus cannot be measured with certainty. This approach gave better results for H$_2$O (see below).

Figure 7 - Relationship between the integrated absorption coefficient (defined as the integrated absorbance / thickness, cm$^{-2}$) of the band at 3630 cm$^{-1}$ assigned to the $\nu_3$ mode of type II H$_2$O and the total alkali content (apfu) in the channels.
For H$_2$O we calculated the absorption coefficients for the principal $v_3$ stretching and the combination bands. In addition to the integrated coefficient, we also calculated, for all bands, the linear molar absorption coefficient, which makes use of the linear intensity instead of the peak area. In some paper, particularly in earlier works, the linear intensity ($A_l$) was in fact used in the Beer-Lambert equation for quantitative purposes.

Figure 8 shows the relationship between the integrated intensity of the bands at 3689, 3630 and 2348 cm$^{-1}$ assigned to H$_2$O$^{[I]}$, H$_2$O$^{[II]}$ and CO$_2$, respectively against the relative SIMS amounts (wt%). Specific molar absorption coefficients ($\varepsilon$) for each sample were obtained on the basis of the Beer-Lambert relationship; the error $\sigma$ associated with each measurement was calculated using the classical statistics of error propagation (e.g., Bellatreccia et al. 2005) considering that the uncertainty on $A$ is $\sim$ 10% (Libowitzky and Rossman 1997), on the sample thickness (t) is < 2 µm, the standard deviation of the density (D) is 2% and the accuracy of SIMS analysis is better than 10%. Average final coefficients and errors for the different bands are summarized in Table 5. Note that in Table 5 we list also the molar absorption coefficients for the combination ($v_3 + 2v_2$) bands of type I and II H$_2$O which can be resolved in the NIR region for thicker sample slabs.

8. Conclusions

We provide in this paper the first integrated molar absorption coefficient for H$_2$O in cordierite based on polarized measurements on oriented crystal sections. Those provided by Goldman et al. (1977) were calibrated using linear (peak height) intensity data. They found very similar values for type I ($\varepsilon = 204$ l·mol$^{-1}$·cm$^{-1}$) and type II ($\varepsilon = 269$ l·mol$^{-1}$·cm$^{-1}$) H$_2$O, and concluded that, considering the analytical error, both types of H$_2$O molecules have the same molar absorption coefficient. We show here that the two water molecules are characterized by significantly different $\varepsilon$ coefficients, and this difference is particularly evident when dealing with integrated absorbance (Table 5). In this latter case, even considering the error in the measurement, the $\varepsilon_i$ coefficient for type II H$_2$O is more than double than that obtained for type I H$_2$O. The logical consequence of this feature is that careful quantification of H$_2$O in cordierite by FTIR spectroscopy requires measuring the different bands due to the different
types of channel water. In Table 5 we also give the value of the $\varepsilon$ coefficient calculated on the basis of the total $\text{H}_2\text{O}^{[\text{I}]} + \text{H}_2\text{O}^{[\text{II}]}$ band intensity versus the total $\text{SIMS}_2\text{O}$ content. This value can be used for a simplified spectroscopic quantification of the total $\text{H}_2\text{O}$ content in the examined cordierite sample.

**Figure 8** - Relationship between the integrated absorption coefficient (defined as the integrated absorbance/thickness, $a_i = \frac{A}{t}$ in cm$^{-1}$) of the band at 3689 cm$^{-1}$ (top), at 3630 cm$^{-1}$ (medium) and 2348 cm$^{-1}$ (bottom) versus the $\text{H}_2\text{O}^{[\text{I}]}$, $\text{H}_2\text{O}^{[\text{II}]}$ and $\text{CO}_2$ contents (apfu) obtained by SIMS, respectively.
For CO\(_2\), the \(\epsilon_{\text{CO}_2}\) calibrated in this work \([19000 \text{ l/(mol cm}^2\text{)}]\) is significantly different from that obtained recently \([\sim 11000 \text{ l/(mol cm}^2\text{)}]\) by Della Ventura et al. (2009). The value obtained here however is an average of measurements done on 8 samples spanning a relatively large CO\(_2\) variation, while the value presented by Della Ventura et al. (2009) was obtained on a single sample only. For this reason, we consider our data to be more reliable.

Powder infrared spectroscopy has been widely used in petrological studies as an analytical method for H\(_2\)O and CO\(_2\) in cordierite (e.g. Vry et al. 1990). However, as discussed by Libowitzky and Rossman (1996) such a procedure cannot provide the absolute quantitative determination of water and/or carbon dioxide. The calibration presented in this study, on the other side, allows a high level of accuracy in the determination of both molecules.

The use of novel techniques in FTIR imaging clearly shows that at the \(\mu\m\)-scale the distribution of H and C in this mineral may be significantly inhomogeneous, and this feature must be taken into account when collecting analytical data for petrological purposes. This feature is probably less important for carbon molecules than it is for H\(_2\)O, whose distribution within the crystal can be strongly affected by the geological history of the mineral after its formation.

Acknowledgements

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CHAPTER 2

SPECTROSCOPY AND X-RAY STRUCTURE REFINEMENT OF SEKANINAITE FROM DOLNÌ BORY (CZECH REP.)

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Abstract

The crystal chemistry of sekaninaite from Dolni Bory, Czech Republic, was characterized by a multi-methodological approach. Particular emphasis was put on the characterization of the channel constituents (i.e. H$_2$O and CO$_2$). Electron-micro-probe analysis shows the sample to be close to the Fe end-member ($X_{Fe} = Fe/(Fe+Mg) = 94\%$) with significant Mn (1.48 wt.%) present; laser ablation mass-spectrometry showed the presence of 0.42 wt.% Li$_2$O. H$_2$O and CO$_2$ contents (1.48 and 0.17 wt.%, respectively) were determined via secondary-ion mass-spectrometry (SIMS). Sample homogeneity was checked by FTIR imaging using a microscope equipped with an FPA detector. Single-crystal FTIR spectroscopy confirmed the presence of two types of H$_2$O groups in different orientations (with prevalence of the type II orientation), and that CO$_2$ is oriented preferentially normal to the crystallographic $c$ axis. Using the Beer-Lambert relation, integrated molar coefficients $\varepsilon_i$ were calculated for both types of H$_2$O ($\varepsilon_{i\, H_2O^{[I]}} = 6000 \pm 2000; \varepsilon_{i\, H_2O^{[II]}} = 13000 \pm 1000$) and for CO$_2$ ($\varepsilon_i\, CO_2 = 2000 \pm 1000$).

Key words: sekaninaite, crystal-structure refinement, EMPA + SIMP analysis, FTIR spectroscopy

1. Introduction

Sekaninaite is the Fe$^{2+}$ dominant member of the cordierite group (Cěrný et al., 1997). The first occurrence of this mineral was reported by Sekanina (1928) in the pegmatites of Dolnì Bory; however, it was definitively described as a new mineral species by Staněk and Miškovský (1964, 1975). Cordierites are framework aluminosilicates with the ideal formula $(\square,Na)(Mg,Fe)_{2}Al_{4}Si_{5}O_{18}(\square,H_2O,CO_2) = XM_2T_9O_{18}Y$ and form a continuous solid solution between the Mg$^{2+}$ end-member (cordierite s.s.) and the Fe$^{2+}$ end-member (sekaninaite). The main structural feature of these minerals is the presence of 6-fold rings of tetrahedra stacked along the $c$ crystallographic axis. These rings form cavities that can accommodate large cations such as Na$^+$, K$^+$ and molecules such as H$_2$O and CO$_2$. The sekaninaite framework can be described as a stacking of pseudo-hexagonal Si/Al layers of tetrahedra and mixed
layers of tetrahedra and octahedra (Fig. 1). Alkali cations, H$_2$O and CO$_2$ fill the resulting pseudo-hexagonal channel, occupying sites on the $c$ axis at (0, 0, 0) for Na, and (0, 0, ¼) for H$_2$O and CO$_2$ (Hochella et al., 1979; Malcherek et al., 2001; Yakubovich et al., 2004). The chemical composition of the framework has the ideal formula 4 Al apfu and 5 Si apfu. Due to the high concentration of alkali cations within the channels (Cěrný et al., 1997; Yakobuvich et al., 2004), charge balance may be restored by Be$^{2+}$ substitution at the tetrahedrally coordinated sites (Armbruster and Irouschek, 1983; Yakobuvich et al., 2004) or Li$^+$ at the octahedrally coordinated sites (Cěrný et al., 1997; Gottesmann and Förster, 2004). Unlike cordierite, sekaninaite is not a widespread mineral, and usually occurs in the albite zone of pegmatitic rocks (Staněk and Miškovský, 1964, Orlandi and Pezzotta, 1994; Guastoni et al., 2004). Other occurrences of sekaninaite were reported in altered bauxitic lithomarges (Ryback et al., 1988) and in Fe-rich pyrometamorphosed rocks (Sharygin et al., 2009; Grapes et al., 2010).

Figure - 1 Schematic view of a portion of the sekaninaite structure which includes the channel parallel along the $c$ axis. Si-containing tetrahedra are shown in dark grey and Al-containing tetrahedra are shown in light grey. The structural position of Na and both orientation types of H$_2$O are shown in the channels.
2. Analytical methodology

Table 1 - Chemical composition (mean of 5 analyses) and chemical formula (apfu), based on 18 oxygen atoms per formula unit, for the studied sekaninaite

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>Range</th>
<th>apfu</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>45.41</td>
<td>45.65-45.16</td>
<td>Si</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01</td>
<td>0.02-0.00</td>
<td>Al</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>31.53</td>
<td>31.84-31.27</td>
<td>ΣT</td>
</tr>
<tr>
<td>FeO</td>
<td>17.55</td>
<td>17.99-17.37</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>1.48</td>
<td>1.52-1.39</td>
<td>Mg</td>
</tr>
<tr>
<td>MgO</td>
<td>0.48</td>
<td>0.53-0.46</td>
<td>Fe</td>
</tr>
<tr>
<td>CaO</td>
<td>0.03</td>
<td>0.05-0.02</td>
<td>Ti</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.90</td>
<td>0.96-0.86</td>
<td>Mn</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.02</td>
<td>0.02-0.01</td>
<td>Li</td>
</tr>
<tr>
<td>Li₂O</td>
<td>0.42</td>
<td>0.43-0.41</td>
<td>ΣOct.</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.48</td>
<td>1.54-1.38</td>
<td>Ca</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.17</td>
<td>0.23-0.11</td>
<td>Na</td>
</tr>
<tr>
<td>Total</td>
<td>99.48</td>
<td></td>
<td>Na</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>K</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ΣCh.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂</td>
</tr>
</tbody>
</table>

All data from EMP analysis except for Li₂O (Nano-LAMS), H₂O and CO₂ from SIMS (see text).

The studied sample is from the type locality of Dolní Bory (Czech Rep.) (Staněk and Miškovský, 1964). The analyzed grains were extracted from a very clear, light blue and almost inclusion-free large crystal that gradually changes toward the rim of the sample into a greenish alteration product of clay minerals. Due to the presence of light elements (Li, H and C), the chemical composition of sekaninaite was determined using a multi-methodological approach. Elements from Si to K (Tab. 1) were analyzed using a Jeol JXA 8200 WD-ED electron micro-probe (EMP) at the Istituto Nazionale di Geofisica e Vulcanologia (INGV), Rome. Working conditions were: 15 kV accelerating voltage, 7 nA sample current, 5 µm beam diameter. Count times were 10 s on the peak and 5 s on the background on both sides of the peak. Standards, spectral lines and crystals used were: albite (NaKα, TAP), pargasite (CaKα, PET), wollastonite (SiKα, PET), K-feldspar (KαKα, PET), kyanite (AlKα, TAP), pargasite (MgKα, TAP), augite (FeKα, LiF), titanium oxide (TiKα, LiF) and spessartine (MnKα, LiF). Data
correction was done using the ZAF method. Sample homogeneity was verified by collecting many points per crystal. Lithium was determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Department of Geological Sciences, University of Manitoba (Winnipeg), using a Merchantek New Wave UP213 laser ablation system. The data were collected from three spots with a Nd: YAG laser, beam diameter of 50 μm, 10 Hz repetition rate, about 5 J/cm² fluence, 30 s background acquisition and 50 s ablation time. Li was standardized against NIST SRM 610.

H₂O and CO₂ were quantified by secondary-ion mass spectrometry (SIMS) using a Cameca IMS4f ion microprobe at the Edinburgh Materials and Micro Analysis Centre, University of Edinburgh. Sputtered secondary ions \(^{1}\text{H}, ^{12}\text{C}\) and \(^{28}\text{Si}\) were measured with an energy offset of 75 V and an energy window of 19 eV, under operating conditions of 4500 V secondary-beam voltage and 8 nA and 10 kV for the primary beam of O\(^-\) ions. Under these conditions, the primary-ion beam sputters an elliptical area with long diameter 25–30 μm and maximum depth of 3 μm. All analyses involved a 3 minute burn-in time followed by 20 cycles of 5 s counts for each isotope. The mean isotope ratios \(^{1}\text{H}/^{28}\text{Si}\) and \(^{12}\text{C}/^{28}\text{Si}\) for the last 10 cycles in each analysis were taken as the final results in order to avoid surface contamination. Analyses expressed as isotopic ratios of \(^{1}\text{H}/^{28}\text{Si}\) and \(^{12}\text{C}/^{28}\text{Si}\) were converted to wt.% H₂O or CO₂ by comparison with the calibration lines produced from fitting two standards analyzed several times throughout the same analytical session. The standards used were the samples ANMH (\(X_{\text{Mg}} = 0.89; \text{H}_2\text{O} = 1.54 \text{ wt%};\) and \(\text{CO}_2 = 0.7 \text{ wt%},\) Thompson et al., 2001) and 8/90 (labeled 81-90 \(X_{\text{Mg}} = 0.75; \text{H}_2\text{O} = 0.81 \%;\) and \(\text{CO}_2 = 1.31 \text{ wt%},\) Thompson et al., 2001).

X-ray diffraction data were collected at the Istituto di Cristallografia, Bari, with a Nonius Kappa CCD area-detector diffractometer (Tab. 2); data collection: COLLECT (Nonius, 1998); cell refinement and data reduction: EvalCCD (Duisenberg et al., 2003), absorption correction: SADABS (Sheldrick, 2008). The structure was solved through the Direct Methods procedure of SIR2008 (Burla et al., 2007) in the orthorhombic space group \textit{Ccmm} (n. 66), with the following unit-cell constants: \(a = 17.2340(15), b = 9.8457(18), c = 9.3463(18) \text{ Å},\) and refined by full-matrix least-squares based on \(F^2\), SHELXL-97 (Sheldrick, 2008); final R indices were, for \(|I|>2σ(I)|\) \(R_1 = 0.0178\) and \(wR_2 =0.0490,\) and for all data \(R_1 = 0.0186\) and \(wR_2 = 0.0499.\)
**Table 2 - Crystal data and structure refinement data for sekaninaite from Dolnì Bory**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Radiation, Wavelength</td>
<td>Mo-Kα, 0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, Space group</td>
<td>Orthorhombic, Cccm</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a = 17.2340(15) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(b = 9.8457(18) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(c = 9.3463(18) \text{ Å})</td>
</tr>
<tr>
<td>Volume</td>
<td>(1585.9(4) \text{ Å}^3)</td>
</tr>
<tr>
<td>Z</td>
<td>16</td>
</tr>
<tr>
<td>Calculated density</td>
<td>(2.726 \text{ Mg} \cdot \text{m}^{-3})</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>(2.315 \text{ mm}^{-1})</td>
</tr>
<tr>
<td>F(000)</td>
<td>1279</td>
</tr>
<tr>
<td>Crystal size</td>
<td>(0.25 \times 0.25 \times 0.12 \text{ mm})</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>(5.25^\circ) to (27.52^\circ)</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>(-22 \leq h \leq 22, -12 \leq k \leq 12, -12 \leq l \leq 10)</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>9441 / 942 ([\text{R}_{int} = 0.0297])</td>
</tr>
<tr>
<td>Completeness to theta</td>
<td>(96.6% \text{ (theta = 27.52(^{\circ}))})</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>(0.7686 \text{ and } 0.5953)</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>942 / 1 / 84</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.162</td>
</tr>
<tr>
<td>Final R indices [(I &gt; 2\sigma(I))]</td>
<td>(R_1 = 0.0178, \text{ wR}_2 = 0.0490)</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>(R_1 = 0.0186; \text{ wR}_2 = 0.0499)</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>(0.0092(4))</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>(0.348 \text{ and } -0.416 \text{ e} \cdot \text{Å}^{-3})</td>
</tr>
</tbody>
</table>

*SHELXL-97 weighting scheme applied: \(w^{-1} = [s^2(F_0^2) + (0.0179P)^2 + 3.4870P]/3\) where \(P = ([F_0^2 + 2F_c^2]/3)\)

Micro-Raman spectra were collected at Porto Conte Ricerche s.r.l., Alghero (Sassari), using a Bruker Senterra Raman microscope equipped with a 532 nm laser operated at 50 mW; 10 acquisitions of 5 s each were accumulated, with a spectral resolution set at 3 to 5 cm\(^{-1}\) (100x lens, NA = 0.9). Raw data were slightly smoothed.

FTIR spectra were acquired with a Nicolet Magna 760 spectrophotometer, equipped with a NicPlan Microscope, a KBr beamsplitter and a liquid nitrogen-cooled MCT detector at the Dipartimento di Scienze Geologiche, Università Roma Tre. The polarized spectra were collected using a gold-wire-grid polarizer on a ZnSe substrate. The nominal resolution is 4 cm\(^{-1}\) and 128 scans were averaged for both spectrum and background. The samples for polarized IR measurements were oriented using a polarizing microscope equipped with a spindle-stage; the program ExcalibrW (Bloss, 1981; Gunter et al., 2005) was used to process
the extinction data and to determine the 2V values. The oriented fragments were transferred to glass slides and doubly polished to thickness below 100 µm. Sample thickness was checked with a Leica DCM 3D optical profilometer at the Laboratorio Interdipartimentale di Microscopia Elettronica (LIME), Università Roma Tre. The nominal vertical resolution was less than 15 nm in confocal mode (20X lens, NA = 0.50) and less than 4 nm in interferometric mode (50X lens, NA = 0.50); sample thickness was averaged for the whole surface of the slab.

FTIR images were collected at the Laboratori Nazionali di Frascati-Istituto Nazionale di Fisica Nucleare (LNF-INFN,) Frascati (Rome) using a Bruker® Hyperion 3000 IR microscope equipped with a 64×64-pixel focal-plane array (FPA) of liquid nitrogen-cooled MCT detectors. Using a 15X objective, each image covers an area of 170 X 170 µm² with a nominal spatial resolution of ~5 µm (Della Ventura et al., 2010). The nominal resolution was set at 4 cm⁻¹ and 64 scans were averaged for each spectrum and background.

Refractive indexes were determined by the double-variation method (Su et al., 1987, Gunter et al., 2004) using standard Cargille liquids as reference.

3. Chemical composition

Figure 2 - Sum of channel cation charges versus Be + Li charges. Cross: this work, diamonds: samples from Dolní Bory (Cěrný et al., 1997); the regression line for these latter samples is reported.
Selected micro-chemical data for the studied sample are reported in Table 1. $\text{Fe}_{\text{tot}}$ was considered as $\text{Fe}^{2+}$. The chemical formula, based on 18 oxygen atoms pfu, is

$$\text{Na}_{0.19}(\text{Mg}_{0.08}\text{Fe}_{1.60}\text{Mn}_{0.14}\text{Li}_{0.19})\text{Al}_{4.05}\text{Si}_{4.95}\text{O}_{18} \cdot 0.54\text{H}_2\text{O} \cdot 0.03\text{CO}_2.$$ 

The chemical composition of the analyzed sample is close to those reported for other samples from the same area (Stanek and Miskovsky, 1964, Hochella et al., 1979, Černý et al. 1997). Sekaninate from Dolnì Bory, like in other pegmatite assemblages, has relatively high contents of Mn, Na and Li, on the opposite it has low concentration in Ti, Mg and K, elements usually abundant in paralava assemblages (Sharygin et al., 2009; Grapes et al., 2010). The Al/Si ratio is almost stoichiometric (4/5) and thus additional tetrahedrally coordinated cations are unlikely to be present. Although we do not have any information on the Fe oxidation state, we can reasonably consider all iron to be divalent, following Černý et al. (1997), who determined via Mössbauer spectroscopy that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ is 0.5% or less for sekaninaites from the same area. $\text{Fe}^{2+}$ is the main constituent at the octahedrally coordinated M site. Significant quantities of $\text{Li}^+$ (0.186 apfu) and $\text{Mn}^{2+}$ (0.137 apfu) are also present, whereas $\text{Mg}^{2+}$ and $\text{Ti}^{4+}$ concentrations are very low. Charge imbalance due to $\text{Na}^+$ in the channels is compensated by $\text{Li}^+$ at the M site. If we consider the sum of channel-cation charges ($\Sigma_{\text{Channel}}$)/(Li + Be) ratio, we clearly see that our sample is located much closer to the 1:1 line compared to the samples analyzed by Černý et al. (1997) (Fig. 2). SIMS data show that the sample is almost $\text{CO}_2$-free and significantly enriched in $\text{H}_2\text{O}$, as reported by previous authors (Yakubovich et al., 2004, Malcherek et al. 2001, Salkress and Bloss, 1980).

4. Single-crystal X-ray results

X-ray structure-refinement data are reported in Table 2, atom coordinates and equivalent isotropic-displacement parameters are reported in Table 3; bond lengths are reported in Table 4. The $a$ and $b$ parameters (Tab. 2) are in line with those reported for samples from the same locality (Hochella et al., 1979; Selkregg and Bloss, 1980; Malcherek et al., 2001) and with those of synthetic iron-cordierite (Borbeski and Schreyer, 1990; Bulbak and Shvedenkova, 2011), whereas the $c$ parameter (and consequently the cell volume) is at least 0.03 Å greater, a value that is more typical of Mg-cordierite. Parameters that, in our case, may increase the $c$ parameter are the absence of Be at the T-sites (see below).
(Yakubovich et al., 2004) and the presence of H\textsubscript{2}O and CO\textsubscript{2} (Tab. 1) in the channels (Armbruster and Bloss, 1982).

<table>
<thead>
<tr>
<th>Site</th>
<th>Wyckoff symbol</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq)</th>
<th>s.o.f.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>4b</td>
<td>0</td>
<td>1/2</td>
<td>1/4</td>
<td>0.0136(2)</td>
<td></td>
</tr>
<tr>
<td>T2</td>
<td>8l</td>
<td>0.18999(4)</td>
<td>0.07921(7)</td>
<td>0</td>
<td>0.01273(17)</td>
<td></td>
</tr>
<tr>
<td>T3</td>
<td>8l</td>
<td>0.13471(4)</td>
<td>0.76594(7)</td>
<td>0</td>
<td>0.01270(17)</td>
<td></td>
</tr>
<tr>
<td>T4</td>
<td>8k</td>
<td>1/4</td>
<td>1/4</td>
<td>0.25011(8)</td>
<td>0.01421(18)</td>
<td></td>
</tr>
<tr>
<td>T5</td>
<td>8l</td>
<td>0.04972(4)</td>
<td>0.30757(7)</td>
<td>0</td>
<td>0.01298(18)</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>8g</td>
<td>0.33688(2)</td>
<td>0</td>
<td>1/4</td>
<td>0.01448(18)</td>
<td>0.873(5) Fe + 0.035(5) Mg + 0.09 Li*</td>
</tr>
<tr>
<td>O1</td>
<td>16m</td>
<td>0.24402(7)</td>
<td>0.89508(12)</td>
<td>0.35809(13)</td>
<td>0.0166(3)</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>16m</td>
<td>0.06074(7)</td>
<td>0.58523(13)</td>
<td>0.34885(14)</td>
<td>0.0165(3)</td>
<td></td>
</tr>
<tr>
<td>O3</td>
<td>16m</td>
<td>0.82705(7)</td>
<td>0.69477(12)</td>
<td>0.35782(14)</td>
<td>0.0167(3)</td>
<td></td>
</tr>
<tr>
<td>O4</td>
<td>8l</td>
<td>0.04328(10)</td>
<td>0.7543(2)</td>
<td>0</td>
<td>0.0210(4)</td>
<td></td>
</tr>
<tr>
<td>O5</td>
<td>8l</td>
<td>0.11931(10)</td>
<td>0.18336(19)</td>
<td>0</td>
<td>0.0209(4)</td>
<td></td>
</tr>
<tr>
<td>O6</td>
<td>8l</td>
<td>0.16213(10)</td>
<td>-0.07670(18)</td>
<td>0</td>
<td>0.0204(4)</td>
<td></td>
</tr>
<tr>
<td>O7</td>
<td>8g</td>
<td>0.0580(6)</td>
<td>0</td>
<td>1/4</td>
<td>0.069</td>
<td>0.03*</td>
</tr>
<tr>
<td>O8w</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>1/4</td>
<td>0.101(6)</td>
<td>0.62(3) O + 0.03* C</td>
</tr>
<tr>
<td>Na</td>
<td>4c</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.035(4)</td>
<td>0.203(10)</td>
</tr>
</tbody>
</table>

Equivalent isotropic U is defined as 1/3 of the trace of the orthogonalised U\textsubscript{ij} tensor. Na and O8w refined with isotropic displacement parameters. C and O7 isotropic displacement parameters fixed at Malcherek et al. (2001) values. *s.o.f. fixed for Li at nano-LAMS (Tab. 1) and for CO\textsubscript{2} at SIMS (Tab. 1) values.

In sekaninaite, the framework consists of five T tetrahedra (Cohen et al., 1977; Armbruster, 1986). Three T-sites (T2, T3 and T5) form the six-membered pseudo-hexagonal ring and the remaining two T-sites (T1 and T4) connect the rings into a chain which extends parallel to the c crystallographic axis. Al occupies the T4 and T5 site (two of the six tetrahedra of the ring are occupied by Al) and the remaining sites (T1, T2 and T3) are occupied by Si (Fig. 1). Be, if present, usually occurs at the T4 site, according to the substitution Na\textsuperscript{+} + Be\textsuperscript{2+} → Al\textsuperscript{3+}. This substitution leads to a decrease of the mean T4-O distance (Tab. 4) as observed by Armbruster (1986). On the other hand, substitution of Mg for Fe leads to shortening of the T4-O distance (Malcherek et al. 2001). Figure 3 shows the T4-O distances from various refinements in the literature as a function of X\textsubscript{Mg} (Fig. 3a) and Be at the T4 site (wt%) (Fig. 3b); samples with more than 1% Be at the T4 site (corresponding to ~ 0.02 apfu) are represented by circles. As we may observe from Figure 3a, samples with
high Be at T4 tend to deviate from the trend described by the Fe$^{2+} \rightarrow$ Mg$^{2+}$ substitution, leading to a decrease in the T4 – O bond length; this trend is evident in Figure 3b. The T4 – O bond length for our sample is reported in Figure 3b as a dashed line; we may reasonably infer that Be in the sample is lower than 0.02 apfu. This conclusion is also corroborated by Figure 2.

**Table 4** - Selected bond lengths (Å) for sekaninaite from Dolní Bory.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Symmetry equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1-O2</td>
<td>1.6289(12)</td>
<td>M-O1</td>
</tr>
<tr>
<td>T1-O2$^{10}$</td>
<td>1.6289(12)</td>
<td>M-O1$^1$</td>
</tr>
<tr>
<td>T1-O2$^{11}$</td>
<td>1.6289(12)</td>
<td>M-O2$^3$</td>
</tr>
<tr>
<td>T1-O2$^{11}$</td>
<td>1.6289(12)</td>
<td>M-O2$^4$</td>
</tr>
<tr>
<td>&lt;T1-O&gt;</td>
<td>1.6289</td>
<td>M-O3$^5$</td>
</tr>
<tr>
<td>T2-05</td>
<td>1.5923(18)</td>
<td>M-O3$^6$</td>
</tr>
<tr>
<td>T2-06</td>
<td>1.6084(19)</td>
<td>&lt;M-O&gt;</td>
</tr>
<tr>
<td>T2-O1$^1$</td>
<td>1.6402(13)</td>
<td>Na-O8w$^{16}$</td>
</tr>
<tr>
<td>T2-O1$^1$</td>
<td>1.6402(13)</td>
<td>Na-O8w</td>
</tr>
<tr>
<td>T2-O1$^1$</td>
<td>1.6203</td>
<td>Na-O8w</td>
</tr>
<tr>
<td>T3-04</td>
<td>1.5799(18)</td>
<td>Na-O4$^8$</td>
</tr>
<tr>
<td>T3-06$^{12}$</td>
<td>1.6198(19)</td>
<td>Na-O4$^2$</td>
</tr>
<tr>
<td>T3-03$^{13}$</td>
<td>1.6404(13)</td>
<td>Na-O2$^{16}$</td>
</tr>
<tr>
<td>T3-03$^{14}$</td>
<td>1.6404(13)</td>
<td>Na-O7$^{15}$</td>
</tr>
<tr>
<td>&lt;T3-O&gt;</td>
<td>1.6201</td>
<td>Na-O7$^{17}$</td>
</tr>
<tr>
<td>T4-03$^2$</td>
<td>1.7528(13)</td>
<td>Na-O5$^{16}$</td>
</tr>
<tr>
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<td>1.7528(13)</td>
<td>&lt;Na-O&gt;</td>
</tr>
<tr>
<td>T4-O1$^3$</td>
<td>1.7532(13)</td>
<td>C-O7$^{15}$</td>
</tr>
<tr>
<td>T4-O1$^1$</td>
<td>1.7532(13)</td>
<td>C-O7</td>
</tr>
<tr>
<td>T5-05</td>
<td>1.7128(19)</td>
<td>Na-C1$^{16}$</td>
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<tr>
<td>T5-04$^3$</td>
<td>1.7146(18)</td>
<td>O7-O8w</td>
</tr>
<tr>
<td>T502$^1$</td>
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<td></td>
</tr>
<tr>
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<td></td>
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<tr>
<td>&lt;T5-O&gt;</td>
<td>1.7437</td>
<td></td>
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</tbody>
</table>

Symmetry operators: #1 x+y+1,z+1/2; #2 x,y-1,z; #3 -x+x+1/2,y-1/2,-z+1/2; #4 -x+1/2,y+1/2,z; #5 x-1/2,y-1/2,z; #6 -x-1/2,-y+1/2,z+1/2; #7 x+1/2,y-1/2,z; #8 x,-y,-z+1/2; #9 -x+1,-y+1,z; #10 -x,-y+1,z; #11 x,-y+1,z+1/2; #12 -x,y,-z+1/2; #13 -x,-y+1,z; #14 x-1/2,y+1/2,z; #15 x,y+1,z; #16 -x+1,y,z+1/2; #17 -x+1,y,-z+1/2.

All atoms were refined with anisotropic-displacement parameters, with the exception of Na and O8w which were refined with isotropic-displacement parameters, and of C and O7 (for CO2) whose isotropic-displacement parameters were fixed at values compatible for ferromagnesium cordierite (Malcherek et al., 2001); the site-occupancy factor (s.o.f.) for Li at the M site was fixed at the nano-LAMS value for Li (Tab. 1); Fe and Mg were refined, constraining the sum of their occupancies to be equal to (1 – Li); s.o.f. were refined for Na and H2O in the channels, and the CO2 occupancy was fixed at the SIMS value. As previously stated, the lack of monovalent charge at the M site due to the presence of Li$^+$, is counter-
balanced by the presence of Na⁺ in the channel; H atoms of the H₂O group could not be detected due to the low concentration of H₂O in the sample (Tab. 1); Fe s.o.f. value is slightly over estimated due to the contribute of Mn. Further details of the crystal structure refinements can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +49 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-425930. The list of $F_o/F_c$ data is available from the author up to one year after the publication has appeared.

**Figure 3** - T₄-O bond lengths for various cordierite samples vs (a) the magnesium number ($X_{Mg}$) and (b) the % Be at the T₄ site. Triangles indicate the samples with % Be in T₄ > 1; the star and the dashed line represents our sample. Data from Hochella *et al.* 1979; Armbruster *et al.* 1986; Malcherek *et al.* 2001, Yakubovich *et al.* 2004.

### 5. Optical properties

The studied sekaninaite is biaxial negative. The measured $2V_\chi$ value is $64\pm2^\circ$, refractive indexes are $\alpha = 1.5640(4)$, $\beta = 1.5740(4)$ and $\gamma = 1.5784(4)$. These values are slightly lower (by 0.004) than those reported by Salkregg and Bloss (1980), probably due to a higher H₂O and Fe contents in the latter.

### 6. FTIR spectroscopy

The single-crystal unpolarized infrared spectrum of sekaninaite (Fig. 4) can be divided into two main regions: (I) 3900 – 3300 cm⁻¹ where absorption bands are due to H₂O
stretching modes (Goldman et al., 1977), and (II) 2600 – 2000 cm\(^{-1}\) where absorption bands are related to the antisymmetric stretching mode of CO\(_2\). As shown by Geiger and Kolesov (2002) and Della Ventura et al. (2009, 2012) for CO\(_2\)-rich samples, the combination modes of CO\(_2\) are also observed, overlapping with H\(_2\)O bands in region I. Additional peaks due H\(_2\)O modes also occur around 1600 cm\(^{-1}\) (bending) and 5250 cm\(^{-1}\) (combination) (Della Ventura et al., 2012).

**Figure 4** - Single-crystal unpolarized-light infrared spectrum of sekaninaite. The two regions from 3900 to 3300 cm\(^{-1}\) and from 2600 to 2000 cm\(^{-1}\) are highlighted. H\(_2\)O bending mode at 1635 cm\(^{-1}\), H\(_2\)O bending first overtone mode at 3241 cm\(^{-1}\) and H\(_2\)O combination mode about 5260 cm\(^{-1}\) are arrowed.

The polarized spectra in the 4000 – 3200 cm\(^{-1}\) range are given in Figure 5a (right). Where the electric vector \(\textbf{E}\) is parallel to the crystallographic axis \(\textbf{c}\) (\(\textbf{E}||\textbf{c}\)), two sharp peaks are observed, the more intense centered at 3575 cm\(^{-1}\), and the weaker at 3689 cm\(^{-1}\). The \(\textbf{E}||\textbf{b}\) spectrum has a very broad peak at about 3630 cm\(^{-1}\) with a pronounced shoulder at 3575 cm\(^{-1}\). The \(\textbf{E}||\textbf{a}\) spectrum shows a broad and very weak multi-component absorption with maxima at 3630 cm\(^{-1}\) and 3595 cm\(^{-1}\).
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Figure 5a - Single-crystal polarized-light infrared spectra of sekaninaite in the ranges 5300-5200 cm\(^{-1}\) (left) and 4000-3200 cm\(^{-1}\) (right). Spectra were collected on (010) 43 \(\mu\)m thick and (100) 47 \(\mu\)m thick oriented slabs.

Figure 5b - Single-crystal polarized-light infrared spectra of sekaninaite in the \(\text{CO}_2\) antisymmetric stretching mode region (left) and \(\text{H}_2\text{O}^{[\text{II}]\text{b}\text{r}}\) bending mode (right). Spectra were collected on the same slabs of Fig. 3b except for the \(\text{E} \parallel \text{b}\) spectrum, which was collected from a (001) 168 \(\mu\)m thick slab.
The polarized spectra in the 5300 - 5200 cm\(^{-1}\) range (Fig. 5a, left) show a fairly sharp peak at 5266 cm\(^{-1}\) for \(E \parallel c\), and a broader peak about 5250 cm\(^{-1}\) for \(E \parallel b\). The \(E \parallel a\) spectrum is featureless.

In region II of the spectrum (Fig. 5b left), only a weak peak at 2348 cm\(^{-1}\) is observed for \(E \parallel a\). Outside these ranges, additional relevant peaks are observed in \(E \parallel c\) at 3241 cm\(^{-1}\) (Fig. 5a right) and 1635 cm\(^{-1}\) (Fig. 5b right). A triplet of very weak components is finally observed at 1552, 1600, and 1635 cm\(^{-1}\) polarized for \(E \parallel a\) and \(E \parallel b\). Note that the peak at 1635 cm\(^{-1}\) is very likely offscale due to detector saturation, even for a slab thickness < 50 μm.

**Figure 6** - FTIR image of the (100) section, 47 μm thick slab of sekaninait. Above: video image of the sample. Below: FPA image of the same sample; integration of the H\(_2\)O stretching bands in the range 3500-3700 cm\(^{-1}\). The chromatic scale is proportional to volatile contents, units are arbitrary.
FPA images of selected sample areas were collected to check for possible inhomogeneity in the volatile distribution across the studied crystals (Della Ventura et al., 2012). Figure 6 shows that there is no significant variation in the H$_2$O contents for the whole sample. Imaging of CO$_2$ distribution was not possible because the CO$_2$ anti-symmetric stretching peak could not be distinguished from the noise in the FPA data due to the low concentration of CO$_2$. However CO$_2$ homogeneity was checked by collecting several random spots on the slab, and the results always gave the same value within esd.

7. FTIR band assignment

Although there are several spectroscopic (FTIR + Raman) works on the channel volatile constituents of Mg-rich cordierite in the literature (Goldman et al., 1977, Geiger and Kolesov, 2002, Della Ventura et al., 2009, 2012), polarized data for Fe-rich cordierite are rare (Kolesov and Geiger, 2000). According to these works, it is now well-established that extra-framework H$_2$O groups occur in the structural channels of cordierite with the molecular plane parallel to (100). However, H$_2$O can be oriented in two different ways: type I H$_2$O (hereafter H$_2$O$^{[I]}$) has its H–H vector oriented parallel to the c axis, and type II H$_2$O (H$_2$O$^{[II]}$) has its H–H vector parallel to the b axis. H$_2$O groups of the latter type are bonded to locally associated channel Na cations as in beryl (Hawthorne and Černý, 1977, Sherriff et al., 1991). The linear CO$_2$ molecules are oriented parallel to the crystallographic a axis (Khomenko and Langer, 2005, Aines and Rossman, 1984).

The band assignment given below follows the criteria proposed by Goldman et al. (1977), Geiger and Kolesov (2002) and Della Ventura et al., (2009), based on single-crystal infrared polarized-light determination on oriented slabs of Mg-rich cordierite. However, as we will see from the band positions and polarization behavior, these criteria are also suitable for sekaninaite.

The peak at 3689 cm$^{-1}$ (Fig. 5a right), polarized for E||c, is assigned to the anti-symmetric stretching mode $\nu_3$ of H$_2$O$^{[I]}$; the corresponding symmetric stretching mode ($\nu_1$) in Mg-cordierite is observed at 3595 cm$^{-1}$ (Paukov et al., 2006) and is polarized for E||b. In the spectra collected for sekaninaite studied here, this component cannot be resolved due to the very high intensity of the 3630 cm$^{-1}$ peak (Fig. 5a). The broad band at 3630 cm$^{-1}$ polarized in E||b is assigned to the antisymmetric stretching mode $\nu_3$ of H$_2$O$^{[III]}$. The corresponding
symmetric stretching band $v_1$ occurs at 3575 cm$^{-1}$ in $E|c$. The weak absorptions at 3575 cm$^{-1}$ in $E|b$ and 3630 cm$^{-1}$ in $E|a$ (Fig. 5a) can be due to slight tilting during sample preparation; the latter could be also ascribed to a very small amount of H$_2$O with its H–H vector parallel to a (Kolesov and Geiger, 2000). A peak at 3595 cm$^{-1}$ observed in $E|a$ was assigned by Della Ventura et al. (2009, 2012) to the $v_3 + 2v_2$ combination mode of CO$_2$. In the present case, because of the very small concentration of CO$_2$, the assignment must be different; the band is probably due to minor tilting of the slab.

The bending mode $v_2$ of H$_2$O[II] is observed at 1635 cm$^{-1}$ (Fig. 5b, right) and is polarized parallel to the c axis (Goldman et al., 1977, Della Ventura et al., 2009); the same behavior is observed for its first overtone mode (Fig. 5a, right) at 3241 cm$^{-1}$ (Herzberg, 1956). On the opposite the bending mode $v_2$ of H$_2$O[II] is much less intense and occurs as three features centered at 1552, 1600, and 1635 cm$^{-1}$ as already observed Goldman et al., (1977). The assignment of these features to H$_2$O modes is supported by the fact that they are absent in samples with low water contents (Della Ventura et al., 2012) and by the fact that they disappear with the other fundamental modes after dehydration (Goldman et al., 1977). The bending mode of H$_2$O[II] is expected to be polarized for $E|b$ however they also appear for $E|a$ (see also Goldman et al., 1977).

In the near-infrared (NIR) region (Fig. 5a, left), the $(v_3 + v_2)$ combination modes at 5266 cm$^{-1}$ (for H$_2$O[II]) and at 5250 cm$^{-1}$ (for H$_2$O[II]) are polarized with $E|c$ and $E|b$, respectively, as is also observed for Mg-cordierite (Goldmann et al., 1977, Della Ventura et al., 2012).

The $v_3$ anti-symmetric stretching vibration mode of CO$_2$ (Fig. 5b, left) at 2348 cm$^{-1}$ is fully polarized for $E|a$.

8. Unpolarized Raman spectroscopy

In region I (Fig. 7), two absorptions are observed: one sharp peak at 3598 cm$^{-1}$ and a second broader peak at about 3580 cm$^{-1}$; the former is related to the symmetric stretching mode $v_1$ of H$_2$O[II] and the latter to the $v_1$ mode of H$_2$O[II] (Kolesov and Geiger, 2000). No bands are present in the Raman spectrum at 1383 cm$^{-1}$ where the CO$_2$ symmetric stretching should be located (Kolesov and Geiger, 2000), in accord with the very small amount of CO$_2$ in the studied crystal; however, two weak absorptions are resolved at 2329 cm$^{-1}$, indicating the
presence of N$_2$ and at 2916 cm$^{-1}$, indicating the presence of CH$_4$ (Cesare et al., 2007) in the sample.

![Graph](image)

**Figure 7** - Background-corrected Raman spectrum of sekaninaite. The symmetric stretching modes for both types of H$_2$O are indicated; intensity in arbitrary units.

### 9. Calibration of a molar absorption coefficients of H$_2$O and CO$_2$ in sekaninaite

The Beer-Lambert law, $C = A / (t \cdot \varepsilon)$, can be used to quantify H$_2$O and CO$_2$ from polarized FTIR spectroscopy in cordierite (Della Ventura et al., 2009, 2012). In this relation, the molar absorption coefficient $\varepsilon$ is matrix specific and must be calibrated by combining the spectroscopic measurements with a second independent analytical method. Rearranging the above equation, $\varepsilon = (A \cdot k) / (t \cdot D \cdot C)$, where $C$(wt.%) is the concentration of the target molecule, $A$ is the infrared absorbance, $t$ is the slab thickness in cm, $D$ is the value of the sample density (g/cm$^3$) and $k$ is a conversion factor needed to convert from wt% to mol·l$^{-1}$; for H$_2$O, $k = 1.8$ (Beran et al., 1993) and for CO$_2$, $k = 4.401$ (Della Ventura et al., 2009). $C$(wt.%) was determined using SIMS, and the absorbance $A$ was calculated as the total integrated absorbance $A_i$ (cm$^{-1}$) = $A_x$ + $A_y$ + $A_z$, where $A_x$, $A_y$ and $A_z$ are the integrated absorptions in each polarization direction (Libowitzky and Rossman, 1996). The peak areas were obtained for each component using the data calculation routine built in the spectrometer software; the background was modeled as linear. Using this method, it is possible to quantify up to a few ppm of H$_2$O or CO$_2$ in the sekaninaite channels, but also
Chapter 2: Spectroscopy and X-ray structure refinement of sekaninaite from Dolní Bory (Czech Rep.)

distinguish the two different types of H₂O groups (H₂O[Ⅰ] and H₂O[Ⅱ]) in a reliable way (Della Ventura et al., 2012). Integrated molar coefficients for both types of H₂O were calculated using the method described in Della Ventura et al. (2012), calculating the concentration of H₂O[Ⅱ] = 2•(Na,K,Ca)ch from the chemical analysis of Table 1 and deriving H₂O[Ⅰ] = H₂Otot - H₂O[Ⅱ]. Molar absorption values were thus obtained for both the principal and combination modes (Tab. 5). It is worth recalling here that the use of the combination modes, where applicable, is very useful as these absorptions can be measured on thicker (and thus easy to prepare) crystal slabs. The error σε associated with ε was obtained using the classical statistics of error propagation (Bellatreccia et al., 2006); the error on A is ~ 10% (Libowitzky and Rossman, 1997), the sample thickness uncertainty was set to 2 µm, the standard deviation of the density (D) is 2% and the accuracy of the SIMS analysis is better than 10%. Final values are ε_i H₂O[Ⅰ] = 6000±2000; ε_i H₂O[Ⅱ] = 13000±1000 and ε_i CO₂ = 2000±1000. Used in the Beer-Lambert relation, these coefficients allow us to quantify H₂O and CO₂ in Fe-rich cordierite from polarized FTIR measurements.

<table>
<thead>
<tr>
<th>V₃</th>
<th>H₂O[Ⅱ] (3689 cm⁻¹) + H₂O[Ⅱ] (3630 cm⁻¹)</th>
<th>ε_i (l/mol·cm²)</th>
<th>ε_l (l/mol·cm)</th>
</tr>
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<tr>
<td></td>
<td>11000±1000</td>
<td></td>
<td>230±20</td>
</tr>
<tr>
<td></td>
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<td>400±100</td>
</tr>
<tr>
<td></td>
<td>13000±1000</td>
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<td>190±20</td>
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<table>
<thead>
<tr>
<th>V₃ + V₂</th>
<th>H₂O[Ⅰ] (5266 cm⁻¹) + H₂O[Ⅱ] (5250 cm⁻¹)</th>
<th>ε_i (l/mol·cm²)</th>
<th>ε_l (l/mol·cm)</th>
</tr>
</thead>
<tbody>
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<td>360±40</td>
<td></td>
<td>11±1</td>
</tr>
<tr>
<td></td>
<td>500±200</td>
<td></td>
<td>25±9</td>
</tr>
<tr>
<td></td>
<td>300±30</td>
<td></td>
<td>7.1±0.8</td>
</tr>
</tbody>
</table>

| V₃       | CO₂ (2348 cm⁻¹)                         | 2000±1000      | 300±200       |

10. Conclusions

Polarized FTIR spectroscopy show the presence of two types of H₂O groups in the structural channels; in particular, due to the relatively high concentration of extraframework alkali cations, H₂O[Ⅱ] is dominant over H₂O[Ⅰ]. FPA images of several samples show that the
sample from Dolní Bory has an homogeneous H$_2$O distribution, unlike most cordierites where many different factors such as fractures, inclusions and secondary alteration may cause very strong inhomogeneity in H$_2$O concentration across a crystal (Della Ventura et al., 2012). Sekaninaite from Dolní Bory contains small amounts of CO$_2$ and, as shown by Raman spectra, trace amounts of N$_2$ and CH$_4$.

The integrated molar absorption coefficients $\varepsilon$ for H$_2$O are very close to those reported for Mg-rich cordierite by Della Ventura et al. (2012). On the other hand, the values of $\varepsilon$ for CO$_2$ obtained here cannot be considered very reliable because of the uncertainty of the SIMS value (which is more than the 50%). However, this value is close to that obtained by Della Ventura et al. (2006) from a CO$_2$-poor cordierite. This suggests that the molar coefficient of CO$_2$ may be dependent on bulk concentration; however, this point needs additional experimental evidence for absolute confirmation.

Acknowledgements

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CHAPTER 3

HT-FTIR MICRO-SPECTROSCOPY OF CORDIERITE.
I: THE CO$_2$ ABSORBANCE AS A FUNCTION OF $T$ FROM IN SITU AND QUENCHED EXPERIMENTS

Abstract

In this work we address the evolution of the intensity of the CO$_2$ bands in cordierite, by comparing data obtained from in situ vs. quenching measurements. A natural well characterized cordierite from Kragero (Arendal region, Norway) was studied up to 1200 °C using a heating stage fitted on a FTIR microscope. Two different oriented sections (001) and (010), respectively, were examined in order to check the effect of the channel orientation on the CO$_2$ release from the matrix. Spectra collected in-situ show that increasing temperatures induces an increase of peak width for all CO$_2$-related bands. The effects on the integrated absorbance $A_i$ are different for the different bands. Most notably, the integrated intensity $A_i$ of the anti-symmetric stretching mode ($\nu_3$) increase up to 800 °C, then progressively decreases to 1000/1200°C, depending on the orientation of the channels respect to the slab surface. Data obtained on quenched sample reveals that there is no variation in the band intensity for $T < 900$ °C. Because CO$_2$ is not expected to change its molecular configuration during heating, the absorbance increase during in situ measurements may be related to an increase in the molar absorption coefficient $\varepsilon$. 
Combined *in situ* and quenched FTIR data revealed that the CO\(_2\) loss from the cordierite matrix starts around 800 °C and is strongly dependent to the thickness and shape of the examined samples. In more details, it is favored for small and tabular shaped grains; while for large and prismatic shaped grains the volatile loss is greatly reduced. Fracturing along direction normal to [001] direction multiplies the diffusion interfaces and enhances the CO\(_2\) loss.

1. Introduction

Microporous minerals are important materials from both a geological and a technological point of view because their structure may permanently host or exchange, under certain circumstances, both useful or hazardous molecular species (Ferrari and Merlino, 2005). Changes in the environmental conditions, such as temperature, pressure \(f_{H_2O}, f_{CO_2}\) or \(f_{O_2}\), may deeply affect both the structural parameters of the matrix and the stability of trapped molecules. In this context, cordierite plays a key role since it represents the only case of a relatively common microporous mineral able to trap significant amounts of molecular H\(_2O\) and CO\(_2\) (Armbruster and Bloss, 1982) under extreme geological conditions, spanning from the amphibolite facies to ultra-high temperature metamorphism to crustal anatexis (Vry *et al.*, 1990). The analysis of volatiles in cordierite can be a very useful tool to define the composition of coexisting fluids during its formation and/or subsequent metasomatism and alteration, thus a deeper knowledge of their diffusion mechanism through the structure is crucial in petrologic studies (Carrington and Harley, 1996). Moreover, a better definition of the ability of cordierite to exchange molecules with coexisting fluids may have implications for technological applications in environmental studies, such as in CO\(_2\) sequestration processes.

Cordierite, with an ideal crystal-chemical formula \((\text{Mg}_{1.5}\text{Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}•n\text{H}_2\text{O},m\text{CO}_2\), can be regarded as a framework silicate (Gibbs, 1966) whose structure consists of 6-fold pseudo-hexagonal Si/Al tetrahedral rings stacked perpendicular the c-crystallographic axis. These ring are held together vertically by tetrahedral Si/Al chain (Gibbs, 1966, Yakubovich *et al.*, 2004). The resulting structure has a very low thermal expansion coefficient (Hocella and Brown, 1986; Bruno and Vogel, 2008) and, because of this, cordierite has important applications in ceramic industry. Mg end-member compositions shows no polymorphic changes up to about
Chapter 3: HT-FTIR micro-spectroscopy of cordierite I: the CO$_2$ absorbance as a function of $T$ from in situ and quenched experiments

1400° C; for higher $T$, cordierite reverts to the hexagonal form indialite (Kitamura and Hiroi, 1982) by a first-order displacive transition. The framework arrangement creates a series of interconnected cages or channels, running along the $c$ crystallographic axis; inside these channels alkali cations and/or volatile molecules, notably CO$_2$ and H$_2$O, are typically allotted (Gibbs, 1966, Goldmann et al., 1977, Della Ventura et al., 2010, 2012). Based on polarized-light infrared spectroscopy, previous authors showed that the linear CO$_2$ molecule is oriented orthogonally to the $c$ crystallographic axis and parallel to the $a$ axis (Armbruster and Bloss, 1982). H$_2$O molecules may occur in two different orientations, i.e. with their H-H direction parallel to the $c$ axis (type I water, H$_2$O$^{[I]}$) or parallel to the $b$ axis (type II water, H$_2$O$^{[II]}$) (Wood and Nassau, 1968, Goldmann et al., 1977), the latter type being associated to alkali cations inside the structural channels (Della Ventura et al., 2012).

Several studies pointed out that the content of volatile constituents within the cordierite channels is strongly dependent on the composition of coexisting fluids during crystal growth (Vry et al., 1990; Carrington and Harley, 1996; Harley et al., 2002; Kurepin, 2010), thus making this mineral an important tool to model the geological process of formation; in addition, H$_2$O and CO$_2$ contents may also affect the stability of cordierite itself (Schreyer 1985; Carey 1995; Harley et al., 2002). Therefore the qualitative evaluation of kinetic behavior of channel constituents is crucial in petrologic studies. Several authors in the past have examined the thermodynamic properties of cordierite during dehydration (Giampaolo and Putnis, 1989; Carey, 1993; Carey, 1995; Paukov et al., 2007; Dachs and Geiger, 2008), however no data are known so far for the possible processes of CO$_2$ desorption, i.e. the extraction of CO$_2$ from the structure as a function of $T$.

In this context, micro FTIR spectroscopy not only may provide quantitative information on the behavior of H and C during heat treatments, but may be a valuable tool to study the kinetics of the process, as it has been proven to be the case in a wide variety of minerals like sulfates (Putnis et al., 1990, Carbone et al., 2008), zeolites (Bish and Carey, 2001), and micas (Tokiwai and Nakashima, 2010a).

Quantitative FTIR spectroscopy is based on the Beer-Lambert relationship which, in its simplified form, is: $A = \varepsilon \cdot t \cdot C$. This equation relates the absorbance of a molecule ($A$) in the FTIR transmission spectra to its concentration ($C$) in a sample of thickness ($t$) via a constant known as the molar absorption coefficient, $\varepsilon$. The absorption coefficient is matrix dependent (Libowitzky and Rossman, 1996) and must be calibrated for any mineral and type of bands.
or, alternatively, evaluated using empirical curves (Paterson, 1982, Libowitzky and Rossman, 1996). However, several authors (e.g. Keppler and Bagdassorov, 1993; Yamagishi et al., 1997; Zhang et al., 2007; Tokiwa and Nakashima, 2010b) revised recently the absorbance changes in minerals and glasses during HT-FTIR experiments and showed that the absorption coefficients measured during in situ data collection change with T. In addition, Zhang et al. (2007) observed recently that, in a variety of minerals, in situ absorbance trends of the same molecular species obtained using HT-FTIR spectroscopy may differ for the different modes (i.e. stretching vs bending or multiphonon bands). The implication of these studies is that one cannot extract quantitative information from in situ HT-FTIR spectra without an accurate preliminary study of the absorbance variation with temperature (Tokiwa and Nakashima, 2010b). In fact, the reason for the change in the molar absorption coefficient ε as a function of T is still not completely understood.

Although the behavior of H2O has attracted significant attention, no studies have so far addressed this problem for CO2 although carbon dioxide is an important constituent of silicate melts (Watson et al., 1982; Watson, 1991; Behrens et al., 2009), and minerals such as beryl (e.g. Wood and Nassau, 1968), cordierite (e.g. Khomenko and Langer, 2005, Della Ventura et al., 2012), feldspathoids (Della Ventura et al., 2006, 2008, Bellatreccia et al., 2009) or various forms of silica (Kolesov and Geiger, 2003). In this work we address the behavior of carbon dioxide absorption in the MIR range for cordierite as a function of temperature and sample orientation. We address in particular the temperature dependence of the CO2 bands by comparing the intensities obtained during in situ and quenching experiments, to investigate the effects of temperature on the molar absorption coefficient ε.

2. Studied samples

Clear and inclusion-free fragments, with a pale blue-violet color were extracted from a large crystal of cordierite Rp 3237 from Kragero (Arendal region, Norway). Chemical composition, crystal-chemical formula, cell parameters, density and optical properties of this sample are given in Della Ventura et al. (2012); for sake of simplicity, a summary of data is reported in Table 1; full explanation of the analytical methods can be found in Della Ventura et al. (2012). This sample was chosen because it is very poor in Fe and has an octahedral composition very close to that of a Mg-end member (Tab. 1).
Chapter 3: HT-FTIR micro-spectroscopy of cordierite I: the CO₂ absorbance as a function of T from in situ and quenched experiments

Table 1 - Microchemical analysis, crystal-chemical formula, cell parameters, density and optical properties for cordierite RP 3237. Data from Della Ventura et. al. (2012). Crystal-chemical formula based on 18 oxygen atoms p.f.u.

<table>
<thead>
<tr>
<th>oxides (wt.%)</th>
<th>St. Dev.</th>
<th>formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>49.55</td>
<td>0.19 Si</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>33.01</td>
<td>0.10 Al</td>
</tr>
<tr>
<td>MgO</td>
<td>12.49</td>
<td>0.12 Σ Tetrahedra</td>
</tr>
<tr>
<td>FeO</td>
<td>1.86</td>
<td>0.14 Mg</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.00</td>
<td>0.00 Fe</td>
</tr>
<tr>
<td>MnO</td>
<td>0.02</td>
<td>0.02 Ti</td>
</tr>
<tr>
<td>CaO</td>
<td>0.00</td>
<td>0.00 Mn</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.24</td>
<td>0.03 Σ Octahedra</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.00</td>
<td>0.01 Ca</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.904</td>
<td>0.04 Na</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.005</td>
<td>0.01 K</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>99.06</td>
<td>Σ Channels</td>
</tr>
</tbody>
</table>
<pre><code>       |          | n(H₂O) | 0.31  |
       |          | m(CO₂) | 0.14  |
       |          | Σ Volatiles | 0.45 |
       |          | **H₂O[II] | 0.10 |
       |          | **H₂O[I] | 0.21  |
       |          | 𝜒_{crd}CO₂ | 0.31 |
</code></pre>

Cell parameters (Å)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>17.085</td>
</tr>
<tr>
<td>b</td>
<td>9.721 (1)</td>
</tr>
<tr>
<td>c</td>
<td>9.353 (1)</td>
</tr>
</tbody>
</table>

Density (g/cm³) | 2.58 (3)

Optic sign | Positive

2Vx (°) | 90.3 (9)

The H₂O and CO₂ contents were quantified by SIMS (secondary-ion-mass-spectrometry) using a Cameca IMS4f ion microprobe at EMMAC, the University of Edinburgh. Procedures follow those described in previous cordierite studies from the Edinburgh laboratory (Harley and Carrington, 2001; Thompson et al., 2001; Harley et al., 2002, Della Ventura et. al., 2012). The crystal-chemical formula, based on 18 oxygen atoms pfu is Na₀.₀₅(Mg₁.₈₉Fe₀.₁₆)Al₁.₉₇Si₅O₁₈·0.₃₁H₂O·0.₁₄CO₂. Fe^tot was considered as Fe^{2+}. 71
Chapter 3: HT-FTIR micro-spectroscopy of cordierite I: the CO$_2$ absorbance as a function of $T$ from in situ and quenched experiments

Preliminary FTIR imaging confirmed an homogeneous distribution of H$_2$O and CO$_2$ across the sample (Della Ventura et al., 2012).

Selected crystal fragments were oriented on (001) and (010) using a polarizing microscope equipped with a spindle-stage; the extinction data were processed using the program ExcalibrW (Bloss, 1981; Gunter et al., 2005). Crystallographic orientation was based on the optical orientation $a = Z$, $b = Y$ and $c = X$ (Deer et al., 2004). The fragments were transferred from the spindle-stage to glass slides and doubly polished. Table 2 gives the final thickness together miscellaneous information for both slabs used in this work; sample thickness was measured using an electronic micrometer with ±5 µm uncertainty and checked using the interference fringes in the FTIR spectra, using the formula $t = 1/[2 \cdot n \cdot (\nu_1 - \nu_2)]$ where $t$ is sample thickness in cm, $n = 1.535$ is the refractive index and $(\nu_1 - \nu_2)$ is the distance between two adjacent fringes in cm$^{-1}$ (Pistorius and DeGrip, 2006).

Table 2 – Miscellaneous data for the studied sections.

<table>
<thead>
<tr>
<th>label</th>
<th>Thickness (µm)</th>
<th>Approximate lateral dimensions (µm)</th>
<th>Crystallographic orientation</th>
<th>Optical directions on plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP 3237_11</td>
<td>77</td>
<td>300 x 250</td>
<td>(001)</td>
<td>Y Z</td>
</tr>
<tr>
<td>RP 3237_14</td>
<td>39</td>
<td>500 x 250</td>
<td>(010)</td>
<td>X Z</td>
</tr>
</tbody>
</table>

3. Experimental methods

HT-FTIR measurements up to 1200 °C were performed using a Linkam TS 1400 XY heating stage. The cordierite slabs were oriented on the horizontal plane using a polarizing microscope and then carefully transferred on a quartz sample holder, which allows good transparency for the MIR domain down to 2070 cm$^{-1}$. The sample holder was inserted into a 17 mm ceramic crucible for the heating runs. Temperature was measured using a type S Pt-10% Rh/Pt thermocouple placed close to the sample; the accuracy was ±1°C according to the manufacturer. Heating ramps were set using a digital controller.

HT-FTIR spectra were acquired using a Bruker™ Hyperion 3000 microscope equipped with a KBr-broadband beamsplitter, a 15 X objective and a liquid nitrogen-cooled MCT detector at Laboratori Nazionali di Frascati-Istituto Nazionale di Fisica Nucleare (LNF-INFN, Frascati, Rome). The nominal resolution was set at 4 cm$^{-1}$ and 128 scans were averaged for
both spectrum and background, for a total collecting time of about 30 seconds. FTIR images were collected using a 64 x 64 pixel focal-plane array (FPA); the nominal resolution was set at 4 cm\(^{-1}\) and 64 scans were averaged for each spectrum and background. With this set up each image covers an area of 170 µm x 170 µm with a nominal spatial resolution of ~5 µm (Della Ventura et al., 2010, 2014).

Two different types of step-heating measurement were performed. In the first series of experiments, the (001) section was heated up to 1000 °C with a rate of 20 °C/min; FTIR spectra were collected for every step. At the end of the run, the sample was allowed to cool down to RT and a spectrum was measured, than was heated up to 1100 °C (rate 100 °C/min) and then cooled down again at RT; spectra were collected at 1100 °C and at RT. Background spectra were collected at the beginning of the experiment and at RT. The second series of experiments was performed heating up the (010) section with a rate of 100 °C/min up to 600 °C; measurements were performed every 100°C during the ramp. Then the sample was cooled down to RT and heated up again up to 600 °C with a rate of 100 °C/min. The same procedure was repeated at 800, 900, 1000, 1100 and 1200 °C. FTIR spectra were collected at RT and every 50 °C during the ramp. In any case, cooling rates were about 200°C/minute down to 200 °C, additional 5 minutes were necessary to cool down from 200 °C to RT. Background spectra were collected before each measurement. After each experiment FPA-FTIR images were collected in order to check the homogeneity of residual CO\(_2\) distribution. We stress that all FTIR spectra on each slab were collected in the same point. A relatively large spot size (~150 µm) was preferred in order to obtain a better average of the CO\(_2\) content. Indeed, as we will see later, major variations may in fact occur at a smaller scale.

4. FTIR spectra of the studied cordierite sections: preliminary considerations on the H\(_2\)O and CO\(_2\) bands

Figure 2 compares the unpolarized-light FTIR spectra of cordierite Rp 3237 collected for both (001) and (010) sections; spectra are scaled to thickness (for peak assignment refer to Tab. 3). Notably, even under unpolarized light, the spectra are significantly different, and partly reflect the polarizing behavior of the respective orientations. For instance, the (001)
spectrum contains all absorption that are expected to be most intense for $E//a$ and $E//b$, while absorptions that are expected to be strongly polarized per $E//c$, i.e. the $\nu_3$ mode of $H_2O^{(l)}$ at 3689 cm$^{-1}$ (e.g. Della Ventura et al., 2010) are very weak. Moreover in the (010) section, the librational bands of CO$_2$ at 2391 and 2306 cm$^{-1}$, which are expected to be polarized for $E//b$ (Tab. 3), are completely absent.

These two sections were chosen such as to check for the effect of the channel orientation on the CO$_2$ release from the matrix; as a matter of fact, as schematically shown in Figure 2, the preferential escape path for the evolving gas, which is expected parallel to the structural channels (Fukuda and Shinoda, 2011) is oriented on the shorter (001) or longer (010) dimension of the sample, respectively.

Assignment of the several bands present on the spectra of cordierite can be based on a large number of unpolarized and polarized-light FTIR studies, see in particular Geiger and Kolesov (2002), Khomenko and Langer (2005), Della Ventura et al. (2009, 2012) and Radica et al. (2013).

To help following the discussion below, Table 3 gives a summary of the most relevant $H_2O$ and CO$_2$ absorptions in the MIR (medium infrared) range, and their polarization directions.
Table 3 — Position, assignment and polarization direction of H$_2$O and CO$_2$ bands of cordierite; note that CO$_2$ antisymmetric stretching $\nu_3$ mode presents residual absorptions per E//b. For explanations and references see text.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Mode</th>
<th>Peak position (cm$^{-1}$)</th>
<th>Polarization direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}$C$^{16}$O$_2$</td>
<td>Antisym stretch $\nu_3$</td>
<td>2348</td>
<td>E//a</td>
</tr>
<tr>
<td></td>
<td>Antisym stretch $\nu_3$ + lib</td>
<td>2391</td>
<td>E//b</td>
</tr>
<tr>
<td></td>
<td>Antisym stretch $\nu_3$ - lib</td>
<td>2306</td>
<td>E//b</td>
</tr>
<tr>
<td></td>
<td>combination $\nu_3$ + $\nu_1$</td>
<td>3708</td>
<td>E//a</td>
</tr>
<tr>
<td></td>
<td>combination $\nu_3$ + $2\nu_2$</td>
<td>3595</td>
<td>E//a</td>
</tr>
<tr>
<td>$^{13}$C$^{16}$O$_2$</td>
<td>Antisym stretch $\nu_3$</td>
<td>2282</td>
<td>E//a</td>
</tr>
<tr>
<td>$^{12}$C$^{16}$O$^{18}$O</td>
<td>Antisym stretch $\nu_3$</td>
<td>2332</td>
<td>E//a</td>
</tr>
<tr>
<td></td>
<td>bending $\nu_2$</td>
<td>1635, 1600, 1560</td>
<td>E//a, E//b</td>
</tr>
<tr>
<td></td>
<td>sym stretch $\nu_1$</td>
<td>3689</td>
<td>E//c</td>
</tr>
<tr>
<td></td>
<td>Antisymm stretch $\nu_3$</td>
<td>3595</td>
<td>E//b</td>
</tr>
<tr>
<td></td>
<td>bending $\nu_2$</td>
<td>1634</td>
<td>E//c</td>
</tr>
<tr>
<td></td>
<td>sym stretch $\nu_1$</td>
<td>3575</td>
<td>E//c</td>
</tr>
<tr>
<td>H$_2$O$^{[II]}$</td>
<td>Antisym stretch $\nu_3$</td>
<td>3630</td>
<td>E//b</td>
</tr>
</tbody>
</table>

5. Experimental Results

5.1 In situ HT-FTIR measurements: the (001) section

Figure 3 shows selected unpolarized-light HT-FTIR spectra collected in situ on the (001), 77 µm thick, section. In this orientation the structural channels are directed normal to the sample surface (Fig. 2). At room $T$, five peaks are observed in the principal CO$_2$ stretching region (Fig. 3b): three of these are related to the anti-symmetric stretching mode of CO$_2$ and its isotopes (2348 cm$^{-1}$: $^{12}$C$^{16}$O$_2$, 2332 cm$^{-1}$: $^{12}$C$^{16}$O$^{18}$O, and 2282 cm$^{-1}$: $^{13}$C$^{16}$O$_2$, Khomenko and Langer, 2005, Della Ventura et al., 2009) and two are assigned to librational sideband peaks at 2391 and 2306 cm$^{-1}$ and are symmetrically sited at ±43 cm$^{-1}$ from the principal $\nu_3$ anti-symmetric stretching peak at 2348 cm$^{-1}$. The temperature increase induces a general broadening of all five bands and an increase in band area ($A_i$). At higher temperatures the 2391 and 2306 cm$^{-1}$ bands shift respectively to lower and to higher energies, converging toward the principal 2348 cm$^{-1}$ band. At 400 °C we observe a doublet with maxima at 2358 cm$^{-1}$ and at 2317 cm$^{-1}$, caused by overlapping of the former 2348-2391 and 2332-2306 cm$^{-1}$ components. The 2282 cm$^{-1}$ peak due to the isotope $^{13}$C$^{16}$O$_2$ is still resolved on the lower frequency side of this broad band. For $T > 900$ °C there is a sudden decrease in intensity of the absorption which is virtually zero at 1000°C.
Figure 3: HT-FTIR micro-spectroscopy of cordierite I: the CO$_2$ absorbance as a function of $T$ from in situ and quenched experiments

Figure 3a displays selected spectra collected in the 3750-3650 cm$^{-1}$ region. In this range we can follow the behavior of the relatively intense and sharp peak at 3708 cm$^{-1}$ which is assigned to the CO$_2$ ($\nu_3 + \nu_1$) combination mode (Table 3, see also Della Ventura et al., 2009, 2012), as a function of increasing $T$. Inspection of Figure 3a shows that this peak shifts to higher frequency and broadens considerably for increasing $T$; for $T > 800^\circ$C it is barely appreciable and at $T = 1000^\circ$C it disappears. The peak parameters of the 3708 cm$^{-1}$ band as a function of $T$ could be easily measured because this band is well isolated from the H$_2$O absorption at 3689 cm$^{-1}$. Spectra were treated with the OriginPro 9™ software using a Lorentzian peak shape function and a linear background; the absorbance contribution due to the 3689 cm$^{-1}$ band could be easily subtracted. The obtained results, i.e. the evolution of the absorbance (both linear and integrated), position and FWHM are displayed in Figure 4.

Figure 3 – In situ FTIR spectra for cordierite Rp 3237, 77 $\mu$m thick (001) section, at selected temperatures in the CO$_2$ ($\nu_3 + \nu_1$) combination region (a) and $\nu_3$ anti-symmetric stretching region (b). For peak assignment see Table 3.
Chapter 3: HT-FTIR micro-spectroscopy of cordierite I: the CO$_2$ absorbance as a function of $T$ from *in situ* and quenched experiments

The integrated absorbance ($A_i$) (Fig. 4a) is almost constant up to about 450 °C, then decrease up to 850 °C. For higher $T$ the intensity decreases with a much faster rate; the band disappears at 950°C. This trend is the result of a decreasing peak height (Fig. 4c) and a simultaneous increasing peak broadening (Fig 4d): the FWHM in fact increases from 6 cm$^{-1}$ to about 18 cm$^{-1}$ and finally decreases for $T > 850$°C. The peak position (Fig. 3 and Fig. 4b) shifts almost linearly to higher energies, from 3708 cm$^{-1}$ at $RT$ to 3715 cm$^{-1}$ at 400 °C, up to about 3720 cm$^{-1}$ at 850 °C. Note that for this section the H$_2$O $\nu_3$ peak at 3689 cm$^{-1}$ (Fig. 2, top curve) is no longer resolved from the background for $T > 200$ °C because of extreme peak broadening (Fig. 3a). The evolution of the 3595 cm$^{-1}$ peak cannot be followed in the unpolarized spectra because of its very weak intensity. As already stated, at 1000 °C no CO$_2$ bands are observed in the higher frequency range, however, after quenching the sample to $RT$ (Fig. 3b), a weak CO$_2$ band at 2348 cm$^{-1}$ shows up, suggesting that at 1000°C weak amounts of carbon dioxide are still present in the sample. This band definitively disappears from the spectrum collected on the quenched sample only for $T > 1100$ °C (Fig. 3b top dashed curves).

Figure 4 – Integrated absorbance (a), peak position (b), peak height (c) and peak FWHM (d) for the 3708 cm$^{-1}$ CO$_2$ combination mode for cordierite Rp 3237, measured on the (001) oriented section. The dashed line at 850 °C is a guide for the eye and denotes the temperature at which the CO$_2$ band starts to decrease drastically.
5.2 In situ HT-FTIR measurements: the (010) section

As expected, trends similar to those described for the (001) section are observed for the (010) section cut out from the same cordierite crystal (Fig. 5). In the H$_2$O stretching region (Fig. 5 left) the 3708 cm$^{-1}$ combination mode of CO$_2$ decreases in intensity, broadens and shifts to higher frequency, up to 3717 cm$^{-1}$ at 900°C. The 3595 cm$^{-1}$ CO$_2$ combination mode, which has a weak intensity and is strongly overlapped with the H$_2$O bands may be resolved exclusively at the lower temperatures (Fig. 2, lower curve).

A linear intensity decrease and peak broadening are also observed for the type II H$_2$O band at 3689 cm$^{-1}$ ($v_3$) and 3575 cm$^{-1}$ ($v_1$) however in this case both peaks shift to lower
frequencies (Fig. 5a). Because the CO$_2$ stretching region for this section is much better resolved due to the absence in the spectra of the librational modes (see above), the peak parameters (intensity, position and FWHM) of the principal 2348 cm$^{-1}$ band (Fig. 5b) could be easily obtained and monitored as a function of $T$, using the data calculation routine built in the spectrometer software. Figure 6 shows that the integrated absorbance ($A_i$) of the 2348 cm$^{-1}$ peak increases up to 850 °C (Fig. 6a) as a result of the simultaneous and significant linear increase of the peak FWHM (Fig. 6d); on the other side, the peak height is constant up to 900 °C (Fig. 6c). For $T > 850$ °C all parameters show a sudden drop (Fig. 6). The peak position does not show any clear behavior; around 400 °C the tip of the peak flattens (Fig. 5) and the peak position cannot be properly measured (Fig. 6b). The CO$_2$ absorptions disappears completely at 1200 °C.

Figure 6 – Integrated absorbance (a), peak position (b), peak height (c) and peak FWHM (d) for the 2348 cm$^{-1}$ CO$_2$ anti-symmetric stretching mode collected on the (010) section for cordierite Rp 3237. The dashed line at 850 °C is a guide for the eye and denotes the temperature at which the CO$_2$ band starts to vanish drastically.
5.3 Measurements at RT on quenched samples

The FTIR spectra collected on the same sections after quenching the sample reveal a totally different situation from that described above. In Figure 7 the FTIR spectra collected on the (010) section in the same spectral range displayed in Figure 5 are displayed. Comparison on these Figures reveals that (1) no band shift or band broadening are retained after cooling the sample at RT; (2) the intensity of the CO$_2$ bands is constant up to 900°C, and, more importantly (3) some CO$_2$ (as it is well visible in the 2500-2400 cm$^{-1}$ region) is still present in the sample heated up to 1200 °C (Fig. 7b). A point to note is that the CO$_2$ peak measured at RT after the sample has been heated a $T > 900$°C is sharper than the same peak measured on the untreated crystal. In fact, a closer inspection of the spectra suggests that, for $T > 900$°C, a second component at lower frequency, which is unresolved at RT, preferentially disappears. This point is presently still not completely understood; one reasonable hypothesis is that at higher concentrations, the CO$_2$ molecules interact to give (at least) two different local coordination environments, characterized by a slightly different vibrational frequency. For lower CO$_2$ concentrations, at $T > 900$°C, this interaction is removed, and only...
one component persists in the spectrum. This being the case, however, the proportionality between the absorption area and the CO$_2$ concentration will be still valid.

5.4 The intensity variation of \textit{in situ} vs quenched data

Figure 8 displays the relative changes in band area $A_{RT\%}$, expressed as the ratio of the integrated absorbance measured at a target temperature ($A_{iT}$) and the absorbance measured at $RT$ ($A_{iRT}$) before the beginning of the heating experiment ($A_{RT\%} = 100 \cdot A_{iTT}/A_{iRT}$).

The shaded region (Fig. 8) represents the estimated error on the ratio calculated using the classic statistic of error propagation, considering that the error on $A_i$ is about ±10 % (e.g. Libowitzky and Rossman, 1997, Bellatreccia \textit{et al.}, 2005). Inspection of Figure 8 clearly shows that the evolution of the absorbance as a function of $T$ is extremely different when we consider the \textit{in situ} measurement vs. the data collected at $RT$ after quenching the sample. For the former case, in the 25°C - 750/800 °C range there is a significant increase in the integrated intensity of CO$_2$. A difference in the absolute values is observed for the different slab orientations, however the general trend is the same. It is worth to note that the 3708 cm$^{-1}$ CO$_2$ combination mode (Fig. 8a and b) has a behavior extremely different from that of the $\nu_3$ mode, and shows only a minor variation up to 850°C. The different behavior of the principal vs multiphonon bands has been recently described for several minerals by Zhang \textit{et al.} (2007) who observed differences in the rate of absorbance variation for different
matrices, and also different trends for the same molecular species in different spectral regions. For \( T > 850 \, ^\circ\text{C} \) there is, for all \( \text{CO}_2 \) modes, a drastic drop in the intensity.

The trend observed for the spectra collected at \( RT \) on quenched samples is displayed as a dashed black line in Figure 8b. The data show that in this case there is no significant intensity variation up to 900 °C, followed by a drop of the intensity in the 900-1200° temperature range. It is also important to note that at 1200°C minor but significant amounts of \( \text{CO}_2 \) (~ 25%) are still retained in the structure. The sudden drop in intensity observed between 800 and 900 °C for the \textit{in situ} experiments cannot be explained as a sudden change of the molar absorption coefficient \( \varepsilon_i \) (Tokiwai and Nakashima, 2010b), but must be exclusively ascribed to progressive loss of \( \text{CO}_2 \) from the channels, as testified by \( RT \) measurements in Figures 7b and 8b.

![Figure 9](image)

Figure 9 – (a) Sample Rp 3237 section (001), relative change in \( \text{H}_2\text{O} \) band area (\( A_{RT\%} \) in %), integration range 3800 to 3400 cm\(^{-1}\)). (b) Sample Rp 3237 (010) section, relative change in band area (\( A_{RT\%} \) in %) of \( \text{H}_2\text{O} \) related absorptions \textit{in situ} (filled squares) and at \( RT \) after quenching (open triangles). The shaded areas represent the estimated error on \( A_{RT\%} \) (see text).

Although the present work was not intended to study the behavior of \( \text{H}_2\text{O} \) in cordierite at \( HT \) (this will be the argument of a forthcoming paper), it is interesting to note that the evolution of the \( \text{H}_2\text{O} \) absorbance as a function of increasing \( T \) is extremely different to that of \( \text{CO}_2 \) (Fig. 9). Due to severe band overlap, for the (001) section we integrated the whole range between 3800 and 3400 cm\(^{-1}\) (Fig. 9a); for the (010) section we could measure independently the intensity variation of the 3689 cm\(^{-1}\) + 3575 cm\(^{-1}\) components, both \textit{in situ} and at \( RT \) after quenching (Fig. 9b). Contrary to \( \text{CO}_2 \) (Fig. 8) the trends for \( \text{H}_2\text{O} \) show in both cases a linear and constant decrease of ~50% of the intensity up to 800°C; in the 800°-900°C range there is a sudden drop and at 950°C the sample is completely anhydrous. Similarly to
what observed for CO$_2$, the data collected on quenched samples show a different scenario: the integrated H$_2$O absorbance (proportional to the amount of water in the sample) is constant up to 800°C and suddenly drops in the 800-900°C range. At 1000°C the sample is completely anhydrous.

6. Discussion

6.1 The thermal behavior of CO$_2$ bands

6.1.1 Temperature dependence of peak position and width

Figure 4a shows a significant frequency shift of both $\nu_3$ (3689 cm$^{-1}$) and $\nu_1$ (3575 cm$^{-1}$) type I H$_2$O peaks of about 15 cm$^{-1}$; this result is consistent with previous studies and has been assigned to a temperature dependence of the H$_2$O vibrational constants (Kolesov, 2008; Fukuda and Shinoda, 2008 and 2011). On the other side, no systematic shift with temperature is observed for the CO$_2$ absorptions at 2348 or 2332 cm$^{-1}$, from -200 °C (Khomenko and Langer, 2005) to 1000 °C (this work, Fig. 5b and Fig. 6b). This issue was studied by Olijnyk et al. (1988) who observed that the principal vibrational modes in solid CO$_2$ do not show any shift with T, but are strongly influenced by pressure changes (see also Hanson and Jones, 1981). Our data, however, show a significant shift, from 3708 to 3720 cm$^{-1}$, for the ($\nu_3 + \nu_1$) combination mode (Fig. 4 and 5).

We also observed a significant peak broadening of all CO$_2$-related bands upon heating (Fig. 4 and 6), in particular of the 2332 cm$^{-1}$ peak which is well resolved only below -200 °C, where its FWHM is just 5-6 cm$^{-1}$ (Khomenko and Langer, 2005).

6.1.2 Temperature dependence of integrated absorbance ($A_i$)

In the introduction we mentioned the change in the molar absorption coefficients $\varepsilon$ with temperature for the OH molecular species, that has been recently addressed by several authors (Zhang et al., 2007, Fukuda and Shinoda, 2008 and 2011, Tokiwai and Nakashima, 2010b). Tokiwai and Nakashima (2010b), during their in-situ FTIR study on muscovite dehydration, identified two distinct stages of intensity decrease: at lower temperatures, they observed a progressive and linear decrease in the $A_i$; at higher temperatures the $A_i$ decrease
was steeper and non-linear. The authors imputed the decrease of $A_i$ at low $T$ exclusively to the effect of the change of molar absorption coefficient $\varepsilon$ with temperature; whereas at high $T$ there is an effective dehydration of the mineral. A similar trend may be easily recognized for H$_2$O in cordierite (Fig. 9), where it is possible to distinguish two different trends: 1) a linear (or quasi-linear) $A_i$ decrease from $RT$ to 700 °C (001 section, Fig. 9a) and 800 °C (010 section Fig. 9b), and 2) a steeper $A_i$ decrease for higher $T$. Quenched data collected at $RT$ on the (010) lamella (Fig. 9b dashed line) clearly proves that up to 800 °C there is no loss of H$_2$O from the sample, while for higher temperatures, the H$_2$O content drops drastically. Based on the Beer-Lambert relationship given above, assuming negligible change in the sample thickness across the studied $T$ range, and considering no H$_2$O loss as evidenced by the quenched measurements, the decreasing trend of Figure 9 for the *in situ* measurements must be assigned to a decrease of $\varepsilon$. On the other side, the sudden and fast $A_i$ decrease for $T > 800^\circ$C may be imputed to the dehydration process.

Interestingly, a similar but reverse trend may be observed for the integrated absorbance of the anti-symmetric CO$_2$ stretching mode at low $T$ (Fig. 8). From $RT$ to ~ 700 °C it is possible to observe a first stage characterized by a strong linear increase of $A_i$, followed by an intermediate stage (~ 100 °C) with no variation of the integrated absorbance. Then there is a second stage characterized by a strong decrease of $A_i$ up to 1200 °C. Quenched data reveal that CO$_2$ loss occurs exclusively above 900 °C. Thus the $A_i$ increase in the first stage may be imputed exclusively to an increase in the molar absorption coefficient $\varepsilon$ with temperature, while in the second stage the $A_i$ decrease may be imputed exclusively to CO$_2$ loss. Note that during the intermediate stage both effects of $\varepsilon$ increase and CO$_2$ loss may be balanced with the result of no or small $A_i$ variation.

In previous *HT-FTIR* studies, all done on H$_2$O/OH spectroscopy, a decrease of the integrated absorbance $A_i$ has been systematically observed (see Prasad *et al.*, 2005, Bonaccorsi *et al.*, 2007; Zhang *et al.*, 2006, 2007; Tokiwai and Nakashima, 2010, among the others), whereas for CO$_2$ we obtain a completely opposite trend, i. e. an increase of $A_i$ with temperature. Such behavior has been so far observed (Zhang *et al.*, 2007) only for the overtone modes of some phyllosicates, although, as they discussed in their work, multi-phonon processes cannot be directly compared to single phonon processes.

At present we have no explanation for the odd behavior of CO$_2$ related absorbance trends, however examination of Figure 8 suggests that: 1) the apparent increase of CO$_2$
absorbance up to ~ 800 °C is due to an increase with temperature of $\varepsilon$; 2) CO$_2$ loss begins around 750/800 °C depending on the investigated slab; and 3) as already observed for H$_2$O/OH in several mineral species (Zhang et al., 2007) the temperature dependence of the principal modes is different from that of multi-phonon bands (Fig. 9a).

6.2 The effect of channel orientation on volatile loss

There are two points to consider when modeling H$_2$O and CO$_2$ devolatilization in cordierite: (1) as shown by Fukuda et al. (2009) and by Radica et al. (this Thesis) for beryl, the volatile diffusion occurs much faster along the structural channels along the [001] crystallographic direction, and (2) as shown by Aines and Rossmann (1984), CO$_2$ does not change its molecular configuration during heating, suggesting that the CO$_2$ loss can be considered as a simple diffusion, although with a much slower rate than H$_2$O (chapter 4). Considering these points, we may infer that in cordierite (and beryl) the CO$_2$ loss must be strongly affected by both particle size and the shape of the studied sample, i.e. the length of the escape path. To check for these issues, we used for our experiments two different crystallographic orientations: the (001), 77 µm thick slab, to simulate the diffusion mechanism for small or tabular shaped grains (although cordierite does not occur as tabular crystals, see for example Deer et al., 2004), where the maximum diffusion pathway is 34 µm, i.e. half slab thickness. On the opposite, the (010) slab, was used to model the case of large or prismatic grains (typical growth habit of cordierite, Deer et al., 2004), where the mean diffusion pathway is about 120 µm, corresponding to half the mean slab dimension along the c axis.

The differences between the two orientations may be observed comparing the in-situ intensities in Figures 8a and 8b. In both samples we observe an inversion in the absorption trends starting at 750/800 °C (Fig. 8). For the (001) slab (Fig. 8a) a sudden decrease of the absorbance occurs between 820 and 950 °C; at 950-1000°C $A_i$ is zero. On the other hand, in the (010) slab the CO$_2$ decrease occurs only for $T > 900$ °C; at 1000°C there is still a significant intensity in the spectra, and the absorbance disappears only at 1200 °C. Note that the experimental duration between the two HT treatments are comparable. Small differences related to slab orientation may be observed also for sample dehydration (Fig. 9). In addition, the dehydration temperatures observed in this work are at least 100 °C, for the (001) slab,
and 200 °C, for the (010) slab, higher than those reported by Aines and Rossman (1984) (600 °C), or by Lepezin and Melenevsky (1977), who gave a range for the beginning of dehydration of 500 - 700 °C.

Quenched data show that only for the (001) slab all CO\textsubscript{2} is lost at 1100 °C (Fig. 3b top dashed curve), while for the (010) slab the average CO\textsubscript{2} content of the grain decreases rather slowly and, at 1200°C, the sample still retains 26% of the starting CO\textsubscript{2} (Fig. 8b dashed line). The H\textsubscript{2}O content, on the other hand, drops drastically down to the 20 % between 800 and 900 °C (Fig. 9b dashed line).

To sum up, in the (001) oriented lamella or in thin and tabular cordierite grains both CO\textsubscript{2} and H\textsubscript{2}O desorption proceeds smoothly even when \( T \) increases with a very fast rate; on the other side, for thicker or prismatic cordierite grains, as simulated by the (010) lamella, both CO\textsubscript{2} desorption and dehydration occur at higher temperatures, at least 50/100 °C higher than in the (001) sample. In other words, the difference in diffusion path length has a significant effect on the temperatures of CO\textsubscript{2} and H\textsubscript{2}O desorption. Because volatile molecules are known to diffuse faster along the channel direction, it follows that longer heating times are necessary to extract all volatile molecules from the core of the grain (see also Chapter 4). With this respect, we also noticed that additional diffusion interfaces, such as cracks or fractures, may significantly promote outward diffusion. In Figure 10 we display

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Figure 10 – Parallel polars light (PPL) optical microscope image and superimposed FPA image of the residual distribution of CO\textsubscript{2} in the (010) cordierite section after the heating experiment; CO\textsubscript{2} poor areas presented diffuse fracturing. Chromatic scale (in cm\textsuperscript{-1}) is proportional to CO\textsubscript{2} content. The dashed square indicates the spot for FTIR in-situ measurements. White arrows indicate fractures developed during the heating.
the FTIR-FPA contour map of residual \( \text{CO}_2 \) in the (010) oriented lamella after the heating experiment. As opposite to single spot measurements that are specifically designed to probe a great portion of the heat-treated slab (dashed square in Figure 10), the higher spatial resolution of FPA image revealed an extremely inhomogeneous distribution of residual \( \text{CO}_2 \). Optical analysis revealed the presence of several 20 µm long fractures oriented normal to the \( c \) direction (arrowed in Figure 10). Notably the fractured area did not show any residual \( \text{CO}_2 \), suggesting a strong role of the fractures in enhancing the loss of carbon dioxide from the matrix.

7. Conclusions

FTIR spectroscopy is one of the most effective methods in Earth and material Science to study \textit{in-situ} the effects of high pressures and temperatures for elements like H and C (Koch-Müller et al., 2003, Iezzi et al., 2006, 2009, Keppler and Smyth, 2006; Hawthorne et al., 2007, Welch et al., 2007, Della Ventura et al., 2010, 2014), however increasing evidence shows that quantitative studies using \textit{in-situ} HT-FTIR spectroscopy are complicated by several factors. First of all, similarly to previous studies done for \( \text{H}_2\text{O}/\text{OH} \) (Yamagishi et al., 1997, Zhang et al., 2006, 2007; Tokiwai and Nakashima, 2010), the present work shows that the molar absorption coefficient \( \varepsilon \) for \( \text{CO}_2 \) in cordierite is strongly dependent on \( T \). In addition, the temperature dependence of the principal modes may be strongly different compared to the multi-phonon modes.

\textit{In-situ} FTIR spectra also revealed that \( \text{CO}_2 \) desorption is strongly dependent on the grain size, thickness of the sample and orientation of the studied section. We observed that volatile loss is favored for small and tabular grains (below 100 µm in thickness); on the opposite, because volatile flux in cordierite occurs preferentially along the structural channel parallel to the \( c \) crystallographic axis and through the crystal interfaces normal to [001], volatile loss is hindered for large sized and prismatic crystals. In this type of grains \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) may be retained inside the sample for higher temperatures. Because of these reasons the process of \( \text{CO}_2 \) desorption from cordierite cannot be ascribed to a first order reaction, where the decrease rate of \( \text{CO}_2 \) is proportional exclusively to \( \text{CO}_2 \) concentration, but, because long distance transport is involved, \( \text{CO}_2 \) desorption must be described as a diffusion
process (see also Chapter 4). Additionally sample fracturing along the direction normal to
the c axis may multiply the diffusion interfaces thus favoring both H$_2$O and CO$_2$ loss.

Comparing H$_2$O and CO$_2$ loss curves it is also possible to infer that from a qualitative
point of view H$_2$O diffuses faster than CO$_2$ inside cordierite structural channels.

We wonder if combination of the size/orientation effect, the different diffusion rates,
and the role of crystal fracturing may be responsible for the scatter of dehydroxylation data
observed in the literature.
CHAPTER 4

HT-FTIR MICRO-SPECTROSCOPY OF CORDIERITE.

II: THE DIFFUSION KINETICS OF CO₂

Abstract

In-situ high temperature FTIR micro-spectroscopy is a powerful tool to study the kinetic processes of minerals at extreme environmental conditions. In recent years additional techniques were implemented in order to improve spectral quality and resolution, in particular synchrotron light (SR-FTIR) sources may provide high S/N (signal-to-noise) data allowing to extract reliable quantitative information. In this work we performed several isothermal heating experiments on (001) oriented sections of a CO₂-rich natural cordierite, a mineral with a great geological and technological relevance. The slices were heat-treated up to 1000 °C using a Linkam TS 1400XY heating stage. Single-crystal were heated to the target temperature; the intensity of the ν₃ anti-symmetric stretching mode of CO₂ at 2348 cm⁻¹ was monitored as a function of heating time. The resulting curves of residual CO₂ were modeled using different approaches to evaluate the kinetic process of CO₂ desorption and diffusion coefficients. In particular, two different versions of the Avrami equations were found to be significantly sensitive to the sample thickness. On the other side, the mono-dimensional plane sheet diffusion approach was found to be more suitable to deal with the examined
purely diffusive process. Fitting of the diffusion coefficients in the Arrhenius space yielded \( \log D_0 = 4.4 \pm 0.7 \text{ m}^2/\text{sec} \) and \( E_a = 204 \pm 15 \text{ kJ/mol} \).

1. Introduction:

Cordierite, ideally \((\text{Mg,Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}\), consists structurally of pseudo-hexagonal rings of Si/Al tetrahedra stacked along the \( c \) crystallographic axis. These rings are linked both laterally and vertically by corner-sharing four-membered tetrahedral chain to give a framework of tetrahedra (Gibbs, 1966). Within this framework there are sites for (Mg, Fe\(^{2+}\)) ions in octahedral coordination that share two edges with one Al, and one edge with a Si tetrahedron. The stacking generates a channel-like open structure running parallel to the \( c \) crystallographic axis, where narrower “bottlenecks” (about 2.5 Å in diameter) alternates to large “cages” (about 5.4 Å along \( b \) and 6.0 Å parallel to \( a \)) (Armbruster and Bloss, 1982). Alkaline cations (like Na\(^+\), K\(^+\) and Ca\(^{2+}\)) and molecular groups (\( \text{H}_2\text{O} \) and \( \text{CO}_2 \)) may be present in significant amounts within the cordierite structural channels. The highest value so far reported for \( \text{H}_2\text{O} \) in the literature is about 2.4 wt.% (Deer et al., 2004), which is very close to the maximum theoretical value of 1 molecule per formula unit in the channel. The highest observed \( \text{CO}_2 \) content is about 2.2 wt.% corresponding to about 0.3 molecules per formula unit. Most notably, water and carbon dioxide are located in the wider parts of the structural channels. Hydrocarbons (Zimmermann, 1981; Mottana et al., 1983; Khomenko and Langer, 1999), CO (Khomenko and Langer 2005; Della Ventura et al., 2009), Ar (Armbruster, 1985; Schreyer, 1985), \( \text{N}_2 \) (Armbruster, 1985; Cesare et al., 2007), Cs (Hawthorne and Černý, 1977, Daniels, 1992) and Fe (Goldmann et al., 1977) were also reported inside the structural channels. The linear \( \text{CO}_2 \) molecules are oriented orthogonally to the \( c \) axis, parallel to the \( a \) crystallographic axis (Aines and Rossman, 1984; Khomenko and Langer, 2005). Extra-framework \( \text{H}_2\text{O} \) groups occur in the structural channels with the molecular plane parallel to (100). However, \( \text{H}_2\text{O} \) may occur in two different orientations: in type I \( \text{H}_2\text{O} \) (hereafter \( \text{H}_2\text{O}^{(I)} \)) the H–H vector is oriented parallel to the \( c \) axis, in type II \( \text{H}_2\text{O} \) (\( \text{H}_2\text{O}^{(II)} \)) the H–H vector is rotated by 90°, parallel to the \( b \) axis (Goldmann et al., 1977). \( \text{H}_2\text{O} \) molecules of the latter orientation are bonded locally to channel alkali cations in a 2:1 ratio (Goldmann et al., 1977).
Chapter 4: HT-FTIR micro-spectroscopy of cordierite II: the diffusion kinetics of CO₂

The potential use of cordierite as a water and carbon dioxide fugacity indicator in rocks has generated much interest in the thermodynamics and structural properties of the gases contained in its channels (Vry et al., 1990; Carrington and Harley, 1996). While there are several studies concerning the thermodynamic parameters of cordierite dehydration (Giampaolo and Putnis, 1989; Carey, 1993; Carey, 1995; Paukov et al., 2007; Dachs and Geiger, 2008), almost no experimental works were devoted to the kinetics of CO₂ expulsion from cordierite and/or cordierite-like structures (Radica et al., chapter 3), partly due to the higher temperatures involved in this process. However several authors pointed out that the CO₂ content in the system not only has a significant influence on the cordierite crystallization (Harley et al., 2002; Kurepin, 2010), but it also affects the H₂O diffusivity out of the structural channels because, for size reason, CO₂ act as a plug in the larger cages (Aines and Rossman, 1984; Vry et al., 1990; Radica et al., this Thesis)

Cordierite is also of interest as a model for extremely small channel zeolite-like minerals (McCruoker, 2005) and for the behavior of water and carbon dioxide trapped in small cavities (Aines and Rossman, 1984).

2. Studied sample

*In-situ* isothermal heating experiments were performed on fragments of a natural cordierite BM 96512 from Cabo de Gata (Almaria region, Spain). The fragments were clear and inclusion-free, with a violet to dark blue color. Chemical composition, crystal-chemical formula, cell parameters, density and optical properties are given in Della Ventura et al. (2012); for sake of simplicity, a summary of data is reported in Table 1. In particular, the H₂O and CO₂ contents were quantified by SIMS (secondary-ion-mass-spectrometry) using a Cameca IMS4f ion microprobe at EMMAC, the University of Edinburgh. Procedures follow those described in previous cordierite studies from the Edinburgh laboratory (Harley and Carrington, 2001; Thompson et al., 2001; Harley et al., 2002; Della Ventura et al., 2012). Fe^tot was considered as Fe^{2+}. The crystal-chemical formula, based on 18 oxygen atoms p.f.u. is Na₀.₀₃(Mg₁.₅₂Fe₀.₄₄)Al₃.₉₈Si₅O₁₈·₀.₂₁H₂O·₀.₀₇CO₂. Preliminary FTIR imaging confirmed an homogeneous distribution of H₂O and CO₂ across the sample (Della Ventura et al., 2012).
Table 1 - Microchemical analysis, crystal-chemical formula, cell parameters, density and optical properties for cordierite studied here. Data from Della Ventura et al. (2012). Crystal-chemical formula is based on 18 oxygen atoms p.f.u.

<table>
<thead>
<tr>
<th>Chemical analysis (wt.%)</th>
<th>BM 96512</th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>49.10</td>
<td>0.31</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>33.10</td>
<td>0.25</td>
</tr>
<tr>
<td>MgO</td>
<td>10.04</td>
<td>0.13</td>
</tr>
<tr>
<td>FeO</td>
<td>5.21</td>
<td>0.12</td>
</tr>
<tr>
<td>TiO$_2$</td>
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<td>0.04</td>
</tr>
<tr>
<td>MnO</td>
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<td>0.07</td>
</tr>
<tr>
<td>CaO</td>
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<td>0.02</td>
</tr>
<tr>
<td>Na$_2$O</td>
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<td>0.02</td>
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<tr>
<td>K$_2$O</td>
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<tr>
<td>H$_2$O</td>
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<td>0.08</td>
</tr>
<tr>
<td>CO$_2$</td>
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<td>0.08</td>
</tr>
<tr>
<td>Total</td>
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<table>
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<tr>
<th>Crystal chemical formula (apfu)</th>
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<tr>
<td>Si</td>
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</tr>
<tr>
<td>Al</td>
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</tr>
<tr>
<td>Σ Tetrahedra</td>
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<tr>
<td>Mg</td>
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<tr>
<td>Fe</td>
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<tr>
<td>Ti</td>
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<tr>
<td>Mn</td>
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<tr>
<td>Σ Octahedra</td>
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<tr>
<td>Na</td>
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</tr>
<tr>
<td>K</td>
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<tr>
<td>Σ Channels</td>
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<td>n(H$_2$O)</td>
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<tr>
<td>m(CO$_2$)</td>
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</tr>
<tr>
<td>Σ Volatiles</td>
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<td>**H$_2$O$^{II}$</td>
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</tr>
<tr>
<td>**H$_2$O$^{I}$</td>
<td>0.13</td>
</tr>
<tr>
<td>$X_{H_2CO_3}$</td>
<td>0.25</td>
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</tbody>
</table>

<table>
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<tr>
<th>Cell parameters (Å)</th>
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<tbody>
<tr>
<td>a</td>
<td>17.135 (7)</td>
</tr>
<tr>
<td>b</td>
<td>9.781 (5)</td>
</tr>
<tr>
<td>c</td>
<td>9.343 (7)</td>
</tr>
</tbody>
</table>

| Density (g/cm$^3$)    | 2.602 (4) |
| Optic sign           | Positive  |
| 2Vx (°)              | 90 (3)    |

3. Experimental methods

*In-situ* heating experiments were performed on cordierite fragments using a high temperature Linkam TS 1400 XY heating stage. Selected crystal fragments were oriented using a polarizing microscope equipped with a spindle-stage; the extinction data were processed using the program ExcalibrW (Bloss, 1981; Gunter *et al.*, 2005). Crystallographic orientation was based on the optical orientation $a = Z$, $b = Y$ and $c = X$ (Deer *et al.*, 2004). The fragments were transferred from the spindle-stage to glass slides and doubly polished.
Sample thickness was measured using an electronic micrometer with ±5 µm uncertainty and checked using the interference fringes in the FTIR spectra, using the formula \( t = 1/(2 \cdot n \cdot (\nu_1 - \nu_2)) \) where \( t \) is sample thickness in cm, \( n \) is the refractive index and \( (\nu_1 - \nu_2) \) is the distance between two adjacent fringes in cm\(^{-1}\) (Pistorius and DeGrip, 2006). Doubly polished fragments were oriented on the horizontal plane using a polarizing microscope and carefully transferred on a quartz sample holder (FTIR frequency cut below 2070 cm\(^{-1}\)). The sample holder was inserted into a 17 mm ceramic crucible for the heating runs. Temperature was measured using a calibrated type S Pt-10% Rh/Pt thermocouple placed close to the sample; the accuracy was ±1°C according to the manufacturer. Heating ramps were programmed using a digital controller.

Conventional light HT-FTIR spectra were acquired using a Bruker™ Hyperion 3000 microscope equipped with a KBr-broadband beamsplitter and a liquid nitrogen-cooled MCT detector at Laboratori Nazionali di Frascati-Istituto Nazionale di Fisica Nucleare (LNF-INFN) Frascati (Rome). Synchrotron light HT FTIR spectra were collected at beamline B22, Diamond Light Source laboratory Oxford (UK). Polarized spectra were collected using a gold-wire-grid polarizer on a ZnSe substrate. A spot size of 50 µm using a 15 X objective was used for data collection in conventional light, while a spot size close to 20 µm with a 20 X objective was used in synchrotron light; the nominal resolution was 4 cm\(^{-1}\) and 128 scans were averaged for both spectrum and background, for a total collecting time of about 30 seconds. FTIR images were collected using a 64 x 64 pixel focal-plane array (FPA), using a 15 X objective; the nominal resolution was set at 4 cm\(^{-1}\) and 64 scans were averaged for each spectrum and background. With this set up each image covers an area of 170 µm x 170 µm with a nominal spatial resolution of ~5 µm (Della Ventura et al., 2010, 2014).

### 3.1 FTIR polarized-light isothermal heating experiments

In order to study the kinetic of CO\(_2\) diffusion within cordierite at high \( T \), two sets of experiments were performed on (001) slabs. This orientation was chosen to ensure a homogenous outward diffusion of CO\(_2\) across the entire slab surface considering that CO\(_2\) diffuses much faster along the structural channels oriented parallel to the \( c \) crystallographic direction (Fig. 1, see Chapter 3). Diffusion through the prismatic faces can be neglected because, as it has already been verified for the structurally related beryl, it is at least two
orders of magnitude lower, as observed by Fukuda et al. (2009) for beryl, and shown for cordierite in the previous chapters.

Figure 1 – Schematic set up (not in scale) of the CO$_2$ diffusion across the sample (white) inside the heating stage during the isothermal kinetic heating experiments. Considering that the ceramic tube heater completely encases the sample in a uniform T controlled environment, and the reduced sample thickness, we assume that there is no T gradient across the grain. Diffusion directions parallel to the c crystallographic axis are indicated as arrows, the diffusion perpendicular to the c direction is negligible (see text for explanation).

Two oriented fragments were double-polished at 60 µm and 19 µm, respectively and broke up into four pieces each. Four fragments of the same 60 µm thick section were heated to 850, 900, 950 and 1000 °C (heating rate 100°C/min) and kept at the target $T$ for two hours (Tab. 3). Polarized spectra were collected using conventional light with both E//a and E//b at RT before the experiment, and at the target $T$, every 5 minutes for the first hour and every 10 minutes for the second hour of isothermal heating. Four fragments of the same 19 µm thick slab were heated to 825, 850, 900 and 1000 °C (heating rate 100°C/min) at different annealing times (Tab. 3). For this second set of samples, spectra were collected using synchrotron light exclusively along the a crystallographic direction at $RT$ and at the target $T$ every 5 minutes. This experimental layout was necessary to get a better S/N because the reduced thickness of the samples coupled with the strong beam absorbance caused by the stage windows, sample holder and polarizers, affected significantly the transmitted signal. The spectra collected for this second set of fragments showed unexpected interference fringes, thus a background correction was needed to extract the intensity data. Heating temperatures were selected on the basis of previous work (Radica et al. chapter 3) which
showed a strong decrease in channel CO$_2$ content around 850 °C. In all cases the lateral dimension of the sample was significantly larger than the beam size.

<table>
<thead>
<tr>
<th>Sample slab (orientation 001)</th>
<th>Thickness (µm)</th>
<th>Annealing temperature (°C)</th>
<th>Annealing time (min)</th>
<th>Light source</th>
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<tbody>
<tr>
<td>BM 96512_T 850</td>
<td>60</td>
<td>850</td>
<td>120</td>
<td>Conventional</td>
</tr>
<tr>
<td>BM 96512_T 900</td>
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<tr>
<td>BM 96512_T 950</td>
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<td>Conventional</td>
</tr>
<tr>
<td>BM 96512_T 1000</td>
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<td>1000</td>
<td>120</td>
<td>Synchrotron</td>
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<td>850</td>
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</tr>
<tr>
<td>BM 96512_T3 1000</td>
<td>19</td>
<td>1000</td>
<td>30</td>
<td>Synchrotron</td>
</tr>
</tbody>
</table>

4. Polarized-light FTIR spectroscopy of cordierite and band assignment

The correct assignment of the absorption peaks in cordierite spectra is a crucial point when using the absorbance data for quantitative purposes (Della Ventura et al., 2012, Radica et al., 2013). In Figure 2 we display the single-crystal polarized infrared spectra of sample BM 96512 collected at RT. H$_2$O and CO$_2$ absorptions are present in 4 different regions of the spectrum: (a) the H$_2$O combination region around 5250 cm$^{-1}$ (Della Ventura et al., 2012) (b) the 3900 – 3300 cm$^{-1}$ region where the H$_2$O stretching modes (Goldman et al., 1977) and the combination modes of CO$_2$ are observed (Geiger and Kolesov, 2002); Della Ventura et al., 2009, 2012); (c) the antisymmetric stretching (2600 – 2000 cm$^{-1}$) region of CO$_2$ (Geiger and Kolesov, 2002) and (d) the H$_2$O bending region around 1600 cm$^{-1}$ (Della Ventura et al., 2012).

Selected polarized spectra in the 3800 – 3200 cm$^{-1}$ range are given in Figure 2b. When the electric vector E is parallel to the crystallographic axis c (E//c), two sharp peaks are observed, one centered at 3575 cm$^{-1}$, and the other at 3689 cm$^{-1}$; a third weaker peak is observed at 3242 cm$^{-1}$. The E//b spectrum features a very broad peak centered about 3630 cm$^{-1}$ with a shoulder around 3595 cm$^{-1}$. The E//a spectrum shows a broad and weak multicomponent absorption with maxima at 3630 cm$^{-1}$ and 3575 cm$^{-1}$; two sharper peaks are present at 3708 and 3595 cm$^{-1}$. The polarized spectra in the 5300 - 5200 cm$^{-1}$ range (Fig. 2a) features a fairly sharp peak at 5266 cm$^{-1}$ for E//c, and a very broad peak about 5250 cm$^{-1}$ for E//b. The E//a spectrum is featureless. In Figure 2c the E//a spectrum in the CO$_2$ region
consists of a very sharp and intense absorption centered at 2348 cm\(^{-1}\), with a weak shoulder at 2332 cm\(^{-1}\) on the low-frequency side. A minor band is observed at 2282 cm\(^{-1}\). The \(E//c\) spectrum is featureless, while the \(E//b\) spectrum shows a minor band at 2348 cm\(^{-1}\) with two side bands at 2391 and 2306 cm\(^{-1}\), respectively. In the \(\text{H}_2\text{O}\) bending region relevant peaks are observed in \(E//c\) at 1634 cm\(^{-1}\) (Fig. 2d). At 1560, 1600, and 1635 cm\(^{-1}\) polarized for \(E//a\) and \(E//b\) a triplet of weak components may be observed.

Figure 2 - Single-crystal polarized-light infrared spectra of BM 96512 cordierite collected at RT in the ranges 5300-5200 cm\(^{-1}\) (a), 3800-3200 cm\(^{-1}\) (b), in the \(\text{CO}_2\) antisymmetric stretching mode region (c) and \(\text{H}_2\text{O}\) bending mode (d). Spectra were collected on (010) oriented 33 µm thick \((E//a\) and \(E//c\)) and (100) oriented 50 µm thick \((E//b)\) oriented slabs. Spectra are scaled to thickness. Band assignment is reported, *=see description in the text.
The vibrational (FTIR and Raman) spectrum is well characterized due to the many spectroscopic works published in the literature (e.g. Goldman et al., 1977, Geiger and Kolesov, 2002, Khomenko and Langer, 2005, Della Ventura et al. 2009, 2012 and references therein). For the band assignment used in this work we follow the work of Della Ventura et al. (2009, 2012), who critically revised the existing literature on the interpretation of the IR spectra of cordierite, and also extending the spectrum analysis to the entire wavenumbers range from 6000 cm\(^{-1}\) (NIR) to 1500 cm\(^{-1}\) (MIR).

Accordingly, the peak at 3689 cm\(^{-1}\) (Fig. 2b), polarized for E//c, is assigned to the antisymmetric stretching mode \(\nu_3\) of H\(_2\)O\[I\]; the corresponding symmetric stretching mode (\(\nu_1\)) in Mg-cordierite is observed at 3595 cm\(^{-1}\) (Paukov et al., 2007) and is polarized for E//b (Fig. 2b). The splitting between these two components [\(\Delta(\nu_3-\nu_1)=94\) cm\(^{-1}\)] suggests that H\(_2\)O\[I\] occurs in cordierite as a relatively free, unbound molecule (Geiger and Kolesov, 2002). The broad band at 3630 cm\(^{-1}\) polarized in E//b is assigned to the antisymmetric stretching mode \(\nu_3\) of H\(_2\)O\[I\]. The corresponding symmetric stretching band \(\nu_1\) occurs at 3575 cm\(^{-1}\) in E//c. The absorptions at 3575 cm\(^{-1}\) for E//b and 3630 cm\(^{-1}\) for E//a (Fig. 2b) may be the result of slight tilting during sample preparation; the latter could be also ascribed to a very small amount of H\(_2\)O with its H–H vector parallel to the \(a\) crystallographic axis (Kolesov and Geiger, 2000). The peaks at 3708 and 3595 cm\(^{-1}\), observed for E//a, are assigned respectively to the \(\nu_3+\nu_1\) and \(\nu_3+2\nu_2\) combination mode of CO\(_2\) (Della Ventura et al., 2009, 2012). The 1634 cm\(^{-1}\) peak (Fig. 2d) polarized parallel to the c axis is assigned to the bending mode (\(\nu_2\)) of H\(_2\)O\[I\] (Goldman et al., 1977, Della Ventura et al., 2009); the same polarization behavior is observed for its first overtone (Fig. 2b) at 3242 cm\(^{-1}\) (Herzberg, 1956). On the opposite, the bending mode \(\nu_2\) of type I H\(_2\)O is much less intense and occurs as three features centered at 1560, 1600, and 1635 cm\(^{-1}\) (Radica et al., 2013). The assignment of these features to H\(_2\)O modes is supported by the fact that they are absent in samples with low water contents (Della Ventura et al., 2009) and by the fact that they disappear with the other fundamental modes after dehydration (Goldman et al., 1977). The bending modes of H\(_2\)O\[I\] are expected to be polarized for E//b, however they also appear for E//a (see also Goldman et al., 1977).

In the NIR region (Fig. 2a), the 5266 cm\(^{-1}\) peak polarized for E//c and the 5250 cm\(^{-1}\) polarized for E//b are assigned to the (\(\nu_3+\nu_2\)) combination modes respectively of H\(_2\)O\[I\] and H\(_2\)O\[I\] (Della Ventura et al., 2012).
In the 2600–2000 cm$^{-1}$ region (Fig. 2c), the most intense band at 2348 cm$^{-1}$ is assigned to the $\nu_3$ antisymmetric stretching mode of the $^{12}$C$^{16}$O$_2$ molecule (Khomenko and Langer, 2005). The minor bands at 2282 and the shoulder at 2332 cm$^{-1}$, which are observed in single-crystal and powder spectra of CO$_2$-rich cordierites (e.g. Le Breton, 1989), have the same polarization behavior as the main band at 2348 cm$^{-1}$. These bands are respectively interpreted as the $\nu_3$ antisymmetric stretching mode of the $^{13}$C$^{16}$O$_2$ and $^{12}$C$^{16}$O$^{18}$O isotope molecules (Khomenko and Langer, 2005). Assignment of the 2348 cm$^{-1}$ band for E/$b$ is unclear; due to position, shape and polarization it could be related to the $\nu_3$ mode of CO$_2$ molecules oriented parallel to the $b$ axis, however there are no further evidence supporting this assumption. The two symmetric bands at 2390 and 2306 cm$^{-1}$ observed for E/$b$ are related to librational, sum and difference motions of the CO$_2$ molecule on the (001) plane (Aines and Rossman, 1984). Final assignment and respective polarization directions are reported in Table 4 for all bands.

### Table 4 – Position, assignment and polarization of H$_2$O and CO$_2$ related peak observed in beryl. * = see description in the text, $^1$ = residual absorptions.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Mode</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$^{\text{H}}$</td>
<td>Bending $\nu_3$</td>
<td>1635*, 1600*, 1560*</td>
<td>E/a, E/b</td>
</tr>
<tr>
<td></td>
<td>Stretch $\nu_1$</td>
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<td>E/c</td>
</tr>
<tr>
<td></td>
<td>Antisymm Stretch $\nu_3$</td>
<td>3595</td>
<td>E/b</td>
</tr>
<tr>
<td></td>
<td>Comb $\nu_1 + \nu_2$</td>
<td>5266</td>
<td>E/c</td>
</tr>
<tr>
<td></td>
<td>Bending $\nu_1$</td>
<td>1634</td>
<td>E/c</td>
</tr>
<tr>
<td></td>
<td>Bending $2\nu_2$</td>
<td>3242</td>
<td>E/c</td>
</tr>
<tr>
<td></td>
<td>Stretch $\nu_3$</td>
<td>3575</td>
<td>E/b, E/a$^1$</td>
</tr>
<tr>
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<td>Antisymm Stretch $\nu_3$</td>
<td>3630</td>
<td>E/b, E/a$^1$</td>
</tr>
<tr>
<td></td>
<td>Comb $\nu_1 + \nu_2$</td>
<td>5250</td>
<td>E/b</td>
</tr>
<tr>
<td>H$_2$O$^{\text{H}}$</td>
<td>Antisymm Stretch $\nu_3$</td>
<td>2348</td>
<td>E/a, E/b$^1$</td>
</tr>
<tr>
<td></td>
<td>Antisymm Stretch $\nu_3 + \text{lib}$</td>
<td>2391</td>
<td>E/b</td>
</tr>
<tr>
<td></td>
<td>Antisymm Stretch $\nu_3 - \text{lib}$</td>
<td>2306</td>
<td>E/b</td>
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<tr>
<td></td>
<td>Comb $\nu_1 + \nu_2$</td>
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<td>E/a</td>
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<tr>
<td>$^{12}$C$^{16}$O$_2$</td>
<td>Comb $\nu_1 + 2\nu_2$</td>
<td>3595</td>
<td>E/a</td>
</tr>
<tr>
<td>$^{13}$C$^{16}$O$_2$</td>
<td>Antisymm Stretch $\nu_3$</td>
<td>2282</td>
<td>E/a</td>
</tr>
<tr>
<td>$^{12}$C$^{16}$O$^{18}$O</td>
<td>Antisymm Stretch $\nu_3$</td>
<td>2332</td>
<td>E/a</td>
</tr>
</tbody>
</table>

5. Results

5.1 Isothermal heating experiments

Figures 3 and 4 show selected polarized light spectra collected on the (001) 60 µm thick section in the CO$_2$ combination region (3750-3550 cm$^{-1}$) for E/$a$ (a), and in the CO$_2$ anti-symmetric stretching region (2450-2200 cm$^{-1}$) for E/$a$ (b) and E/$b$ (c). In particular, the
spectra displayed in Figure 3 are those collected at room $T$ before the experiments, (dashed lines) and in situ just after reaching the target $T$ indicated on the figure (solid lines). High temperature polarized measurements confirms the trends observed in Radica et al. (chapter 3): the $\nu_3 + \nu_2$ combination peak clearly broadens and shifts to higher frequency, at about $3720 \text{ cm}^{-1}$, while, for $T > 850^\circ\text{C}$, the $\nu_3 + 2\nu_2$ combination peak of CO$_2$ at $3595 \text{ cm}^{-1}$ and the H$_2$O absorptions at 3630 and 3575 cm$^{-1}$ disappear. A weak shoulder can be observed around 3680 cm$^{-1}$ (Fig. 3a). In the 2450-2200 cm$^{-1}$ region, the 2348 cm$^{-1}$ and the 2332 cm$^{-1}$ components broadens without shifting. Note that at high $T$, the 2332 cm$^{-1}$ peak intensity is almost comparable with that of the 2348 cm$^{-1}$ peak. The 2282 cm$^{-1}$ peak is hidden under the low-frequency tail of the broadened 2348-2332 cm$^{-1}$ band (Fig. 3b). For $E//b$ the high temperature behavior of the CO$_2$ sidebands is observed. In particular we observe the convergence of both components at 2391 and 2306 cm$^{-1}$ toward the central 2348 cm$^{-1}$ band, with a major shift (30 cm$^{-1}$) observed for the 2391 cm$^{-1}$ band, due to a $\nu_3$ + libration mode (Aines and Rossman, 1984) with respect the 2306 cm$^{-1}$ ($\nu_3$ – libration mode), whose shift is 9 cm$^{-1}$ (Fig. 3c).

Figure 3 – Conventional light polarized FTIR spectra in (a) the CO$_2$ combination region for $E//a$, and anti-symmetric stretching region for (b) $E//a$, and (c) $E//b$; sample BM96512, 60 µm thick (001) section. Dashed line: RT spectrum before the heating experiments. HT spectra collected in situ just after reaching the target $T$ (time = 0 min). Peak position at RT and at selected $T$ are indicated. For peak assignments see Table 4 and text.
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Figure 4 compares the spectra collected at RT before the experiments (dashed line) and the RT spectra collected on the quenched sample after 120 min annealing at the same temperatures as in Figure 3. Inspection of Figure 4 confirms a decrease in the integrated absorption of all CO$_2$ related peaks; the magnitude in decrease is directly proportional to the temperature, with the only exception of the 2348 cm$^{-1}$ absorption polarized parallel to the $b$ crystallographic axis, which presents a constant $A_t$ of about 40% of the starting intensity. A similar behavior was observed by Fukuda and Shinoda (2011). It is worth of note that after the heat-treatment no H$_2$O related absorption are present in the spectra, even at the lowest 850°C temperature (Fig. 4a). In addition, no peak shifts are observed.

![Figure 4](image_url)

Figure 4 – Room T polarized light FTIR spectra, sample BM96512 60 µm thick collected before the experiment (dashed curves) and after 2 hours at the indicated temperatures (solid curves). Spectra in the CO$_2$ combination region for $E//a$ (a), and anti-symmetric stretching region of with $E//a$ (b) and $E//b$ (c).

Figure 5 shows the CO$_2$ loss curves expressed as $A_t \% = 100 \cdot A_t / A_0$ where $A_t$ is the $A_i$ at time = t and $A_0$ is $A_i$ at time = 0, i.e. just after the sample reached the target temperature; data obtained with $E//a$ for the $\nu_3$ mode at 2348 cm$^{-1}$ for the 60 µm thick BM96512 and the 19 µm thick BM96512 (001) sections are displayed. Errors on the CO$_2$ loss curves are accounted as ±10% of the integrated absorbances $A_i$ (Libowitzky and Rossman, 1997), hence, following the error propagation rules, the estimated error is expressed as $\sigma A_t \% = A_t \% \cdot 0.1 \cdot \sqrt{2}$.
Figure 5 – Isothermal plots of residual CO\textsubscript{2} within the cordierite channels ($A_{t\%} = 100 \cdot A_t/A_0$ of the 2348 cm\textsuperscript{-1} band) as a function of time; sample BM96512, (001) section with E//a. Shaded areas represent the estimated error on the absorption. (a) 60 µm thick section, (b) 19 µm thick section.

5.2 Reaction kinetics

5.2.1 Avrami rate equations

Figure 5 shows that for $T > 800^\circ\text{C}$ the CO\textsubscript{2} content decreases significantly as a function of time. As a first step, we modeled the results of Figure 5 by using the same formalism employed by previous authors for their dehydration experiments (Hancock and Sharp, 1972; Giampaolo and Putnis, 1989), i.e. by assuming that CO\textsubscript{2} loss from cordierite may be described as a first order reaction. In such a case, the rate is exclusively proportional to the concentration of CO\textsubscript{2}, because no chemical reactions are involved during CO\textsubscript{2} loss other than simple desorption. A first order reaction follows the general Avrami formula (Avrami, 1939, 1940, 1941) of exponential decay:

$$y = 1 - \exp(-f(t)) \text{ or } A_t = A_0 \cdot \exp(-f(t))$$

(1)

where $y = 1 - A_t/A_0$ is the fraction of CO\textsubscript{2} lost at time $t$ (min), $A_t$ is the integrated absorbance ($A_i$) at time $t$, $A_0$ is $A_i$ at time $0$ and $f(t)$ is a time dependent exponential function. $f(t)$ is usually described by two parameters $k$ and $m$. The coefficient $k$, the rate constant, describes the way the decrease depends on the concentration of the reactant. The exponential factor $m$ is an empirical factor used to model the reaction mechanism. Curves with the same value of $m$ are isokinetic and indicate that the reaction type does not change within the examined range of temperature or fraction loss. The kinetic parameter $k$ may be
used, via the Arrhenius equation, to calculate the activation energy $E_a$ (kJ/mol) of the process leading to CO$_2$ loss from the structural channels:

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right)$$

(2a)

Linearized:

$$\ln k = \ln \alpha - \frac{E_a}{RT}$$

(2b)

where $R$ is the universal gas constant (kJ/mol K), $T$ is the temperature in K and $\alpha$ is the frequency factor.

Because various equations can fit the same data set equally well, very different values of the empirical activation energy can be derived from the same experiments. Thus the activation energy is only meaningful in terms of the rate equation used to fit the data. In order to test for the best model to describe the CO$_2$ loss form cordierite, we fitted our data (Fig. 6) with two of the most commonly used equations in kinetic studies for minerals:

$$A_t = A_0 \cdot \exp\left[-k \cdot t^m\right]$$

(3a)

Hereafter referred as Avrami JMAK (Avrami, 1939, 1940, 1941; Hancock and Sharp, 1972; Carbone et al., 2008), and:

$$A_t = A_0 \cdot \exp\left[-(k \cdot t)^m\right]$$

(3b)

referred as Avrami Putnis (Giampaolo and Putnis, 1989, Putnis et al., 1990, Putnis, 1992). It is important to note that in the latter formula the rate constant $k$ has always the dimension of $t^{-1}$, while in the former case the dimension of $k$ is $t^m$ and thus depends on the fitted curve.

Figure 6 shows the results of fitting the above equations to the experimental data for the $\nu_3$ anti-symmetric stretching mode of CO$_2$ for both sections 60 µm and 19 µm thick, respectively; fitted parameters are compared in Table 5. Figure 7 shows the values of the fitted parameters in the Arrhenius space. The activation energies $E_a$ calculated from the
Arrhenius equation (equation 2b above) for each of the aforementioned datasets are reported in Table 6.

Table 5 – Avrami JMAK and Avrami Putnis fitted values and its associated errors ($\sigma$). $\ln k$ and $R^2$ are also reported.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Avrami JMAK</th>
<th>Avrami Putnis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BM 96512 60 µm thick</td>
<td>BM 96512 19 µm thick</td>
</tr>
<tr>
<td></td>
<td>m</td>
<td>a</td>
</tr>
<tr>
<td>1000</td>
<td>0.54</td>
<td>0.03</td>
</tr>
<tr>
<td>950</td>
<td>0.80</td>
<td>0.03</td>
</tr>
<tr>
<td>900</td>
<td>0.97</td>
<td>0.04</td>
</tr>
<tr>
<td>850</td>
<td>1.17</td>
<td>0.40</td>
</tr>
<tr>
<td>825</td>
<td>0.51</td>
<td>0.06</td>
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Figure 6 – Evolution of integrated CO₂ absorbance ($\nu_3$ anti-symmetric stretching mode) as a function of time for the experimental data set collected for the BM 96512 60 µm thick (a, b) and 19 µm thick (c, d). Curves are fitted by Avrami JMAK equation (left column) and Avrami Putnis (right column) for each temperature.
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Table 6 – Arrhenius equation parameters and activation energies $E_a$ for each of the dataset obtained via Avrami JMAK and Avrami Putnis equation.

<table>
<thead>
<tr>
<th></th>
<th>Avrami JMAK</th>
<th>Avrami Putnis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BM 96512 60 µm</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ln $A$</td>
<td>36.5±1.2</td>
<td>18.1±1.4</td>
</tr>
<tr>
<td>$E_a/R$</td>
<td>48.5±1.5</td>
<td>26.9±1.7</td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>403±12</td>
<td>224±14</td>
</tr>
<tr>
<td><strong>BM 96512 19 µm</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ln $A$</td>
<td>3.9±1.9</td>
<td>11.8±1.2</td>
</tr>
<tr>
<td>$E_a/R$</td>
<td>5.9±2.2</td>
<td>16.6±1.4</td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>49±16</td>
<td>138±12</td>
</tr>
</tbody>
</table>

Figure 7 – Arrhenius plots for cordierite BM 96512, 60 µm thick (a, b) and 19 µm thick (c, d).

Examination of Table 6 shows that two different sets of results are obtained when using the two (JMAK vs Putnis) equations, suggesting that the Avrami formalism is not suitable to describe the CO$_2$ desorption along the structural channels. This point will be discussed in more details below.
5.2.2 Mono-dimensional plane sheet diffusion

In the previous paragraph, we showed that the process of CO$_2$ loss in cordierite is not related exclusively to the starting CO$_2$ content, but depends strongly on the shape and size of the examined sample. Therefore, we modeled the data on the basis of a mono-dimensional diffusion from a plane sheet of finite thickness (Fig. 8), using the equation (Carlslaw and Jeager, 1959; Crank, 1975; Ingrin, 1995; Tokiwai and Nakashima, 2010a):

$$ A_t = A_0 \cdot \sum_{n=0}^{\infty} \left\{ \frac{8}{(2n+1)^2\pi^2} \right\} \cdot \exp \left\{ \frac{-D(2n + 1)^2\pi^2t}{L^2} \right\} $$

(4)

where $A_t$ is the $A_i$ at time = t, $A_0$ is $A_i$ at time = 0, $D$ is the diffusion coefficient in m$^2$/sec, t is the time in sec and $L$ is sample thickness in m, $n$ is the index of summation.

In order to apply equation (4) the following consideration were done: 1) the CO$_2$ concentration $C$ may be replaced by the integrated absorbances $A_i$, because the CO$_2$ content and its absorbance in the FTIR spectrum are related by the Beer-Lambert equation; 2) any CO$_2$ at the crystal surface was removed using a gentle flow of N$_2$ in the microscope chamber; 3) the diffusion normal to the slab surface is homogeneous, because the CO$_2$ diffusion occurs exclusively along the c crystallographic direction (Fukuda et al., 2009; Radica et al. Chap. 3); moreover FPA images collected after the experiments on the 60 µm thick section, confirmed an homogenous distribution of residual CO$_2$ (Fig. 9).
The diffusivity of a given species in a particular medium is described by the Arrhenius equation in the form:

\[ D = D_0 \cdot \exp \left(-\frac{E_a}{RT}\right) \]  

(5)

with \( D \) is the diffusion coefficient, \( D_0 \) the pre-exponential factor, \( E_a \) the activation energy, which is the amount of energy required for a particle to pass the potential barrier between its equilibrium position and an adjacent one. \( R \) is the ideal gas constant, and \( T \) the absolute temperature in K. The parameters \( E_a \) and \( D_0 \) are obtained from the Arrhenius plot -\( \log D \) vs. \( 1/T \), where the diffusion coefficients plot in a straight line:

\[ \log D = \log D_0 - \frac{E_a}{R} \cdot \ln 10 \cdot \frac{1}{T} \]  

(6)

Hence, the activation energy \( E_a \) is derived from the slope of the line and \( D_0 \) is the intercept; \( \ln 10 \) is needed to convert from log units (diffusion coefficients) to \( \ln \) units (Arrhenius equation).
Figure 10 shows the results obtained by fitting the equation (4) to the experimental data for the CO$_2$ $\nu_3$ mode in the spectra of both 60 $\mu$m and 19 $\mu$m thick sections, while Table 7 lists the diffusion coefficients $D$ obtained from the calculations. Figure 11 displays the data in the Arrhenius space. $E_a$ values calculated from equation (6) are listed in Table 8.

Figure 10 – Evolution of CO$_2$ integrated absorbance (as a function of time) of the $\nu_3$ anti-symmetric stretching mode for the experimental data sets obtained for the 60 $\mu$m (a) and 19 $\mu$m thick (b) sections. Curves are fitted using the mono-dimensional plane sheet diffusion equation (4).
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Table 7 – Values obtained using the mono-dimensional plane sheet diffusion model and associated errors. -logD and $R^2$ are also reported.

<table>
<thead>
<tr>
<th>BM 96512 60 µm</th>
<th>Temp (°C)</th>
<th>$10^3/T$</th>
<th>D</th>
<th>σ_D</th>
<th>-logD</th>
<th>σ_-logD</th>
<th>$R^2$</th>
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</thead>
<tbody>
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<table>
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<th>D</th>
<th>σ_D</th>
<th>-logD</th>
<th>σ_-logD</th>
<th>$R^2$</th>
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</thead>
<tbody>
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<tr>
<td>900</td>
<td>0.85</td>
<td>3.02E-14</td>
<td>2.99E-15</td>
<td>13.52</td>
<td>0.10</td>
<td>0.944</td>
<td></td>
</tr>
<tr>
<td>850</td>
<td>0.89</td>
<td>1.07E-14</td>
<td>7.20E-16</td>
<td>13.97</td>
<td>0.07</td>
<td>0.914</td>
<td></td>
</tr>
<tr>
<td>825</td>
<td>0.91</td>
<td>7.45E-15</td>
<td>1.27E-15</td>
<td>14.13</td>
<td>0.17</td>
<td>0.939</td>
<td></td>
</tr>
</tbody>
</table>

Table 8 – Arrhenius equation parameters (5) and activation energies $E_a$ for each of the dataset obtained via mono-dimensional plane sheet diffusion equation (4).

<table>
<thead>
<tr>
<th>BM 96512 60 µm</th>
<th>-logD</th>
<th>$E_a/(R \ln10)$</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0±0.9</td>
<td>11.1±1.1</td>
<td>213±21</td>
<td></td>
</tr>
<tr>
<td>BM 96512 19 µm</td>
<td>5.4±0.7</td>
<td>9.6±0.8</td>
<td>183±15</td>
</tr>
<tr>
<td>All points</td>
<td>4.4±0.7</td>
<td>10.7±0.8</td>
<td>204±15</td>
</tr>
</tbody>
</table>

Figure 11 – Arrhenius plot using values of the diffusion coefficient D obtained fitting the equations (4) for the $\nu_3$ anti-symmetric stretching mode for both 60 µm and 19 µm thick sections. The combined diffusion law is reported, line parameters are reported in Tab. 8.
6. Discussions: Kinetic of CO₂ extraction

The kinetic of CO₂ expulsion from cordierite channels in the temperature range from 825 °C to 1000 °C was calculated using the integrated absorbance (Aᵢ) changes in the MIR region. Isothermal heating experiments were performed on oriented cordierite slabs doubly polished along the direction normal to the c crystallographic axis; FTIR spectra were collected in situ. Hereafter we discuss the differences on the calculated activation energies (Eₐ) of CO₂ expulsion on the basis of the used analytical approach or the effects of the sample thickness.

1) From Table 6 we observe that, when using the Avrami approach, calculation of the activation energies Eₐ on the basis of two different equations (JMAK and Putnis), yields very different values, spanning from 403 kJ/Mol to 49 kJ/Mol. The differences are not only related to the different analytical approach, but mostly to the different sample thickness. The value calculated with the Avrami JMAK equation are in fact reduced by almost one order of magnitude for the thinner sample with respect the thicker one, while those calculated using the Avrami Putnis equation are only halved.

2) Data reported in Table 8 suggest that when using the mono-dimensional diffusion model, the thickness has no effect on the resulting D₀ or Eₐ values, thus confirming that, unlike to what observed for H₂O in muscovite (Tokiwai and Nakashima, 2010a) the CO₂ diffusion in cordierite can be well described by this formalism.

3) In the previous section we mentioned that the m parameter in the Avrami equation is dependent of the reaction mechanism (Putnis et al., 1990). Examination of Figure 12 shows two distinct trends between the m values obtained for the different sections: the values fitted for the 60 µm thick sample in fact decrease progressively as a function of T, suggesting a progressive change of the expulsion mechanism. On the other hand, those fitted using the data collected on the 19 µm thick sample are constant in the whole T range considered. Considering that the two experimental sets of data differ just for the thickness of the studied crystal slab, and that in this temperature range no significant change in CO₂ expulsion mechanism are expected (also see point 2 above), we may conclude that the m values in the Avrami approach are sensitive to the sample thickness. In addition, because the m values are constant
exclusively for thinner 19 µm we may conclude that Avrami formalism could be
suitable to describe the behavior of very small, possibly powdered, samples.

4) The same procedures were adopted to model the absorbance trends for CO$_2$
sidebands polarized per E//b (Fig. 3c) in the 60 µm sample data set. In Table 9 we
compare the calculated activation energies $E_a$, ln$A$ and $-\log D_0$ obtained for each
different approach. Only small differences are observed with the $E_a$ calculated using
the $v_3$ mode collected for E//a; in particular, the Avrami Putnis and the mono-
dimensional plane sheet diffusion method yield very similar $E_a$ values (see also Tab. 6
and 8).

Table 9 – Arrhenius equation parameters and activation energies $E_0$ for the sidebands in sample BM 96512 60 µm via Avrami JMAK, Avrami Putnis and mono-dimensional plane sheet diffusion equations.

<table>
<thead>
<tr>
<th></th>
<th>Avrami JMAK</th>
<th>Avrami Putnis</th>
<th>1D diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>ln$A$</td>
<td>31.4±1.2</td>
<td>18.0±1.5</td>
<td>-log$D_0$</td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>348±13</td>
<td>222±14</td>
<td>$E_0$ (kJ/mol)</td>
</tr>
</tbody>
</table>
Scattering of the $E_a$ values confirms that the Avrami approach cannot be used to evaluate the kinetic parameters of CO$_2$ extraction. However, based on the above assumptions, it is possible to infer that the most reliable activation energy for CO$_2$ expulsion from cordierite provided by the Avrami formalism is $E_a = 138\pm12$ kJ/mol, i.e. the value obtained using the Avrami Putnis equation on the thinner sample data set. Note that this value is very close to those obtained by previous authors for the dehydration of cordierite (Giampaolo and Putnis, 1989; Lepezin and Melenevsky, 1977; Zimmermann, 1981).

![Figure 13 – Arrhenius diagram of various diffusion coefficients $D$ for different silicates or silicate melts for H$_2$O and CO$_2$. Numerical values and references in Tab. 10.](image)

We calculated also the diffusion coefficient $D$ and $E_a$ for CO$_2$ in cordierite using the mono-dimensional plane-sheet diffusion approach (Crank, 1995). We discussed in the previous paragraph how CO$_2$ likely diffuses across cordierite through a simple diffusion mechanism for temperatures between 825 and 1000 °C. Diffusion coefficients of volatile molecular species in silicates are expected to be tightly related to the molecule dimension and the diffusing structure. It is also widely accepted that for more compact silicate structures and/or larger molecules diffusing rates are smaller and activation energies larger. As we may observe from Figure 13 the diffusing rates calculated for CO$_2$ in cordierite (this
work) are almost one order of magnitude lower than \( \text{H}_2\text{O} \) diffusion coefficients calculated in the isostructural beryl (Fukuda et al., 2009).

It is difficult to draw a direct comparison between our data and the diffusion coefficients available in the literature for minerals; the reason is that, beryl and cordierite behave as microporous structures trapping H and C as \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) molecules, while the vast majority of the existing data have been collected on minerals where H is present as an OH\(^-\) group. Moreover no data are available for \( \text{CO}_2 \) diffusion in minerals (excluding C diffusion in carbonates, e.g. Anderson, 1972; Labotka et al., 2000). Thus in the next paragraph we are forced to compare our data with those derived for basically different processes.

Figure 18 and Table 6 give selected examples of diffusion rates for the most common hydrous minerals. In Figure 18 we may observe that the diffusion coefficients measured for \( \text{CO}_2 \) in beryl are close to the OH\(^-\) diffusion coefficients obtained in other ring silicates like tourmaline (Desbois and Ingrin, 2007), layer silicates like muscovite (Graham, 1981), amphiboles like kaersutite (Ingrin and Blanchard 2000), or in disilicates like epidote (Graham, 1981). However, it is important to note that structural OH\(^-\) probably diffuses inside these structures in the form of H\(^+\) (Zhang et al., 2010) thus the diffusing species is much smaller compared to molecular \( \text{CO}_2 \) and \( \text{H}_2\text{O} \). Our data suggest that the structural channels of cordierite and beryl act more likely as fast paths for the mobility of large molecular groups compared to similar silicate structures, and for this reason the diffusing behavior is more similar (in terms of diffusion coefficients, not in the mechanism) to the one typically observed for grain boundary diffusion, such as, for example, \( \text{H}_2\text{O} \) in quartzite (Farver and Yund, 1991) or to the behavior of \( \text{CO}_2 \) in non-crystalline materials, like silicate melts (Watson et al., 1982; Watson, 1991).

### Table 10 – Comparison of the experimental data for \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) diffusion in various silicate minerals and melts found in the literature.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Diffusing molecule</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>( \Delta G (\text{kJ/mol}) )</th>
<th>( \log D_0 ) (m(^2)/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhyolite</td>
<td>( \text{CO}_2 )</td>
<td>800-1100</td>
<td>1000</td>
<td>75</td>
<td>-7.2</td>
<td>Watson, 1991</td>
</tr>
<tr>
<td>Basalt</td>
<td>( \text{CO}_2 )</td>
<td>1350-1500</td>
<td>1500</td>
<td>195</td>
<td>-3.4</td>
<td>Watson et al., 1982</td>
</tr>
<tr>
<td>Muscovite</td>
<td>( \text{D/H}_2\text{O}, \text{D}_2\text{O} )</td>
<td>450-750</td>
<td>200 or 400</td>
<td>121</td>
<td>-8.0</td>
<td>Graham, 1981</td>
</tr>
<tr>
<td>Epidote</td>
<td>( \text{D/H}_2\text{O}, \text{D}_2\text{O} )</td>
<td>250-650</td>
<td>200 or 400</td>
<td>90</td>
<td>-7.4</td>
<td>Graham, 1981 in Ingrin and Blanchard, 2006</td>
</tr>
<tr>
<td>Kaersutite</td>
<td>( \text{D}_2\text{O} )</td>
<td>600-900</td>
<td>0.1</td>
<td>104±12</td>
<td>-8.7</td>
<td>Ingrin and Blanchard, 2000</td>
</tr>
<tr>
<td>Tourmaline (par c)</td>
<td>( \text{D/Ar}, \text{D}_2 )</td>
<td>700-800</td>
<td>0.1</td>
<td>106.3±36.8</td>
<td>-9.8</td>
<td>Desbois and Ingrin, 2007</td>
</tr>
<tr>
<td>Quarzite</td>
<td>( \text{H}_2\text{O} )</td>
<td>450-800</td>
<td>100</td>
<td>113</td>
<td>-7.6</td>
<td>Farver and Yund, 1991</td>
</tr>
<tr>
<td>Beryl</td>
<td>( \text{H}_2\text{O} )</td>
<td>500-700</td>
<td>50-150</td>
<td>133</td>
<td>-6.6</td>
<td>Fukuda et al., 2009</td>
</tr>
</tbody>
</table>
7. Conclusions

In this work we evaluate the kinetic parameters and diffusion rates of CO\textsubscript{2} along the structural channels of cordierite for increasing thermal conditions. High-quality polarized-light \textit{in-situ} HT-FTIR data up to 1000 °C could be obtained for very thin samples thanks to the increased brilliance of a synchrotron radiation light source (SR-FTIR, Della Ventura \textit{et al.}, 2014), compensating for the degradation of the IR signal resulting from the use of a polarizer and the heating stage.

Isothermal heating experiments were performed on (001) oriented cordierite slabs that ensure a homogeneous CO\textsubscript{2} desorption out from the slab surface (Radica \textit{et al.} chapter 3). Inspection of the spectra collected at high-\textit{T} shows a significant peak broadening of all CO\textsubscript{2} peaks, while no peak shift were observed for the \textit{\nu}_3 mode at 2348 cm\textsuperscript{-1}. Polarized spectra collected at RT after the heating experiments for the 60 µm thick sample confirms a decrease in the integrated absorption of all CO\textsubscript{2} peaks; the magnitude of decrease is directly proportional to the temperature. No H\textsubscript{2}O bands are present in the spectra after the heat-treatments, indicating that, differently from CO\textsubscript{2}, for \textit{T} > 850°C H\textsubscript{2}O is totally lost from the cordierite matrix.

Because no changes in CO\textsubscript{2} speciation occur during desorption, CO\textsubscript{2} loss can be described as a simple diffusion mechanism. The mono-dimensional plane-sheet diffusion approach is not influenced by thickness; calculated activation energies are larger, about 204±15 kJ/mol. Measured diffusion coefficients (\textit{D}) for CO\textsubscript{2} along the structural channels are almost two order of magnitude lower than those for H\textsubscript{2}O in the isostructural beryl, and very close to those of H\textsuperscript{+} in hydrated minerals or CO\textsubscript{2} in silicate melts.
CHAPTER 5

KINETICS OF INCORPORATION OF CO₂ IN CORDIERITE AND BERYL: AN FTIR-FPA SPECTROSCOPY STUDY

Abstract

In this work, we address experimentally the diffusion of CO₂ into cordierite and beryl, two isostructural microporous rock-forming minerals, using FTIR spectroscopy coupled with FPA (focal-plane-array of detectors) imaging. Fragments of a natural, almost Mg end-member cordierite and CO₂-free synthetic beryl were used as starting materials; the cordierite crystallites were degassed before the experiments. Starting crystals were treated in a CO₂-saturated atmosphere at different pressure, temperature and time conditions, using a non end-loaded piston-cylinder apparatus. Ag-carbonate was used as the source for carbon dioxide. After the high pressure experiments, the recovered crystals were oriented using a spindle stage, cut and doubly polished, and analyzed using polarized micro-FTIR spectroscopy to study the distribution of CO₂ across the sample and quantify its concentration. The IR data show that pressure plays a major role on the incorporation of gaseous CO₂ in both cordierite and beryl, whereas the effect of temperature is limited. The spectroscopic data show that the diffusion of CO₂ occurs preferentially along the structural channels parallel the c-axis direction. Diffusion coefficients (D) for beryl were calculated using the monodimensional diffusion equations; obtained values are in the order of 10⁻¹⁴ m²/s between 700 – 900°C. Fitting of the diffusion coefficients in the Arrhenius plot yielded – logD₀ = 7.2±0.7 m²/sec and an activation energy Eₐ = 122±15 kJ/mol. Sample cracks formed
during the high pressure experiments were found to enhance significantly the gas diffusion within the samples.

1. Introduction

Microporous and mesoporous minerals are important from both a geological and a technological viewpoint. Initially these attributes were only referred to zeolites, however in the last decade the IUPAC nomenclature was extended to non-zeolitic minerals (McCusker et al., 2001; McCusker, 2005). Among these phases, cordierite plays a key role because it represents the only case of a widespread microporous mineral (pore size under 2 nm, Rouquérol et al., 1994; McCusker et al., 2001) that is able to trap significant amounts of molecular H$_2$O and CO$_2$ (Schreyer and Yoder 1964; Mirwald et al., 1979; Newton and Wood, 1979; Armbruster and Bloss 1982; Kurepin 1985) under extreme geological (P, T) conditions. Cordierite stability extends from the amphibolite facies to ultra-high temperature metamorphism to crustal anatexis conditions (Mirwald and Schreyer, 1977; Vry et al., 1990; Carrington and Harley, 1996; Smith 1996; Kalt 2000; Harley et al., 2002; Bertoldi et al., 2004; Sarkar et al., 2010). The analysis of the volatile constituents of cordierite can used to determine the composition of the fluid phase during crystallization (Vry et al., 1990; Carrington and Harley, 1996; Harley et al., 2002; Kurepin, 2010). H$_2$O and CO$_2$ contents affect the stability of cordierite (Schreyer 1985; Carey 1995; Harley et al., 2002). Therefore, a quantitative determination of its channel constituents is crucial in petrologic studies.

Among the wide range of cordierite occurrences, the most investigated is the ultra high-temperature metamorphism of pelitic rocks. Dehydration melting of biotite-bearing pelites with moderate to high $X_{Mg}$ variations ($X_{Mg}/X_{Mg+Fe} > 0.5$) is often controlled by cordierite-forming reactions in migmatites and leuco-granites at 200–700 MPa and 700–900°C (Fitzsimons, 1996; Harley et al., 2002). Thus understanding the role of cordierite as an H$_2$O and CO$_2$ bearing phase is essential for understanding melting processes and for thermodynamic calculation of fluid activities during these events (Harley and Thompson, 2004). Kurepin (2010) made calculations of the dependence of H$_2$O and CO$_2$ contents in cordierite as a function of P, T and fluid composition for the aforementioned P-T conditions, and his thermodynamic model showed a non-ideality of thermodynamic behavior of H$_2$O
and CO₂ mixing. In addition evaluation of the H₂O and CO₂ activities showed that cordierites in high temperature and pressure assemblages were formed under fluid-saturated conditions over a wide range of H₂O/CO₂ ratios (Vry et al., 1990; Kurepin, 2010).

In order to understand these mechanisms, several experimental studies on the solubility of volatile components in cordierite have been performed, in particular H₂O (Schreyer and Yoder 1964; Mirwald et al., 1979, Harley and Carrington, 2001 among the others), CO₂ (Armbruster and Bloss, 1982, Armbruster, 1985; Le Breton and Schreyer, 1993), and mixed H₂O – CO₂ (Johannes and Schreyer 1981; Thompson et al., 2001).

As a result of these studies, there is agreement that pressure exerts a stronger influence on the solubility of both H₂O and CO₂ than does temperature. Both H₂O and CO₂ contents slightly decrease with increasing temperature, while increasing pressure favors higher concentrations (e.g. Fig. 1, modified after Harley and Thompson, 2004). It is important to note that the maximum H₂O content obtained at 700 MPa is about 2.4 wt.%, which is close to the maximum theoretical value of 2.9 wt.% or 1 molecule per formula unit in the channel (Deer et al., 2004). The maximum calculated value for CO₂ is about 2.2 wt.% (Deer et al., 2004) corresponding to about 0.3 molecules per formula unit.

![Figure 1](image_url)

Figure 1 – (a) Pressure – temperature phase diagram of the isopleths of H₂O (expressed in wt.%) for X_Mg = 0.75 cordierite coexisting with pure H₂O fluid, as calculated by Harley and Carrington (2001); (b) isopleths of CO₂ (expressed in wt.%) for X_Mg = 0.80 cordierite in a pure fluid after Thompson et al., (2001) and Harley et al., (2002).

Studies on X_CO₂, where X_CO₂ = CO₂/(CO₂+H₂O), partitioning between melt and cordierite have shown that H₂O tends to be incorporated preferentially into the cordierite structure, while CO₂ preferentially remains in the melt (Fig. 2b and Johannes and Schreyer,
1981). This behavior is only slightly changed at higher temperatures (Harley and Carrington, 2001), while $X_{\text{CO}_2}$ increases with increasing pressure, facilitating CO$_2$ uptake (Johannes and Schreyer, 1981). Moreover, increasing $X_{\text{CO}_2}$ decreases significantly the amount of H$_2$O+CO$_2$ diffused into the mineral. In particular, there is a decrease of H$_2$O (Fig. 2a) probably because the presence of CO$_2$ obstructs its diffusion to the channel ways. This behavior, which is observed also in natural samples (Vry et al., 1990), can be explained by the configuration of the CO$_2$ molecule inside the channels. Another factor that decreases the total amount of diffused fluids is the alkali content within the structural channels (Johannes and Schreyer, 1981; Vry et al., 1990). There is evidence suggesting that CO$_2$ (and possibly alkali cations) may act as plugs in the channel ways obstructing inward and outward molecule diffusion, drastically slowing down the time of degassing and re-equilibration in case of pressure drop (Johannes and Schreyer, 1981; Kalt, 2000). This behavior complicates the possibility to predict the diffused molecules coexisting with mixed H$_2$O and CO$_2$ fluids, although a theoretical approach has been attempted by Kurepin (2010).

![Figure 2](image)

**Figure 2** (a) variation of the volatile composition in cordierite ($X_{\text{Mg}} = 0.68$) channels with fluid-saturated, intermediate H$_2$O - CO$_2$ fluid composition. The lines show the calculated values at Thompson et al. (2001). Squares = H$_2$O, triangles = CO$_2$, circles = total number of molecules per formula unit (modified after Thompson et al., 2001). (b) partition curves showing $X_{\text{CO}_2}$ fractioning between cordierite and coexisting fluid at 500 MPa and 600°C for two different synthetic cordierites A and B (modified after Johannes and Schreyer, 1981).

The experiments were performed with small cordierite grains as starting materials (about 200 µm in Armbruster and Bloss, 1982 and Armbruster, 1985; 125-250 µm in Thompson et al., 2001) in order to maximize the surface-to-volume ratio, and were carried out for a long duration (up to a few weeks) in order to achieve fluid/mineral equilibration. However there is still no agreement on the results, among the different authors. For
instance, Johannes and Schreyer (1981) obtained different results as a function of different starting material (Fig. 2b) or grain size of cordierite, and Le Breton and Schreyer (1993) observed a nonlinear behavior of the CO$_2$ contents between 15 minutes to 3 weeks experimental runs. Major problems arise with CO$_2$ diffusion, because its “sluggish” nature delays or even prevents sample saturation. Thus, the study of the run products cannot be addressed by conventional bulk methods, such as coulometric titration (Armbruster and Bloss, 1982; Johannes and Schreyer, 1981) or powder FTIR spectroscopy (Vry et al., 1990) or single spot micro-analytical techniques, such as SIMS (secondary ion mass spectrometry) (Thompson et al., 2001), which do not allow characterizing the inhomogeneous distribution of the target element.

The aim of this work is to examine the interaction of cordierite single grains with a CO$_2$–rich fluid under different experimental $P$, $T$ and $t$ conditions and to determine the diffusion behavior of CO$_2$ within the crystals at controlled $P$-$T$ conditions. In particular, we performed several short duration experiments on relatively large samples (max dimension 2 mm across) in order to observe the diffusion behavior of CO$_2$ in the early stages of the experiment. Along to cordierite, we investigated the behavior of isostructural beryl that is also known to trap significant amounts of H$_2$O and CO$_2$ inside its channels (e.g. Wood and Nassau, 1968). Differently from the used cordierite fragments, the beryl crystals had a perfect prismatic hexagonal habit that make easier the orientation of the crystal recovered after the run, and to evaluate the anisotropy of diffusion coefficients. Based on previous literature data, we expected neither saturation nor sample homogenization with respect the CO$_2$ content. Therefore we made extensive use of FPA imaging to preliminarily characterize the run products and to locate the single-spot analyses for quantitative measurements. Recent works on cordierite (Della Ventura et al., 2009, 2012) and other microporous minerals of the haüyine-sodalite group (Bellatreccia et al., 2009) or feldspathoids such as leucite (Della Ventura et al., 2008) have shown that FTIR-imaging is crucial when dealing with volatile or channel constituents which may be strongly zoned across the samples. Moreover, several experimental studies (e.g. Zhang et al., 2006; Watson and Baxter, 2007) have shown that growth imperfections and/or stress induced deformations may lead to preferential “fast–paths” complicating the diffusion behavior across apparently homogeneous crystals.
Chapter 5: Kinetics of incorporation of CO\textsubscript{2} in cordierite and beryl: an FTIR-FPA spectroscopy study

1.1 Cordierite and beryl: structural details

Cordierite is a framework alumino silicate with the ideal formula (□,Na)(Mg,Fe)\textsubscript{2}Al\textsubscript{4}Si\textsubscript{5}O\textsubscript{18}(□,H\textsubscript{2}O,CO\textsubscript{2}) and a continuous solid solution between the Mg\textsuperscript{2+} end-member and the Fe\textsuperscript{2+} end-member (sekaninaite) exists (e.g. Černý et al., 1997, Radica et al., 2013). The cordierite framework can be described as a stacking of pseudo-hexagonal Si/Al layers of tetrahedra and mixed layers of tetrahedra and octahedra (Fig. 3a). Alkali cations such as Na, K, Ca, and molecules such as H\textsubscript{2}O and CO\textsubscript{2} may be allotted within the resulting pseudo-hexagonal channel, occupying sites on the c axis at the height of the narrow “bottle necks” for Na, and of the large cavities for H\textsubscript{2}O and CO\textsubscript{2} (Gibbs, 1966, Hochella et al., 1979; Malcherek et al., 2001; Yakubovich et al., 2004).

Figure 3 - Schematic view of a portion of the cordierite (a) and beryl (b) structures emphasizing the channels parallel the c axis. Si-containing tetrahedra are shown in blue, Al in tetrahedral and octahedral coordination is shown in orange, Be-containing distorted tetrahedra in dark gray and Mg-octahedra in dark green. The structural position of the channel alkali cations, both orientation types of H\textsubscript{2}O and CO\textsubscript{2} are shown (modified after Radica et al., 2013)

Beryl (ideal formula (□,Na)Be\textsubscript{3}Al\textsubscript{2}Si\textsubscript{6}O\textsubscript{18}(□,H\textsubscript{2}O,CO\textsubscript{2}) is isostructural with cordierite (Fig. 3b). Its framework is constituted by 6-fold Si-centered tetrahedral rings stacked along the c axis. The hexagonal rings are interconnected parallel to [001] by distorted Be-centered tetrahedra. Al occupies the octahedral sites (Gibbs et al., 1968). Beryl also has structural
channels running along the c axis that can contain alkali cations and volatile molecules (Wood and Nassau, 1968).

Extra-framework H₂O groups occur in the structural channels with the molecular plane parallel to (100). In both cordierite and beryl H₂O can be oriented in two different ways: type I H₂O (hereafter H₂O[I]) has its H–H vector oriented parallel to the c axis, and type II H₂O (H₂O[II]) has its H–H vector normal to the c axis (parallel to the b axis in cordierite). H₂O groups of the latter type are locally associated with channel cations (Goldmann et al., 1977; Hawthorne and Černý, 1977). Winkler et al. (1994) proposed that H₂O[I] in synthetic Mg-cordierite is rotationally disordered about [001] and that a purely static description is inappropriate to describe its behavior in the channel cavity. They proposed a model whereby the H...H vector remains parallel to [001] and the H₂O molecule rotates in two different positions about its center of mass with an estimated hopping time of about 6 picoseconds at room temperature; this feature however cannot be observed by using FTIR spectroscopy. The linear CO₂ molecules are systematically oriented normal to the c axis and parallel to the crystallographic a axis for cordierite (Aines and Rossman, 1984; Kolesov and Geiger, 2000; Khomenko and Langer, 2005).

The molecular dimension of H₂O is 2.8 X 3.2 X 3.7 Å and CO₂ is 2.8 X 2.8 X 5.0 Å (Wood and Nassau, 1968). However the CO₂ molecule barely fits inside the cage, so once inside it tends to be wedged to the structure behaving as a “plug” (Aines and Rosmann, 1984; Vry et al., 1990). On the opposite, the smaller H₂O polar molecules are bonded to the structure mainly by electrostatic interactions with the structural oxygens (H₂O[I]) and alkali cations (H₂O[II]).

The maximum H₂O and CO₂ content in both cordierite and beryl is constrained by the available space in the channels that corresponds roughly to 1 molecule per formula unit (about 2.5 - 2.9 wt% of H₂O or about 6.9 - 7.1 wt% of CO₂; Deer et al., 2004). While the theoretical maximum water content has been observed in nature for both minerals (2.90 wt%, in a cordierite-biotite gneiss: Fediuk, 1971; 2.68 wt.% in a pegmatite beryl: Erämetsä et al., 1973), the highest CO₂ contents so far recorded of only 1.97 wt. % (0.26 molecules p.f.u.) was observed for a cordierite occurring in a granulate from Cauchon Lake (Vry et al., 1990). Cordierites with high CO₂ and CO are typically found in granulitic facies rocks, while in amphibolite facies H₂O specimens prevails (Zimmerman, 1981).
2. Experimental and analytical procedure

2.1 Starting materials

For the experiments described here, cordierite RP 7344 (Fig. 4 left) from Karur, Tamil Nadu (India) were used as starting material; the crystals were provided by Mr. Renato Pagano. The fragments are clear and inclusion-free, with a color from pale blue-violet with yellow nuances, typical of its pleochroic nature. The sample composition, crystal-chemical formula, cell parameters, density and optical properties of this sample can be found in Della Ventura et. al. (2012) and are reported in Table 1 for simplicity. Chemical data collected over three analytical points.

$\text{Fe}^{\text{tot}}$ was considered as $\text{Fe}^{2+}$ allotted in the octahedral sites. However we remark that some $\text{Fe}^{2+}$ can be also present in the tetrahedral site (Geiger et al., 2000). The chemical formula, based on 18 oxygen atoms p.f.u. is $\text{Na}_{0.08}(\text{Mg}_{1.98}\text{Fe}_{0.09})\text{Al}_{3.93}\text{Si}_5\text{O}_{18}\cdot0.51\text{H}_2\text{O}\cdot0.03\text{CO}_2$; due to the very high magnesium number ($X_{\text{Mg}} = 95.6\%$) the selected sample can be considered as a Mg end-member of the Mg-Fe cordierite series. Untreated cordierite presents significant $\text{H}_2\text{O}$ and very low $\text{CO}_2$. Preliminary FTIR analysis confirmed an homogeneous distribution of $\text{H}_2\text{O}$ and $\text{CO}_2$ across the sample (Della Ventura et. al., 2012) and showed that water is mostly present as $\text{H}_2\text{O}^{[\text{II}] ol}$ because of the high Na contents in the structural channels (Della Ventura et. al., 2012).
Beryl samples are part of the very first Li$_2$O and MoO$_3$ flux-grown synthetic emeralds, made by P.G. Hautefueille and A. Perrey in 1888 in Paris (Bellatreccia et al., 2008) and currently kept in the mineralogical collection of the Muséum National d'Histoire Naturelle, Paris. The crystals were obtained after 15 days of growth at 800°C, because higher temperatures lead to formation of phenakite (Hautefueille and Perrey, 1888, 1890). Beryl
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crystals show a perfect prismatic hexagonal habitus with a maximum length of 1 mm and width of 0.5 mm (Bellatreccia et al., 2008).

Figure 5 – Crossed polarizers optical microscope picture of a 1 mm long and 0.2 mm wide, double-polished beryl slab (Pa_340 d bis). The dark part at the center of the grain consists of molybdenum inclusions (Bellatreccia et al., 2008). Tiny inclusions, remnants of the natural beryl seeds used for the synthesis are observable at the left side.

The used batch consists of fairly large (max. dimensions 1 mm X 0.5 mm) emerald-green hexagonal prismatic beryls. Close examination of these samples reveals the presence of tiny dark inclusions (EDS spectra indicates the presence of molybdenum, Bellatreccia et al., 2008) and beryl seeds within the grains (Fig. 5). Cracks may occasionally be present.

A crystal-chemical study for these beryls is reported in Bellatreccia et al. (2008) and data are summarized in Table 1. Chemical data collected over six analytical points. The crystal-chemical formula (Be calculated by stoichiometry) based on 36 oxygen atoms p.f.u. is Na$_{0.02}$K$_{0.01}$(Al$_{3.77}$Cr$_{0.23}$)Be$_6$Al$_{0.18}$Si$_{11.82}$O$_{36}$F$_{0.12}$ (Bellatreccia et al., 2008). Octahedral Al was calculated as: Al$^{VI}$ = Al$^{tot}$ – Al$^{IV}$ where Al$^{IV}$ = 12 – Si (all elements in apfu), i.e. assuming that all aluminum exceeding the amount needed to fill the tetrahedral rings is allotted to the octahedral sites. The final composition is close to the stoichiometric composition except for the Cr$_2$O$_3$ content which ranges from 1.45 to 2.95 wt.%, the Cr being responsible for the characteristic emerald green color. The c/a ratio of 0.9961 (Bellatreccia et al., 2008) is typical
of normal-type beryls (Aurisicchio et al., 1988) characterized by the substitution of \( \text{Al}^{3+} \rightarrow \text{Me}^{2+} \) at the octahedral site. Normal beryls usually compensates the charge unbalance with alkali cations inside the structural channels and may show both type of water where the \( \text{H}_2\text{O}^{[\text{II}]} / \text{H}_2\text{O}^{[\text{I}]} \) ratio depends on the Na in the channels (Aurisicchio et al., 1994). Following the classification proposed by Hawthorne and Černý (1977), the studied synthetic beryl may be considered as “alkali-free beryl” (total alkali ≤ 0.1 Wt.%), with a composition similar to those occurring inside vugs of predominantly graphic pegmatites and schlieren and pocket-type bodies in granites.

As expected, preliminary FTIR single-crystal unpolarized spectra of untreated samples showed no \( \text{CO}_2 \) related absorptions at around 2360 cm\(^{-1}\), however small traces of \( \text{H}_2\text{O} \), indicated by the weak absorptions at 3643 and 3587 cm\(^{-1}\), are present (Fig. 6).
2.2 Experimental procedure

Several cordierite fragments with size ranging from 1.5 to 0.2 mm were separated from a large single crystal. Before the experiments the fragments were blown through an abrasive cylinder to remove sharp edges and then the grains were pre-treated at 1250 °C for 24 hour in order to remove all H₂O and CO₂ from the sample (Chapter 3). Grains showed no evident variation in color or clarity, however cracking of larger grains occurred during the heat-treatment.

The experiments were carried in 3 x 9 mm Pt capsules; silver carbonate was used as a CO₂ source to saturate the system with carbon dioxide during HT/HP treatment. As a matter of fact Ag₂CO₃ decomposes according to the 2Ag₂CO₃ → 2Ag₂O + 2CO₂ reaction at 210 °C, yielding a theoretical CO₂ content ≈16 wt.%. Al₂O₃ powder (Al₂O₃ = 99.72 wt.%, SiO₂ = 0.07 wt.%, others = 0.21 wt.%) was mixed in 1 to 1 ratio by wt. with Ag₂CO₃, and added to the charge. The aluminum oxide powder was used to prevent the contact between the crystals and the capsule walls after the silver carbonate disappearance due to its decomposition. Layers of Ag₂CO₃/Al₂O₃ mix were alternated to layers of starting crystals (Fig. 7a). Explorative runs were performed to check different setups (Tab. 2, experiments QP1-12, QP1-14 and QP1-15); these trials lead to capsule failure. Capsules containing both beryl and cordierite or exclusively beryl or cordierite (Tab. 2) were prepared; each capsule contained from 4 to 7 grains, for a total crystal weight of about 2 to 10 milligram of sample. All components used to prepare the tubes were dried up at 110 °C in order to avoid water contamination. The capsules were crimped and welded on both sides. After each run the capsule, if possible, was pierced to check the presence of CO₂ in excess.

Table 2 - Experimental conditions and set up.

<table>
<thead>
<tr>
<th>Code experiment</th>
<th>Set up</th>
<th>Sample</th>
<th>Mineral</th>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>Time</th>
<th>Note</th>
</tr>
</thead>
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<td>QP 25</td>
<td>Crd_pr 1</td>
<td>Cordierite</td>
<td>750</td>
<td>200</td>
<td>4</td>
<td>Al₂O₃ and Ag₂CO₃ not mixed</td>
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<td>&quot;</td>
<td>QP 25</td>
<td>Crd_pr 2</td>
<td>Cordierite</td>
<td>750</td>
<td>200</td>
<td>4</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
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<td>Crd_pr 3</td>
<td>Cordierite</td>
<td>750</td>
<td>200</td>
<td>4</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>QP 25</td>
<td>Crd_pr 4</td>
<td>Cordierite</td>
<td>750</td>
<td>200</td>
<td>4</td>
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<td>24</td>
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<tr>
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<td>QP 19-25</td>
<td>Crd_pr 6</td>
<td>Cordierite</td>
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<td>42</td>
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<tr>
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<td>QP 19-25</td>
<td>Crd_pr 7</td>
<td>Cordierite</td>
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<td>250</td>
<td>4</td>
<td>Failed</td>
</tr>
</tbody>
</table>
Chapter 5: Kinetics of incorporation of CO$_2$ in cordierite and beryl: an FTIR-FPA spectroscopy study

All experiments were performed using a non-end loaded piston cylinder apparatus (QUICKpress™ design by Depths of the Earth Co.) at the HP-HT Laboratory of Experimental Volcanology and Geophysics of Instituto Nazionale di Geofisica e Vulcanologia (INGV, Rome, Italy). Experiments were conducted using two different set-ups (Tab. 2): experiments coded QP34-xx were performed using a standard 19 mm assembly (Moore et al., 2008) with an oxygen fugacity set at NNO +2 (Freda et al., 2008, Masotta et al., 2012a) and pressure ranging from 300 to 800 MPa. Experiments coded QP1-xx in a 19-25 and 25 mm assemblies with comparable oxygen fugacity and pressure ranging from 150 to 300 MPa; the 25 mm...
assembly may accommodate up to 4 samples in a single run (Fig. 7b, modified after Masotta et al., 2012b). We used a NaCl-Pyrex-Graphite-crushable-MgO-pyrex assembly with capsule surrounded by pyrex powder instead of pyrophyllite powder to avoid water infiltration. Temperature was controlled using a factory calibrated C-type (W95Re5 – W74Re26) thermocouple with a ±5 °C uncertainty (Holtz et al., 2001). Error on pressure of ±25 MPa is associated with the piston cylinder NaCl calibration method (Baker, 2004, Masotta et al., 2012b). Heating rates were set to 100 °C/min; the isobaric quenching rate ranged from 50 °C/s (25 mm assembly) to 100 °C/s (19 mm and 19-25 mm assembly) in the first 5 seconds (Masotta et al., 2012b). Experiments were performed in the pressure range 200 – 700 MPa, temperature range 700 – 900 °C; run duration varied from 1 to 72 hours.

![Figure 7](image)

Figure 7 – (a) Schematic section of the layered crystal/filler assemblage within the capsule, (b) schematic cross section a 19-25 mm and 25 mm furnace assemblies (modified after Masotta et al., 2012b).

### 2.3 Analytical methods

BSE-SEM images were collected at INGV using a field emission scanning electron microscope (FE-SEM) Jeol 6500F equipped with an energy-dispersive (EDS) detector. Samples were coated with Au before the analysis.

FTIR spectra were acquired using a Bruker™ Hyperion 3000 microscope equipped with a KBr-Broadband beamsplitter and a liquid nitrogen-cooled MCT detector at Laboratori Nazionali di Frascati-Istituto Nazionale di Fisica Nucleare (LNF-INFN,) Frascati (Rome). Polarized spectra were collected using a gold-wire-grid FTIR polarizer on a ZnSe substrate. The spot size was variable; a 15x objective and a conventional light source (Globar) was employed, with a nominal resolution of 4 cm⁻¹ averaging 128 scans for both spectrum and background. The FTIR images were collected with the same device using a 64 x 64 pixel focal-
plane array (FPA) of liquid nitrogen-cooled MCT detectors. Using a 15x objective, each image covers an area of 170 µm x 170 µm with a nominal spatial resolution of ~5 µm (Della Ventura et al., 2010, 2014). The nominal resolution was set at 4 cm\(^{-1}\) and 64 scans were averaged for each spectrum and background.

For polarized IR measurements, the cordierite samples were oriented on (010) using a polarizing microscope equipped with a spindle-stage; the program ExcalibrW (Bloss, 1981; Gunter et al., 2005) was used to process the extinction data. Beryl samples were oriented (hk0) using the external hexagonal prismatic morphology. The oriented fragments were transferred to glass slides and doubly polished to thickness usually below 400 µm.

Sample thickness was checked using an electronic micrometer with ±5 µm uncertainty and double checked using the interference fringes in the FTIR spectra, based on the formula \(t = 1/[2 \cdot n \cdot (v_1 - v_2)]\) where \(t\) is sample thickness in cm, \(n = 1.535\) is the refractive index and \((v_1 - v_2)\) is the distance between two adjacent fringes in cm\(^{-1}\) (Pistorius and DeGrip, 2006). For some samples, thickness were also checked with a Leica DCM 3D optical profilometer at the Laboratorio Interdipartimentale di Microscopia Elettronica (LIME), Università Roma Tre. The nominal vertical resolution was less than 15 nm in confocal mode (20X lens, NA = 0.50) and less than 4 nm in interferometric mode (50X lens, NA = 0.50); sample thickness was averaged for the whole surface of the slab.

The CO\(_2\) content of run samples were calculated from polarized FTIR spectra using the Beer-Lambert relationship, \(C = (A \cdot k) / (t \cdot D \cdot \varepsilon)\), where \(\varepsilon\) (l mol\(^{-1}\) cm\(^{-2}\)) is the molar absorption coefficient, \(C\) (wt.%) is the concentration of the target molecule, \(A\) is the measured absorbance, \(t\) is the slab thickness in cm, \(D\) is the value of the sample density (g/cm\(^3\)) and \(k\) is a conversion factor needed to convert from wt% to mol\(^{-1}\); for CO\(_2\), \(k = 4.401\) (Della Ventura et al., 2009, 2012). \(A\) was calculated as total integrated absorbance \(A_i\) (cm\(^{-1}\)) = \(A_x + A_y + A_z\) for trimetric cordierite and \(A_i\) (cm\(^{-1}\)) = 2\(A_x + A_y\) for dimetric beryl, where \(A_x, A_y\) and \(A_z\) are the integrated absorptions along each polarization direction (Libowitzky and Rossman, 1996). The peak areas were obtained for each component using the data calculation routine built in the spectrometer software; the background was modeled as linear. Using this method, it is possible to quantify even few ppm of CO\(_2\) in the channels (Della Ventura et al., 2009). Integrated absorbance values were obtained for the principal \(\nu_3\) anti-symmetric stretching modes of CO\(_2\) (Fig. 8) at 2348 cm\(^{-1}\) polarized for \(E//a\) for cordierite (Della Ventura et al., 2009) and at 2360 cm\(^{-1}\) polarized for \(E\perp c\) for beryl (Charoy et al., 1996).
The density was set at 2.577 g/cm$^3$ for cordierite (Sample RP 7344 in Della Ventura et al., 2012) and 2.657 g/cm$^3$ for beryl (Tab. 1). The integrated molar absorption coefficients for cordierite, $\varepsilon_{\text{ICO}_2} = 19000\pm2000$ was taken from Della Ventura et al. (2012), while for beryl $\varepsilon_{\text{ICO}_2} = 70000\pm7000$ was recalculated after Charoy et al. (1996). The error $\sigma_C$ associated with C was obtained using the classical statistics of error propagation (Bellatreccia et al., 2005); the error on A is $\sim$ 10% (Libowitzky and Rossman, 1997), the sample thickness uncertainty was $\pm$5 µm, the standard deviation of the density (D) is 2%.

Figure 8 – FTIR polarized light spectra for E//a in a 130 µm thick cordierite slab, and E⊥c in a 153 µm thick beryl slab both treated at 700 MPa and 900 °C for 24 hour. Spectra scaled to sample thickness.
3. Results

3.1 Run products

After the run, the mineral grains were embedded in a fine white-grayish powder. XRD diffraction pattern of this powder revealed the presence of residual alumina (corundum) and metallic silver together with traces of silver carbonate/oxides.

Beryl grains usually presented a brown-red reaction/alteration coating of a few microns. This coating was not observed for shorter duration experiments. On the opposite, cordierite grains usually presented a very thin metallic coating around the edge and inside the major cracks. In Figure 9a, we present a crossed polars optical microscope image of a (010) cordierite section. Beside the very heterogenous aspect of the grain indicated by the interference colors, the sample shows several major cracks filled with a metallic material; in section the filling color ranges from a silver to a dark black tone. Two-hour treated cordierite also presented the same type of cracks, although the crack filling is incomplete (Fig. 9b). A closer examination of the slabs (especially near the edges of the grain) reveals a system of about 20 µm wide cracks oriented normally to the c crystallographic axis (dashed yellow square in Fig. 9c). BSE-SEM images showed in fact (top side of Fig. 9d) the presence of two systems of smaller cracks, one parallel to the larger cracks observed in optical microscopy, and a second system normal to the c axis. SEM-EDS spots revealed that the metallic filling is constituted mainly by Ag due to the Ag₂CO₃ added to the charge (Fig. 9e). Cordierite treated at 700° C did not show these micro-cracks at any pressure conditions and the grains were always very clear after the extraction. The beryl samples after the run presented some fracturing due to differential stress, but never presented any micro-cracking at any pressure and temperature.
Figure 9 – (a) Crossed polars light (XPL) picture of a (010) 130 µm thick cordierite slab (Crd_pr 33, 700 Mpa, 900° C, 24 hours): in the top part of the sample there is a large brown area corresponding to a crack completely filled with silver/silver carbonate particles. (b) XPL picture of a (010) 127 µm thick cordierite slab (Crd_pr 13, 200 Mpa, 700° C, 2 hours): the highlighted area corresponds to a crack partially filled by Ag probably due to the short duration of the experiment. (c) XPL picture of a (010) 292 µm thick cordierite slab (Crd_pr 18, 350 Mpa, 800° C, 24 hours): the sample presents diffuse small cracks perpendicular to the c crystallographic direction (dashed yellow square). (d) BSE-SEM image of a (010) 110 µm thick cordierite slab (Crd_pr 5, 200 Mpa, 900° C, 24 hours showing additional systems of cracks 2 µm wide, perpendicular and parallel to the c axis, respectively (dashed yellow square). EDS spectra of (e) spot 1 (crack) and (f) spot 2 (cordierite) indicated in Figure 9d.
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The formation of these systems of micro-fractures may be due to the different response of beryl and cordierite to thermal shocks. Hochella and Brown (1986) observed that, during heating, the channel structure of cordierite contracts along the $c$ axis due to a twisting of the tetrahedral framework, partially driven by the octahedral site expansion along the $a$ and $b$ axis (see also Khosrovani and Sleight, 1999). This mechanism is enhanced for high $X_{\text{Mg}}$, as it is the case of the samples studied here (Tab. 1 and solid line in Fig. 10a). On the opposite, the thermal expansion of the Be tetrahedra and Al octahedra in beryl is less pronounced than in cordierite, and this prevents the shortening along the $c$ axis. Indeed Morosin (1972) observed that a small degree of Cr$_{3+}$ → Al$_{3+}$ substitution, as in emeralds, causes expansion in both $a$ and $c$ axis (dashed line Fig. 10b).

The set of fractures parallel to the $c$ crystallographic direction along the (010) and (100) cleavage planes may be due to the thermal expansion along the $a$ and $b$ crystallographic directions. On the other hand, the set of micro-cracks oriented normal to the $c$ crystallographic axis may be caused by the local stress caused by contraction along the $c$ axis. When this stress overrides the lattice strength, probably for $T > 700 \, ^\circ\text{C}$, an extension fracture occurs along the (001) cleavage plane (Coulomb, 1776). The presence of cracking is random, and is not preferentially related to specific $T$ or $P$ conditions. This process may be favored by the fluid circulation inside the cracks; in our case, the fluid circulation is witnessed by the silver carbonate filling the voids. This is a notable point to consider: the fact that the cracks are filled by Ag indicates that they developed during the experiment, and not

Figure 10 – Selected thermal expansion curves for cordierite and indialite (a), and for beryl and emerald (b) (from Hochella and Brown, 1986). The White Well cordierite (Fig 10a, solid lines) is a natural almost Mg end-member containing alkali cations in the channels with a composition similar to our starting sample. The gem quality beryl curve (Fig 10b, dashed lines) contains small amounts of Cr.
as a consequence of the decompression at the end of the run. One may argue that in such a case the cracks could have provided a favorable path for the CO$_2$ diffusion across the sample. However, considering that the fractures are all filled by Ag, we consider this possibility as unlikely. In addition, we note that only cordierite is affected by this phenomenon, while beryl did not show any evidence of cracking. In the following, the diffusion coefficients that will be discussed were obtained mostly on the beryl samples.

### 3.2 CO$_2$ diffusion in cordierite and beryl: preliminary considerations

The main problem in experimental studies on CO$_2$ (as well as H$_2$O) diffusion in minerals is the difficulty to quantify the amount of carbon dioxide (and hydrogen) but also its distribution within the matrix. Carbon can be quantitatively analyzed only using SIMS; besides the non-easy access to this facility, few SIMS laboratories are equipped to work with this element, the analysis of which requires non-conventional cautions and standardization. In addition, as already shown by Della Ventura et al. (2009, 2012) and Bellatreccia et al. (2009) in microporous minerals, CO$_2$ is frequently zoned, and the lack of the zoning patterns may significantly alter the data and their interpretation. Preliminary FTIR-FPA imaging for CO$_2$ revealed an extreme heterogeneity in carbon dioxide concentrations across the crystals, thus each sample was carefully examined by FPA to locate the area suitable for analytical spots (Fig. 11).

Selected FPA images are given in Figure 11. The interpretation of those relative to beryl (Fig 11c, 11d) is much easier due to the well-developed morphology of the samples; it is evident that the CO$_2$ diffusion proceeds exclusively from the basal (001) pinacoids through the crystal, following the structural channel. A similarly observation was reported by Fukuda et al. (2009) for H$_2$O diffusion in beryl. For cordierite, due to the strongly irregular shape of the grains, the interpretation of the images given in Figures 11a and 11b is less straightforward. Considering that cordierite is isostructural with beryl, however, it is likely that also in this case the CO$_2$ diffusion proceeds along the channels parallel to the c crystallographic direction (see also Chapter 3). Figure 11b, in particular, shows the strong enhancement of the CO$_2$ diffusion along a cracks well evident in the center of the grain. An additional source of uncertainty, for cordierite, is the fact that, under high T and $P_{H2O}$ conditions, it has the strong tendency to give reaction rims (e.g. Deer et al., 2004) typically
consisting of clay-like products (pinite). In such a case, a possible negative effect (a kind of plug effect) on the CO$_2$ diffusion could result. In the system studied here, however, this problem is minimized because the experimental system was very poor in H$_2$O; we did not examined by EMPA the rims of the crystals after the experiments, however optical observations did not show any presence of reaction products.

All samples recovered after the experiments were previously examined by FTIR imaging, and on the basis of the results we located the most suitable area for the analytical spot, usually on the first 20/30 µm from the edge. We carefully avoided measurements spots close to fractures (see below). In the case of controversial data, detailed IR transects were performed; the beam size was kept as small as possible, usually at 20x20 µm$^2$ and the highest absorbance values were selected as representative of the CO$_2$ content of the sample.

### 3.3 CO$_2$ contents

The maximum CO$_2$ contents (in ppm) measured in the experimental samples, considering the above considerations, are summarized in Table 3 for cordierite and Table 4 for beryl. Slab thickness and the experimental conditions are also given. Samples from the
same capsule prepared multiple times are indicated with brackets. Measurements indicated with F were performed on fractures in order to compare the fracture contents with those at the grain edges. The presence of brown-red coating (RC) in beryls and Ag crack filling (HF, SF) in cordierite is also reported. Failed capsule featuring pale white solid filling are indicated with WM.

Table 3 – CO$_2$ contents (in ppm) obtained for the studied cordierites. Integration range 2300-2400 cm$^{-1}$, $\varepsilon_r=19000\pm2000$. Sample thickness estimated standard error (ESE) is reported in brackets. Sample thicknesses with ESE = ±5 µm were obtained using an electronic micrometer, sample thicknesses with ESE < ±5 µm were obtained using the optical profilometer. F = analytical spot on fracture, HF = Heavy filled cracks, SF = Slightly filled cracks, WM = White solid mass, 1 = grain with diffuse fracturing, 2 = calculation performed on unpolarized FTIR spectrum.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (µm)</th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Maximum measured CO$_2$ concentration (ppm)</th>
<th>CO$_2$ (ppm)</th>
<th>Note</th>
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</thead>
<tbody>
<tr>
<td>Crd_pr 5</td>
<td>153 (5)</td>
<td>200</td>
<td>900</td>
<td>24</td>
<td>316</td>
<td>49</td>
<td>HF</td>
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<tr>
<td>Crd_pr 8</td>
<td>152 (5)</td>
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<td>800</td>
<td>48</td>
<td>237</td>
<td>36</td>
<td>SF</td>
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<td>Crd_pr 12 (F)</td>
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<td>700</td>
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<td>388</td>
<td>59</td>
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<tr>
<td>Crd_pr 12</td>
<td>171 (5)</td>
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<td>700</td>
<td>24</td>
<td>146</td>
<td>22</td>
<td>SF</td>
</tr>
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<td>SF</td>
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<tr>
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<td>500</td>
<td>900</td>
<td>1</td>
<td>111</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Crd_pr 15 (F)</td>
<td>241 (5)</td>
<td>500</td>
<td>900</td>
<td>1</td>
<td>1455</td>
<td>221</td>
<td>F</td>
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<tr>
<td>Crd_pr 16</td>
<td>196 (5)</td>
<td>500</td>
<td>700</td>
<td>24</td>
<td>187</td>
<td>28</td>
<td>SF</td>
</tr>
<tr>
<td>Crd_pr 17</td>
<td>224 (1)</td>
<td>500</td>
<td>900</td>
<td>24</td>
<td>405</td>
<td>61</td>
<td>HF</td>
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<tr>
<td>Crd_pr 18 (F)</td>
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<td>476</td>
<td>72</td>
<td>SF, F</td>
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<tr>
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<td>800</td>
<td>24</td>
<td>268</td>
<td>40</td>
<td>SF</td>
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<tr>
<td>Crd_pr 19 (F)</td>
<td>324 (1)</td>
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<td>800</td>
<td>24</td>
<td>928</td>
<td>139</td>
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<td>800</td>
<td>24</td>
<td>307</td>
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<td>SF</td>
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<td>500</td>
<td>800</td>
<td>48</td>
<td>405</td>
<td>65</td>
<td>HF</td>
</tr>
<tr>
<td>Crd_pr 22 (F)</td>
<td>185 (5)</td>
<td>200</td>
<td>800</td>
<td>20</td>
<td>1346</td>
<td>205</td>
<td>1, WM</td>
</tr>
<tr>
<td>Crd_pr 25 (F)</td>
<td>237 (5)</td>
<td>200</td>
<td>800</td>
<td>20</td>
<td>1017</td>
<td>154</td>
<td>1</td>
</tr>
<tr>
<td>Crd_pr 23 (F)</td>
<td>140 (5)</td>
<td>200</td>
<td>800</td>
<td>24</td>
<td>936</td>
<td>145</td>
<td>HF, F</td>
</tr>
<tr>
<td>Crd_pr 23</td>
<td>140 (5)</td>
<td>500</td>
<td>800</td>
<td>24</td>
<td>425</td>
<td>66</td>
<td>HF</td>
</tr>
<tr>
<td>Crd_pr 24</td>
<td>90 (5)</td>
<td>500</td>
<td>800</td>
<td>24</td>
<td>418</td>
<td>67</td>
<td>HF</td>
</tr>
<tr>
<td>Crd_pr 29 (F)</td>
<td>175 (5)</td>
<td>700</td>
<td>800</td>
<td>10</td>
<td>2419</td>
<td>370</td>
<td>SF, F</td>
</tr>
<tr>
<td>Crd_pr 29</td>
<td>175 (5)</td>
<td>700</td>
<td>800</td>
<td>10</td>
<td>939</td>
<td>144</td>
<td>SF</td>
</tr>
<tr>
<td>Crd_pr 27</td>
<td>99 (5)</td>
<td>700</td>
<td>800</td>
<td>48</td>
<td>308</td>
<td>49</td>
<td>WM</td>
</tr>
<tr>
<td>Crd_pr 26</td>
<td>81 (5)</td>
<td>200</td>
<td>800</td>
<td>24</td>
<td>158</td>
<td>26</td>
<td>WM</td>
</tr>
<tr>
<td>Crd_pr 30</td>
<td>198 (5)</td>
<td>200</td>
<td>800</td>
<td>24</td>
<td>285</td>
<td>43</td>
<td>HF</td>
</tr>
<tr>
<td>Crd_pr 28</td>
<td>160 (5)</td>
<td>200</td>
<td>800</td>
<td>48</td>
<td>364</td>
<td>56</td>
<td>WM</td>
</tr>
<tr>
<td>Crd_pr 31 (bis)</td>
<td>75 (5)</td>
<td>500</td>
<td>800</td>
<td>&gt; 33</td>
<td>4449</td>
<td>731</td>
<td>F, WM</td>
</tr>
<tr>
<td>Crd_pr 32 (bis)</td>
<td>53 (5)</td>
<td>700</td>
<td>700</td>
<td>24</td>
<td>1022</td>
<td>181</td>
<td></td>
</tr>
<tr>
<td>Crd_pr 33</td>
<td>130 (5)</td>
<td>700</td>
<td>900</td>
<td>24</td>
<td>1622</td>
<td>252</td>
<td>HF</td>
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</tbody>
</table>
Table 4 – CO₂ content (in ppm) measured for the studied beryl samples. Integration range 2300-2406 cm⁻¹, εᵢ=70000±7000. Estimated standard error (ESE) on sample thickness is reported in brackets. Sample thicknesses with ESE = ±5 µm were obtained using an electronic micrometer, sample thicknesses with ESE < ±5 µm were obtained using the optical profilometer. F = analytical spot on fracture, RC = Reddish Coating, WM = White solid mass, 1 = eroded grain edge.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Thickness (µm)</th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Maximum measured CO₂ concentration (ppm)</th>
<th>CO₂ concentration CO₂(ppm)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pa_340 a</td>
<td>243.2 (0.6)</td>
<td>200</td>
<td>700</td>
<td>2</td>
<td>65</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Pa_340 b</td>
<td>194.5 (0.7)</td>
<td>200</td>
<td>700</td>
<td>24</td>
<td>82</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Pa_340 c (340)</td>
<td>92 (2)</td>
<td>200</td>
<td>900</td>
<td>24</td>
<td>69</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Pa_340 c (88)</td>
<td>101.2 (0.4)</td>
<td>200</td>
<td>900</td>
<td>24</td>
<td>72</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Pa_340 c (380)</td>
<td>380 (5)</td>
<td>200</td>
<td>900</td>
<td>24</td>
<td>80</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Pa_340 d (bis)</td>
<td>125 (5)</td>
<td>500</td>
<td>700</td>
<td>24</td>
<td>699</td>
<td>106</td>
<td>RC</td>
</tr>
<tr>
<td>Pa_340 e (bis)</td>
<td>101 (1)</td>
<td>500</td>
<td>900</td>
<td>24</td>
<td>829</td>
<td>122</td>
<td>RC</td>
</tr>
<tr>
<td>Pa_340 f</td>
<td>252 (5)</td>
<td>200</td>
<td>900</td>
<td>72</td>
<td>89</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Pa_340 g (bis)</td>
<td>77 (5)</td>
<td>500</td>
<td>900</td>
<td>24</td>
<td>1434</td>
<td>211</td>
<td>F</td>
</tr>
<tr>
<td>Pa_340 h</td>
<td>240 (5)</td>
<td>200</td>
<td>800</td>
<td>20</td>
<td>nd</td>
<td>nd</td>
<td>WM</td>
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<tr>
<td>Pa_340 k</td>
<td>248 (5)</td>
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<td>800</td>
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<td>78</td>
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<td>Pa_340 l (bis)</td>
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<td>500</td>
<td>800</td>
<td>24</td>
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<td>Pa_340 j</td>
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<td>800</td>
<td>24</td>
<td>679</td>
<td>101</td>
<td></td>
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<tr>
<td>Pa_340 o</td>
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<td>800</td>
<td>10</td>
<td>1071</td>
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<tr>
<td>Pa_340 m</td>
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<td>nd</td>
<td>WM</td>
</tr>
<tr>
<td>Pa_340 l</td>
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<td>200</td>
<td>800</td>
<td>24</td>
<td>nd</td>
<td>nd</td>
<td>WM</td>
</tr>
<tr>
<td>Pa_340 p</td>
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<td>800</td>
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<td>RC</td>
</tr>
<tr>
<td>Pa_340 n (bis)</td>
<td>180 (5)</td>
<td>200</td>
<td>800</td>
<td>48</td>
<td>nd</td>
<td>nd</td>
<td>WM</td>
</tr>
<tr>
<td>Pa_340 q</td>
<td>180 (5)</td>
<td>500</td>
<td>800</td>
<td>&gt; 33</td>
<td>nd</td>
<td>nd</td>
<td>WM</td>
</tr>
<tr>
<td>Pa_340 t</td>
<td>118 (5)</td>
<td>500</td>
<td>800</td>
<td>10</td>
<td>1320</td>
<td>201</td>
<td>F</td>
</tr>
<tr>
<td>Pa_340 t (bis)</td>
<td>152 (5)</td>
<td>500</td>
<td>800</td>
<td>10</td>
<td>515</td>
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<td>RC</td>
</tr>
<tr>
<td>Pa_340 s</td>
<td>106 (5)</td>
<td>700</td>
<td>900</td>
<td>24</td>
<td>2489</td>
<td>383</td>
<td>RC, F</td>
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<tr>
<td>Pa_340 s (bis)</td>
<td>101 (5)</td>
<td>700</td>
<td>900</td>
<td>24</td>
<td>1531</td>
<td>237</td>
<td>RC</td>
</tr>
<tr>
<td>Pa_340 r</td>
<td>107 (5)</td>
<td>700</td>
<td>700</td>
<td>24</td>
<td>1795</td>
<td>276</td>
<td></td>
</tr>
<tr>
<td>Pa_340 z</td>
<td>125 (5)</td>
<td>700</td>
<td>800</td>
<td>24</td>
<td>1211</td>
<td>184</td>
<td>RC</td>
</tr>
</tbody>
</table>

CO₂ concentration measured for the 24 hour experiment for both cordierite and beryl are plotted in Figure 12 as a function of temperature (a and c) and as a function of pressure (b and d).
Chapter 5: Kinetics of incorporation of CO$_2$ in cordierite and beryl: an FTIR-FPA spectroscopy study

Figure 12 – CO$_2$ concentration for the 24 hour runs for beryl (a and b) and cordierite (c and d), plotted as a function of temperature (left) and pressure (right).

Figure 13 – CO$_2$ concentration measured for the same P, T annealing condition, reported on the side, and for different run times. All samples are annealed in presence of silver carbonate. Log scale was used for clarity.
Inspection of Figure 12 shows that $T$ plays only a minor role on the CO$_2$ solubility for both cordierite and beryl. Major variations are observed with pressure. In particular, beryl shows a steep increase in CO$_2$ content from 200 MPa to 500 MPa and from 500 MPa to 700 MPa. The CO$_2$ contents in cordierite, on the other side, show only a smaller increase from 200 MPa to 500 MPa, than from 500 MPa to 700 MPa.

Figure 13, shows the effect of the annealing time on the CO$_2$ amount incorporated in cordierite and beryl. The logarithmic scale was chosen for clarity. Longer duration experiments had only a slight effect on the amount of CO$_2$. At least over the first 72 hours all samples treated with different run times present a concentration variable within the error bars.

4. Diffusion coefficients of CO$_2$ for cordierite and beryl

The early work on diffusive mass transport was undertaken at the end of the 19th century by the German physiologist Adolf Fick (Zhang and Cherniak, 2010), who related the diffusive mass flux ($J$) to the variation of the concentration of a component ($C$) in space ($x$) times the negative of a diffusion coefficient ($D$) (Fick’s first law $J = -D(\partial C/\partial x)$). However in diffusion studies, it is often necessary to determine how a concentration profile evolves with time given the initial concentration distribution. For this purpose it is necessary to describe how the concentration is related to both space and time ($t$), i.e. the $C(x,t)$ function, which is expressed by the Fick’s second law of diffusion: $\partial C/\partial t = D \partial^2 C/\partial x^2$.

Diffusion is a temperature-dependent phenomenon, where the increased kinetic energy associated with higher temperature improves atoms mobility. In the site-jumping model, the diffusivity ($D$) is proportional to the jump frequency (Zhang and Cherniak, 2010), and varies with $T^{-1}$ in log-linear fashion. The diffusivity of a given species in a particular medium is described by the Arrhenius equation:

$$D = D_0 \times \exp\left(-\frac{E_a}{RT}\right)$$

where $D$ is the diffusion coefficient, $D_0$ the pre-exponential factor, $E_a$ the activation energy, which is the amount of energy required for a particle to overcome the potential barrier
between its equilibrium position and an adjacent one. \( R \) is the ideal gas constant, and \( T \) is the absolute temperature in K. The parameters \( E_a \) and \( D_0 \) are derived from the Arrhenius plot relating \( \log(D) \) vs \( 1/T \), in which the diffusion coefficients plot on a straight line described by:

\[
\log(D) = \log(D_0) - \frac{E_a}{R} \cdot \ln(10) \cdot \frac{1}{T}
\]

The activation energy \( E_a \) is calculated from the slope of the line and \( D_0 \) is the intercept on the ordinate axis.

As shown above, both structural considerations and our FTIR imaging clearly shows that the diffusion proceeds from the (001) crystal face into the grain. In order to obtain the diffusion coefficient \( (D) \), the \( CO_2 \) concentration profiles (Fig. 14) were fitted by a simple mono dimensional diffusion equation (Crank, 1975, Zhang and Cherniak, 2010):

\[
C = C_0 \cdot \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)
\]

where \( C \) is the concentration at depth \( x \) (m) from the sample rim, \( C_0 \) is the maximum concentration, \( D \) is the diffusion coefficient (m\(^2\)/s), \( t \) is the time duration (s), and \( \text{erfc} \) is the complementary error function. \( C_0 \) and \( D \) parameters were fitted using the OriginPro 9™ software. FTIR-FPA images were collected before each FTIR diffusion profile in order to find the most suitable analytical areas. \( CO_2 \) contents in beryl were measured along traverses parallel to the \( c \)-axis usually from the middle of the (001) edge. Diffusion through the prismatic faces can be neglected because it is at least two order of magnitude slower (Fukuda et al., 2009). Diffusion profiles in cordierite grains were also performed along traverses parallel to the \( c \)-axis, on grains oriented using the spindle stage as explained above. \( C \) and \( C_0 \) where fitted on data profiles obtained by integrating the principal \( \nu_3 \) anti-symmetric stretching modes of \( CO_2 \) at 2348 cm\(^{-1}\) polarized for \( E//a \) for cordierite and at 2360 cm\(^{-1}\) polarized for \( E\perp c \) for beryl (Fig. 8). In order to reduce border effects and/or slab surface unevenness, \( C \) and \( C_0 \) were scaled to the 1880 cm\(^{-1}\) peak area, corresponding to a lattice overtone (Aines and Rossman, 1984), whose intensity and shape is dependent only of sample thickness and orientation. This expedient was possible because \( D \) is dependent on the \( C/C_0 \) ratio and not on their absolute values.
Figure 14 - (a, b) selected CO\textsubscript{2} diffusion profiles obtained for the antisymmetric stretching mode along the \textit{c} crystallographic axis direction. (c) Example of a diffusion profile obtained across two fractures about 115 µm and 190 µm from the crystal edge. In (a) and (b) the dashed lines are the fitted curves; open squares in (b) are data points excluded from fitting (see text). Below each profile the corresponding FPA CO\textsubscript{2} image is displayed where the analytical transect is indicated by a dashed red line.

Figure 14 (a and b) shows the most common situation where, due to slight underestimation of the CO\textsubscript{2} content close to the crystal rim, a deviation from the ideal inverse error-function (\textit{erfc}) trend of a component diffusing inside a matrix (Zhang and Cherniak, 2010) is typically observed. In such a case the concentration profiles were fitted excluding these points (Fig. 14b), as suggested by Fukuda \textit{et al}. (2009). The third example (Fig. 14c) shows the case of an analytical transect across a fracture. In such a case multiple maxima located in correspondence of the fracture(s) are observed. Obviously these profiles could not be used for the \textit{D} determination. Below each diffusion profile we reported the optical images and FPA CO\textsubscript{2} contour maps of the areas where the FTIR transects (dashed red line) were collected.

Table 5 – Diffusion coefficients for CO\textsubscript{2} along the structural channels of beryl and cordierite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>D (m\textsuperscript{2}/sec)</th>
<th>1000/T (K)</th>
<th>Log D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pa_340 j</td>
<td>500</td>
<td>800</td>
<td>24</td>
<td>6.2E-14</td>
<td>0.93</td>
<td>-13.21</td>
</tr>
<tr>
<td>Pa_340 d (bis)</td>
<td>500</td>
<td>700</td>
<td>24</td>
<td>2.4E-14 \div 1.7E-14</td>
<td>1.03</td>
<td>-13.62 \div -13.76</td>
</tr>
<tr>
<td>Pa_340 r</td>
<td>700</td>
<td>700</td>
<td>24</td>
<td>1.9E-14 \div 1.1E-14</td>
<td>1.03</td>
<td>-13.72 \div -13.97</td>
</tr>
</tbody>
</table>
Chapter 5: Kinetics of incorporation of CO$_2$ in cordierite and beryl: an FTIR-FPA spectroscopy study

| \textbf{Pa$_{340}$ o} & 700 & 800 & 10 & 8.9E-14 \div 4.9E-14 & 0.93 & -13.05 \div -13.31 |
| \textbf{Pa$_{340}$ k} & 200 & 800 & 20 & 7.2E-14 \div 6.1E-14 & 0.93 & -13.15 \div -13.21 |
| \textbf{Pa$_{340}$ t} & 500 & 800 & 10 & 9.5E-14 \div 7.0E-14 & 0.93 & -13.02 \div -13.15 |

Calculated $D$ coefficients are reported in Table 5; activation energy ($E_a$) and pre-exponential factor (-log$D_0$) were determined fitting the data on the basis of the Arrhenius equation. Mean activation energy ($E_a$) for beryl data is 122±15 kJ/mol with a pre-exponential (-log$D_0$) factor of 7.2±0.7. Figure 15 shows the calculated diffusion coefficients in the Arrhenius space, the solid line with errors (dashed lines) is the best fit of the Arrhenius equation for all the data points in Table 5.

![Figure 15 - Arrhenius plot for diffusion coefficients of CO$_2$ in beryl (black squares 700 MPa, gray triangles 500 MPa and open circles 200 MPa) from the data reported in Table 5. Solid line with errors (dashed lines) is the best fit of the Arrhenius equation for all the data points.](image-url)
5. Discussion

In this chapter we address an old problem, i.e. the diffusion of CO$_2$ across minerals of geological relevance, in the present case cordierite and beryl, using a modern methodology, such as FTIR micro-spectroscopy coupled with imaging (Della Ventura et al., 2014), to characterize the distribution and the amount of gas inside the sample. Because of the non-conventional procedure set up and used during this work, in this section we will discuss the problems and the advantages of this methodology by comparing the data obtained during our work with those obtained by previous authors.

5.1 The solubility of CO$_2$ in cordierite and beryl

Tables 3 and 4 summarize the CO$_2$ contents measured in the first 20 µm from the (001) edge of cordierite and beryl treated samples, inferred to represent the maximum content diffused into the phase. For cordierite, our experiments are in agreement with previous studies in showing that the CO$_2$ solubility within the mineral increases as a function of pressure, while temperature has only a minor effect. However while our data indicate a slightly increase in CO$_2$ for increasing T, previous authors (e.g. Johannes and Schreyer, 1981, Harley and Thompson, 2004) observed a slight but significant opposite trend. Figure 13 in addition shows that the CO$_2$ contents are not influenced by the duration of the experiment, opposite to what found by Le Breton and Schreyer (1993), at least in the range from 2 hours to 3 days. This last finding is in agreement with the work of Johannes and Schreyer (1981) who concluded that equilibration can be obtained even after just 1 hour. No literature data are available for the experimental solubility of CO$_2$ in beryl; however, due to the close structural similarities between the two minerals, we obtain trends similar to those observed for cordierite (Fig. 12).

A notable point is that, in comparison with the literature data, we observed a large difference in the absolute CO$_2$ content incorporated into cordierite, which is more than one order of magnitude lower. For instance, Johannes and Schreyer (1981) and Armbruster and Bloss (1982) reported, for cordierites treated at 500 MPa and 800°C, CO$_2$ contents in the 1–2 wt. % range, while under the same conditions we measured a CO$_2$ content of ~ 0.04 wt. %.
Armbruster and Bloss (1982) reported values as high as 3.13 wt% CO$_2$ in the White Well cordierite treated at 600°C, 600 MPa for 4 weeks. This point is extremely important, thus considering that we are comparing completely different experimental and analytical techniques, below we will discuss some factors that may explain such differences.

1) The cordierite used here as a starting material has significant amounts of alkaline cations (Tab. 1) in its structural channels; Vry et al. (1990) observed that in natural cordierite the total content of CO$_2$ + alkali cations may induce a volatile deficiency of both H$_2$O + CO$_2$ during equilibration with the surrounding fluid because of a “plug effect” affecting the diffusion rate of the relatively large CO$_2$ molecule from the fluid into the mineral. However, while Johannes and Schreyer (1981) used synthetic and thus alkali-free crystals as starting material for their experiments, Armbruster and Bloss (1982) used a natural cordierite from White Well containing 0.05 Na apfu, thus the alkali content alone cannot explain such a huge discrepancy.

2) One problem could be looked for in the sample handling and preparation for the analyses. Figure 9 shows that the thermal/baric treatment of the sample during the experiments induces development of a series of micro-fractures close to the edges of the cordierite crystals. These micro-fractures may induce the formation of a CO$_2$-rich (see above) but fragile external layer which could be removed during sample slicing and polishing for FTIR analyses. In order to test for this hypothesis, and check the effect of longer fluid-mineral interaction time, we performed some longer duration (10 days) experiments at 500 MPa, 800 °C, adding silver oxalate (Ag$_2$C$_2$O$_4$) to the charge and using a Tuttle-type H$_2$O cold seal pressure vessel (CSPV) at Institut für Mineralogie, Leibniz Universität Hannover (Germany). The choice of this alternative experimental set up was due to the fact that such long duration experiments could not be performed with the used Quickpress, where the experiment duration is limited to few (1-3) days. The results are displayed in Figure 16a where we show the FPA image of CO$_2$ distribution in cordierite. From this image it is possible to observe that the outer zone of the grain consists of 150/200 µm thick strongly fractured layer, presenting a fairly high CO$_2$ content, while the core of the grain is almost CO$_2$ free. Because of this thick layer it was not possible to orient the grain by optical means and consequently determine the actual CO$_2$ content by using polarized data. However, using unpolarized data we can estimate a rough content in this layer of at least 0.42±0.09 wt.%.

Figure 16b displays the FPA contour map of CO$_2$ in a synthetic beryl treated at the same $P,T,t$
conditions. Contrary to cordierite, synthetic emeralds did not develop significant thermally induced micro-fractures along the grain edges. Figure 16b shows that the 10 days treated beryl still presents a prismatic hexagonal habitus and no thick alteration layers were formed; CO$_2$ diffusion occurred, as usual, from the (001) pinacoidal face of the grain and along cracks (dashed line). This “edge effect” may thus strongly affect the CO$_2$ content measured for the experimentally-treated grains as well as the diffusion of CO$_2$ into cordierite.

![Figure 16 – FTIR – FPA image of the CO$_2$ distribution in cordierite Crd_pr 38 (left) and beryl Pa_340 v (right) treated with a CSPV for 10 days at 500 MPa and 800 °C. The beryl crystal is oriented parallel to c- crystallographic axis; white dashed line are cracks. The cordierite sample is randomly oriented, the white dashed line marks the boundary of the altered layer.](image)

5.2 The effect of fractures on the CO$_2$ content

The second most notable feature from Tables 3 and 4 is the difference between the data measured at the edges of the grain and those measured in correspondence of fractures (labeled with “F” in the notes). CO$_2$ contents observed in correspondence of fractures may be several times higher than the value calculated at the edge of the grain, this effect is more pronounced in cordierite samples than in beryl samples, where the CO$_2$ content measured on fractures are rarely higher than the CO$_2$ content measured on the edges. An example is reported in Figure 17. Sample Crd_pr 25 and Crd_pr 30 were treated at the same conditions (200 MPa and 800 °C for 24 hours), however sample Crd_pr 25 was re-run after a thermal shock due to a technical problem occurred during the heating ramp; after the experiment, optical examination of the grains revealed the presence of diffuse fracturing across the
crystals. FTIR analyses showed that the amount of CO\textsubscript{2} in sample Crd_pr 30 was lower than in sample Crd_pr 25, indicating that the fracturing favored CO\textsubscript{2} solubility all across the grain, in line with the general observation that grain-boundary diffusion and diffusion along interfaces, like cracks, can be several order of magnitude faster than lattice diffusion (Zhang and Cherniak, 2010). One final point to note is that, although no water was present in the experimental tubes, the spectra of Figure 17 show the presence of minor water (3000 ppm) in the run products. This water originated from the moisture present in the chemicals used for the sample preparation.

Figure 17 - Polarized FTIR spectra of Crd_pr 25 (above) and Crd_pr 30 (below) both treated at 200 MPa and 800 °C for 24 hours. The anti-symmetric stretching peaks of CO\textsubscript{2} are highlighted. Spectra scaled to sample thickness. Sample Crd_pr 25 presents diffuse fracturing and a much higher CO\textsubscript{2} content, for explanation see text.
5.3 The CO$_2$ diffusion in microporous structures

Figure 18 – Diffusion coefficients $D$ for different silicates or silicate melts for H$_2$O and CO$_2$ from the literature plotted onto the Arrhenius diagram. For numerical values and references see Table 6.

Because of the well-developed hexagonal prismatic habitus, the beryl samples were excellent candidates to evaluate the diffusivity of CO$_2$ in these channel-like structures. In Table 5 we list the diffusion coefficients determined from different beryl samples treated at different $T$, $P$ conditions, as well as the activation energy ($E_a$) necessary to induce the diffusion process. From Table 5 we may notice that pressure variation from 200 to 700 MPa has little effect on the diffusion coefficients. It is also interesting to note that while the overall CO$_2$ content inside the beryl samples is greater at higher pressure (Figure 12), the diffusing rate remains constant. On the opposite, the diffusion coefficient for cordierite was more difficult to evaluate because of the very irregular shape of the crystals.

From a general point of view, diffusion coefficients of molecular species in silicates are expected to be tightly related to the dimension of the diffusing molecule and the hosting structure. It is also widely accepted that for more compact silicate structures and/or larger molecules diffusing rates are smaller and activation energies larger. As we may observe from
Figure 18 the diffusing rates calculated for CO$_2$ (this work) and H$_2$O (Fukuda et al., 2009) in beryl are very close, even though CO$_2$ molecule are larger than the H$_2$O molecule (the overall dimension of H$_2$O is 2.8 x 3.2 x 3.7 Å and for CO$_2$ is 2.8 x 2.8 x 5.0 Å: Wood and Nassau, 1968). On the other hand, the CO$_2$ diffusion coefficients for beryl (this work) are greater than the diffusion coefficient calculated for the outward CO$_2$ diffusion from the cordierite channels (chapter 4). In addition, Vry et al. (1990) observed that, in cordierite, the inward diffusion is quicker than outward diffusion. These authors concluded that the difference between inward and outward diffusion rates may be caused by alkali cations and CO$_2$ itself, that, acting as plugs in the channel, preferentially slows down the outward volatile diffusions.

It is difficult to draw a direct comparison between our data and the diffusion coefficients available in the literature for minerals; the reason is that, beryl and cordierite behave as microporous structures trapping H and C as H$_2$O and CO$_2$ molecules, while the vast majority of the existing data have been collected on minerals where H is present as an OH$^-$ group. Moreover no data are available for CO$_2$ diffusion in minerals (excluding C diffusion in carbonates, e. g. Anderson, 1972; Labotka et al., 2000). Thus in the next paragraph we are forced to compare our data with those derived for basically different processes.

Figure 18 and Table 6 give selected examples of diffusion rates for the most common hydrous minerals. In Figure 18 we may observe that the diffusion coefficients measured for CO$_2$ in beryl are close to the OH$^-$ diffusion coefficients obtained in other ring silicates like tourmaline (Desbois and Ingrin, 2007), layer silicates like muscovite (Graham, 1981), amphiboles like kaersutite (Ingrin and Blanchard 2000), or in disilicates like epidote (Graham, 1981). However, it’s important to note that structural OH$^-$ probably diffuses inside these structures in the form of H$^+$ (Zhang et al., 2010) thus the diffusing species is much smaller compared to molecular CO$_2$ and H$_2$O.

Our data suggest that the structural channels of cordierite and beryl act more likely fast paths for the mobility of large molecular groups compared to similar silicate structures, and for this reason the diffusing behavior is more similar to the one typically observed for grain boundary diffusion, such as, for example, H$_2$O in quartzite (Farver and Yund, 1991) or to the behavior of CO$_2$ in non-crystalline materials, like silicate melts (Watson et al., 1982; Watson, 1991).
Table 6 – Experimental data for $H_2O$ and $CO_2$ diffusion in various silicate minerals and melts found in the literature

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Diffusing molecule</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$logD_0$ (m$^2$/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhyolite</td>
<td>$CO_2$</td>
<td>800 - 1100</td>
<td>1000</td>
<td>75</td>
<td>-7.2</td>
<td>Watson, 1991</td>
</tr>
<tr>
<td>Basalt</td>
<td>$CO_2$</td>
<td>1350 - 1500</td>
<td>1500</td>
<td>195</td>
<td>-3.4</td>
<td>Watson et al., 1982</td>
</tr>
<tr>
<td>Muscovite</td>
<td>$D/H_2O$, $D_2O$</td>
<td>450-750</td>
<td>200 or 400</td>
<td>121</td>
<td>-8.0</td>
<td>Graham, 1981</td>
</tr>
<tr>
<td>Epidote</td>
<td>$D/H_2O$, $D_2O$</td>
<td>250-650</td>
<td>200 or 400</td>
<td>90</td>
<td>-7.4</td>
<td>Graham, 1981 in Ingrin and Blanchard, 2006</td>
</tr>
<tr>
<td>Kearsutite</td>
<td>$D/D_2$</td>
<td>600-900</td>
<td>0.1</td>
<td>104±12</td>
<td>-8.7</td>
<td>Ingrin and Blanchard, 2000</td>
</tr>
<tr>
<td>Tourmaline (par c)</td>
<td>$D/Ar$, $D_2$</td>
<td>700-800</td>
<td>0.1</td>
<td>106.3±36, 8</td>
<td>-9.8</td>
<td>Desbois and Ingrin, 2007</td>
</tr>
<tr>
<td>Quarzite</td>
<td>$H_2O$</td>
<td>450 - 800</td>
<td>100</td>
<td>113</td>
<td>-7.6</td>
<td>Farver and Yund, 1991</td>
</tr>
<tr>
<td>Beryl</td>
<td>$H_2O$</td>
<td>500 - 700</td>
<td>50-150</td>
<td>133</td>
<td>-6.6</td>
<td>Fukuda et al., 2009</td>
</tr>
<tr>
<td>Cordierite</td>
<td>$CO_2$</td>
<td>825 -1000</td>
<td>0.1</td>
<td>198</td>
<td>-4.7</td>
<td>Chapter 4</td>
</tr>
</tbody>
</table>

6. Conclusions

In this study we combined micro-FTIR spectroscopy and FPA imaging to study the carbon dioxide diffusion in cordierite and beryl. The starting crystals were treated at different pressure and temperature in a $CO_2$ rich atmosphere using a non end-load piston–cylinder designed for short term experiments and able of very fast heating ramps and cooling rates. Because of the relative short duration of the experiments and the slow diffusion rates of $CO_2$ in the structural channels we did not expect a complete homogenization of the sample, thus in this work we made extensive use of FTIR-FPA imaging as primary tool to characterize the distribution of $CO_2$ in the run product and locate correctly the most suitable points for FTIR analysis. The results showed that $CO_2$ diffusion in both minerals occurs exclusively along the structural channels parallel to the $c$ crystallographic axis; FTIR micro-spectroscopy showed that the final $CO_2$ content is strongly influenced by pressure, while temperature has a minor effect. Surprisingly, however, the $CO_2$ contents introduced into cordierite were even two order of magnitude lower than expected. Cracks and fractures, produced during the thermal treatment, were found to enhance significantly the $CO_2$ diffusion across cordierite, while beryl was less affected by this kind of phenomenon. The calculated activation energies and diffusion coefficients for $CO_2$ along beryl structural channels were found to be close to values typical of grain boundary diffusion and melts, or $H^+$ in the most common hydrated minerals.
CHAPTER 6

THE DIFFUSION OF CO₂ AND H₂O IN A SYNTHETIC SECTOR-ZONED BERYL: A MULTI-ANALYTICAL STUDY

Abstract

In this work we investigate the strong inhomogeneous distribution of CO₂ and H₂O across a synthetic beryl characterized by a peculiar hourglass structure due to the Cr distribution during the crystal growth. The sample was treated at 800°C, 500 MPa, in a CO₂-rich atmosphere. A combination of analytical techniques and, in particular, polarized-light FPA imaging, revealed an additional pathway of carbon dioxide diffusion along the zoning discontinuity. Using high-resolution synchrotron-light mapping it was possible to distinguish between the enhancement of the CO₂ diffusion along the hourglass trace and a fracture in the grain. High-resolution FESEM images revealed that no physical discontinuities are present in the matrix, at least at the scale of tenth of nanometers. Therefore, the hourglass zone boundary may be considered as a planar defect possibly due to the mismatch induced by the different growth rates of each sector. The H₂O diffusion follows an extremely different pattern: combining TOF-SIMS and FTIR-FPA a significant depletion of H₂O[II] along the hourglass boundary where a significant amount of Na was replaced by K.
1. Introduction

Diffusion of hydrogen-oxygen species in minerals as a function of $T$ and $P$ has been addressed by numerous experimental studies (e.g. Ingrin and Blanchard, 2006; Watson and Baxter, 2007; Farver, 2010 and references therein) due to the extremely important consequences that this processes may have in Earth Science systems. Accordingly, diffusion may occur in three different ways: (i) intra-crystalline (volume), (ii) grain boundary (Fukuda et al., 2009) and (iii) planar defects diffusion (Zhang et al., 2006). Intra-crystalline diffusion is the slower mechanism, whereas grain boundary and planar defects act as fast-pathways for the travelling of ions or molecular species across the mineral (e.g. Zhang et al., 2006).

Several rock forming minerals are structurally characterized by atomic arrangements which leave free space to the molecular diffusivity in the form of connected cavities or channels: notable examples are the zeolite-type feldspathoids, and ring silicates such as beryl and cordierite. Diffusion along these connected structural cavities is typically faster than the volume diffusion. In other words there is evidence that diffusivity along structural channels can be assimilated to fast mobility diffusion. In this work we address some particular aspects of the diffusivity of CO$_2$ in beryl, after the more general experimental work described in chapter 5 of this Thesis. The chapter deals in particular with a peculiar diffusion pattern observed for an hourglass-zoned crystal.

Figure 1 – a) Schematic view of beryl crystal structures parallel to the crystallographic $c$ axis. Blue = Si tetrahedra; orange = Al sites and gray = Be sites. b) Schematic section of beryl channel parallel to [0001], modified after Fukuda and Shinoda (2011). c) Sketch of the hourglass zoning inside a beryl (modified after Hollister, 1970)
Beryl is a relatively rare rock-forming mineral, and is found as an accessory constituent in pegmatites, in cavities of granitic rocks and occasionally in metamorphic rocks (Deer et al., 1986). A rare occurrence in a volcanic syenitic ejectum has also been reported (Della Ventura et al., 2000). It is structurally a ring silicate with ideal formula Be$_3$Al$_2$Si$_6$O$_{18}$, consisting of six-member hexagonal rings of tetrahedra. The vertical stacking of these rings forms a succession of interconnected cages arranged along the c axis (Fig. 1a). The cages have a maximum diameter of about 5.0 Å and a minimum diameter of 2.8 Å (Gibbs et al., 1968); channel height is about 4.7 Å (Fukuda and Shinoda, 2011).

Figure 1b shows a schematic section of the structural channel parallel to [001], where different atoms and/or molecular groups may be hosted. H$_2$O and CO$_2$ are the main constituents in beryl channels (Wood and Nassau, 1968, Aines and Rossman, 1984) and are located in the wider sites of the channels (2a position in Fig. 1b). Larger ions like Cs$^+$ and K$^+$ (Hawthorne and Černý, 1977) and possibly OH groups (Wickersheim and Buchanan, 1959, Aurisicchio et al., 1994) may also be located in the 2a position, while smaller cations like Na$^+$ (Wood and Nassau, 1968) occur at the narrower 2b site (Fig. 1b).

Polarized FTIR data show that the linear CO$_2$ molecules are oriented orthogonally to the c axis (Wood and Nassau, 1968; Aines and Rossman, 1984). Extra-framework H$_2$O occur in the structural channels with the molecular plane parallel to (100) and may present two different orientations (Fig. 1b): in type I H$_2$O (hereafter H$_2$O$^{[I]}$) the H–H vector is oriented parallel to the c axis and in type II H$_2$O (H$_2$O$^{[II]}$) the H–H vector is rotated by 90° orthogonally to the c axis (Wood and Nassau, 1968, Bellatreccia et al., 2008). H$_2$O molecules of this latter type are locally bonded to alkali cations sited in the 2b position (Goldmann et al., 1977; Hawthorne and Černý, 1977).

H$_2$O and CO$_2$ diffusion in beryl has been recently studied by Fukuda et al. (2009) and in this thesis (chapter 5); the available data show without doubt that mobility of molecules across the mineral occurs exclusively along the structural channels.

In this work we describe the crystal-chemistry of one beryl grain recovered from one of the CO$_2$ diffusion experiments described in chapter 5 of this Thesis. Preliminary FTIR-FPA data showed a peculiar inhomogeneity of CO$_2$ and H$_2$O in this sample, thus the crystal has been characterized in detail using a multidisciplinary approach. The volatile distribution, in particular, has been studied by high-resolution synchrotron-radiation (SR) FTIR-FPA imaging under polarized light. The data clearly demonstrate that careful determination of the
inhomogeneous distribution of volatile species is mandatory when studying the distribution mechanisms and coefficients across mineral matrixes.

2. Materials and Methods

The single-crystal used as starting product for the diffusion experiments (sample label 103_391_c) described here, is a synthetic beryl from the very first attempt to produce Li₂O and MoO₃ flux-grown emeralds; the crystals were obtained after 15 days of annealing at 800°C, whereas higher temperatures lead to formation of phenakite (Hautefeuille and Perrey, 1888, 1890). Batches of these syntheses are currently kept in the mineralogical collection of Muséum National d'Histoire Naturelle in Paris (MNHN), and some grains were kindly donated to us to be used for scientific research. The batch consists of fairly large (~1.0 mm X 0.5 mm) emerald-green prismatic crystals, showing a particular sector (hourglass) zoning of Cr (Fig. 1c, see also Liedl et al., 2014); this type of feature had already been mentioned by Bellatreccia et al. (2008) for grains from a different batch kept at the Museum of Mineralogy of University La Sapienza (Rome).

Some crystals were used for the experiments described below; one of these samples, recovered after the run, has been fully characterized by a combination of methods, and the results will be discussed in this text. One additional, untreated crystal from the same batch, was oriented using its prismatic morphology, embedded and doubly polished for EMPA-WDS chemical imaging and single spot analysis using a JEOL JXA 8200 WD-ED electron microprobe at INGV (Rome). Working conditions were 15 kV accelerating voltage, 7 nA sample current, 5 µm beam diameter, counting times: 10 seconds on the peak and 5 seconds on the background on both sides of the peak. The standards, spectral lines and crystals used were: albite (NaKα, TAP), wollastonite (SiKα, PET), k-feldspar (KKα, PET), kyanite (AlKα, TAP). Data correction was performed using the ZAF method. BeO content was calculated by stoichiometry.

Selected results are reported in Figure 2 and will be useful to compare the observed chemical inhomogeneity before and after the thermal treatment. The BSE image (Fig. 2, top) clearly shows the sector zoning mentioned above. The XRF maps reveal that the zoning visible in the BSE image is related to the distribution of Cr; this element is in fact significantly enriched in the outer sector. A slight inhomogeneity is also observed for Si that is enriched in
the inner sector, while both Al and K are slightly enriched in the outer sector. The eventual zoning of Na is unclear from these images, due to its low concentration. Selected microchemical data are given in Table 1, for the high Cr and Low Cr sectors, respectively. In line with the data presented by Bellatreccia et al. (2008), the Cr content is close to 2.0 wt% in the high-Cr zones, while being < 1.0 wt% in the low-Cr zones. The Na content is too low to allow conclusions on its distribution based on EMP, while the K content, although very low, is clearly slightly higher in the Cr-rich areas, as indicated by the XRF images of Figure 2.

Differently from the crystal studied by Bellatreccia et al. (2008), which showed traces (~ 30 ppm) of H₂O, several single-spot spectra collected at random on the sample studied here showed the crystal to be completely anhydrous and, obviously, CO₂-free. This point is particularly important for the discussion below.

The experiments were done using 3 x 9 mm Au capsules; silver oxalate was used as a CO₂ source to saturate the system with carbon dioxide during HT/HP treatment. Ag₂C₂O₄
decomposes into $2\text{Ag} + 2\text{CO}_2$ at 140 °C, yielding a theoretical $\text{CO}_2$ content ≈29 wt.%. $\text{Al}_2\text{O}_3$ powder ($\text{Al}_2\text{O}_3 = 99.72$ wt.%, $\text{SiO}_2 = 0.07$ wt.%, others = 0.21 wt.%) was mixed in 1 to 1 ratio by wt with $\text{Ag}_2\text{C}_2\text{O}_4$, and added to the charge. The aluminum oxide powder was used to prevent the contact between the crystals and the capsule walls after the silver oxalate disappearance due to its decomposition, and helped to dissipate the differential stress that may arise during the experiment. All components used to prepare the tubes were dried up in oven at 110 °C in order to avoid moisture contamination, however, despite this precaution, FTIR data (see below) revealed significant $\text{H}_2\text{O}$ in the sample after the run.

Table 1 - Microchemical analysis for the beryl in Figure 2, data points were collected in the high Cr sector (HighCr) and low Cr sector (lowCr and lowCr2). Crystal-chemical formulae were recalculated based on 18 oxygen atoms p.f.u. The tetrahedral site-population was constrained to be 9 apfu, Be was calculated by stoichiometry

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<th>HighCr</th>
<th>lowCr</th>
<th>lowCr2</th>
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<td>$\text{SiO}_2$</td>
<td>62.44</td>
<td>63.87</td>
<td>65.09</td>
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<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>20.15</td>
<td>19.59</td>
<td>19.34</td>
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<tr>
<td>$\text{Cr}_2\text{O}_3$</td>
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<td>0.91</td>
<td>0.70</td>
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<tr>
<td>$\text{BeO}$</td>
<td>13.55</td>
<td>13.62</td>
<td>13.76</td>
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<tr>
<td>$\text{Na}_2\text{O}$</td>
<td>0.01</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>$\text{K}_2\text{O}$</td>
<td>0.09</td>
<td>0.06</td>
<td>0.04</td>
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<tr>
<td>Total</td>
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<td>98.06</td>
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<th>5.756</th>
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<td>$\text{Al}^{IV}$</td>
<td>0.240</td>
<td>0.140</td>
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<td>Be</td>
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<td>3.001</td>
<td>3.001</td>
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<td>$\Sigma$ Tetrahedra</td>
<td>8.997</td>
<td>9.001</td>
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<table>
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<th>1.950</th>
<th>2.118</th>
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<td>$\text{Al}^{VI}$</td>
<td>0.131</td>
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<td>$\Sigma$ Octahedra</td>
<td>2.081</td>
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<table>
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<tr>
<th></th>
<th>0.001</th>
<th>0.004</th>
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<tbody>
<tr>
<td>Na</td>
<td>0.010</td>
<td>0.007</td>
<td>0.004</td>
</tr>
<tr>
<td>$\Sigma$ Channels</td>
<td>0.012</td>
<td>0.010</td>
<td>0.005</td>
</tr>
</tbody>
</table>

The experiments were performed using an externally heated vessel at Institut für Mineralogie, Leibniz Universität Hannover (Germany). The temperature uncertainty at the sample position is estimated to be ±10 °C and pressure was automatically controlled to be within 5 MPa (Behrens, 2010); oxygen fugacity within the vessel was close to NNO. The sample was treated at 800 °C and 500 MPa for 4 days. The X-ray diffraction pattern of the
powder added within the tube revealed the presence of residual alumina (corundum) and metallic silver, together with traces of silver oxide. The beryl sample was separated from the residual powder, oriented using its perfect prismatic morphology, embedded in epoxy resin and doubly polished to 63 µm; sample thickness was determined using an electronic micrometer with ±5 µm uncertainty.

Preliminary FTIR spectra were acquired using a Bruker™ Hyperion 3000 microscope equipped with a KBr broadband beamsplitter and a liquid nitrogen-cooled MCT detector at Laboratori Nazionali di Frascati-Istituto Nazionale di Fisica Nucleare (LNF-INFN,) Frascati (Rome). High-resolution spectra were acquired at beamline B22, Diamond Light Source Laboratory (Oxford, UK) using a similar set up except a synchrotron FTIR source instead a Globar source. The polarized spectra were collected using a gold-wire-grid polarizer on a ZnSe substrate. A 15 x objective in conventional light and 36 x objective in synchrotron light were employed; the nominal resolution was 4 cm$^{-1}$ and 128 scans were averaged for both spectrum and background. FTIR images were collected with a 64 x 64 pixel focal-plane array (FPA) of liquid nitrogen-cooled MCT detectors. The nominal resolution was set at 4 cm$^{-1}$ and 64 scans were averaged for each spectrum and background; each image covers an area of 170 µm x 170 µm with a nominal spatial resolution of ~ 5 µm (Della Ventura et al., 2010, 2014).

Time of Flight – Secondary Ion Mass Spectroscopy (TOF – SIMS) data were collected on a ION – TOF TOF.SIMS 5™ mass-spectrometer at Dipartimento di Matematica e Fisica, University of Roma Tre, using a ToF-SIMS V instrument equipped with a 30 keV Bi liquid metal ion gun (BiLMIG). Sample surface sputtering procedure was performed before the measurements.

3. Results

3.1 TOF-SIMS mapping

Figure 3 shows the distribution of selected chemical components across the beryl extracted from the vessel after the T/P treatment, obtained by TOF-SIMS imaging. Inspection of Figure 3a shows that the crystal has a well evident hourglass growth structure, which is visible in optical microscopy under both parallel and crossed polars. Figure 3b indicates that,
as already discussed above, the hourglass zoning is essentially due to the Cr$^{3+}$ distribution across the crystal; in particular comparing Figure 3a and Figure 3b it is possible to observe that the Cr$^{3+}$ zoning is also the main responsible for the difference in birefringence in the different sides of the grain: higher birefringence (darker-yellow colors in Fig. 3a) is associated with higher Cr content, while a lower Cr content is associated with a lower birefringence (pale yellow/white in Fig. 3a). Such a distribution has been recently characterized in 3D by Liedl et al. (2014) on a crystal from the same batch and later used for microchemical analyses (see below) using µ-CT X-ray tomography.

Figure 3c and 3d show a peculiar distribution of K$^+$ and Na$^+$ which indicates that, despite these elements are present as accessory constituents inside the structural channels, their content also is inhomogeneously distributed and follows the hourglass pattern; in agreement with XRF images (Fig. 2), TOF-SIMS data show that the K content is slightly higher in the outer sector while Na seems to be inversely correlated to K (compare Fig. 3c with Fig. 3d).

3.2 Polarized-light FTIR spectra, band assignment, and volatile contents

Figure 4 shows selected single-crystal polarized-light FTIR spectra collected for the treated sample close to the (001) edge of the grain, were the maximum CO$_2$ (and H$_2$O) content is expected (this thesis, chapter 5). The single-crystal polarized infrared spectrum of beryl has been studied by several authors, after the early work of Wood and Nassau (1967, 1968) and Aines and Rossman (1984) who clearly showed that the beryl channels may in fact host H$_2$O in two different orientations, and CO$_2$ molecules. A detailed analysis of the beryl spectrum is behind the scope of the present work and will be given in chapter 7, thus we will describe briefly only those absorptions that will be used for the measurements discussed.
below. In the 4000-3200 cm\(^{-1}\) range, when the electric vector \(E\) is parallel to the \(c\) crystallographic axis (\(E//c\)), two very sharp and intense peaks occur at 3699 cm\(^{-1}\) and 3602 cm\(^{-1}\). Based on the literature data (Wood and Nassau, 1967, Charoy et al., 1996, Kolesov and Geiger, 2000b, Gatta et al., 2006, Della Ventura et al., 2007, Adamo et al., 2008, Bellatreccia et al., 2008) the former peak is assigned to the \(\nu_3\) mode of type I \(\text{H}_2\text{O}\), while the latter peak is assigned to the \(\nu_1\) mode of type II \(\text{H}_2\text{O}\). In the same range, the \(E\perp c\) spectrum consists of a very broad multi-component absorption with maxima at 3724, 3675 and 3605, with a shoulder around 3591 cm\(^{-1}\); pertinent to the following discussion is the 3675 cm\(^{-1}\) band that is assigned to the \(\nu_3\) mode of type II \(\text{H}_2\text{O}\).

In the 2600-2000 cm\(^{-1}\) range, the very sharp and asymmetric peak centered at 2360 cm\(^{-1}\) for \(E//c\) is assigned to the \(\nu_3\) mode of \(\text{CO}_2\) (Wood and Nassau 1967, Charoy et al., 1996); in the same range the \(E\perp c\) spectrum is featureless, in agreement with the fact that the \(\text{CO}_2\) molecule is aligned \(\perp\) to the \(c\) crystallographic axis (see Fig. 1).

![Figure 4 - Single-crystal polarized-light infrared spectra of the experimentally treated beryl (solid lines). Data collected on a 63 µm thick, (hk0) oriented slab. The single-crystal unpolarized-light FTIR spectrum (dashed line) of an untreated beryl sample from the same batch is reported for comparison. Spectra scaled to thickness.](image)

Both the \(\text{H}_2\text{O}\) and \(\text{CO}_2\) contents were quantified from the polarized data collected close to the sample edge, where the content of these molecules is maximum (see below).
Chapter 6: The diffusion of CO$_2$ and H$_2$O in a synthetic sector-zoned beryl: a multi-analytical study

The Lambert-Beer equation: $C = \left(\frac{A_{\text{tot}} \cdot k}{\varepsilon \cdot D \cdot t}\right)$, was used, where $C$ is the concentration in wt%, $A_{\text{tot}}$ is the total integral absorbance in cm$^{-1}$ ($A_{\text{tot}} = A_i/c + 2 \cdot A_{i\perp}c$: Libowitzky and Rossman, 1996), $D$ is the sample density in g·cm$^{-3}$ and $t$ is the sample thickness in cm. $k_{\text{H}_2\text{O}} = 1.8$ (Beran et al., 1993) and $k_{\text{CO}_2} = 4.401$ (Della Ventura et al., 2009, 2012) were used to convert H$_2$O and CO$_2$, respectively, from mol·l$^{-1}$ to wt.%. The critical point in the Lambert-Beer equation is the integral molar absorption coefficient, $\varepsilon$, which is matrix-dependent and needs to be calibrated for the mineral under investigation; alternatively it can be derived from empirical curves such as the one proposed by Libowitzky and Rossman (1997). For beryl, $\varepsilon_{\text{H}_2\text{O}}$ values are available in the literature, however their use is complicated by the fact that H$_2$O occurs in two different molecular configurations, which absorb the IR beam at different wavenumbers. In addition, previous authors have used either integrated or linear absorbance data, thus it is difficult to compare results from different methods. We give in Table 2 the contents derived using both the $\varepsilon_{\text{H}_2\text{O}}$ coefficients calculated from the curve of Libowitzky and Rossman (1997) for H$_2$O$^\text{I}$ and H$_2$O$^\text{II}$, independently, and the $\varepsilon_{\text{H}_2\text{O}}$ values given by Charoy et al. (1996) and Goldman et al. (1977), as proposed by Fukuda et al. (2009). Table 2 gives also the CO$_2$ content calculated using the $\varepsilon$ value recalculated after Charoy et al. (1996). The error $\sigma_C$ associated with C was obtained according to Bellatreccia et al. (2005). For sake of comparison we also list in Table 2 the CO$_2$ content obtained using the $\varepsilon_i$ calibrated by Della Ventura et al. (2012) for the closely (structurally) related cordierite.

As a general comment, it is evident from Table 2 that the choice of the absorption coefficient is crucial when quantifying the amount of H$_2$O and CO$_2$ in beryl: using the curve of

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Mode, position and polarization</th>
<th>$\varepsilon_i$ (l·mol$^{-1}$·cm$^{-2}$)</th>
<th>$C$ (wt.%)</th>
</tr>
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<tbody>
<tr>
<td>Type I H$_2$O</td>
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<td>0.79±0.11</td>
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<th>$C$ (wt.%)</th>
</tr>
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<tbody>
<tr>
<td>Type I H$_2$O</td>
<td>$\nu_3$ at 3699 cm$^{-1}$, $E//c$</td>
<td>197</td>
<td>0.94±0.13</td>
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<tr>
<td>Type II H$_2$O</td>
<td>$\nu_4$ at 3602 cm$^{-1}$, $E//c$</td>
<td>256</td>
<td>0.44±0.06</td>
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<tr>
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<td>1.38±0.19</td>
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<table>
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<th>Mode, position and polarization</th>
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<td>CO$_2$</td>
<td>$\nu_3$ at 2360 cm$^{-1}$, $E\perp c$</td>
<td>70000±7000</td>
<td>0.21±0.04</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$\nu_4$ at 2360 cm$^{-1}$, $E\perp c$</td>
<td>19000±2000</td>
<td>0.79±0.13</td>
</tr>
</tbody>
</table>
Libowitzky and Rossman (1997) the final total H₂O content is in fact halved with respect the result obtained when using the coefficients calibrated by other authors. In addition, the relative amount of type I / type II water is also reversed. Therefore, until the ε coefficients are calibrated for beryl, the values reported in Table 2 must be considered just indicative of the real H₂O and CO₂ contents. For CO₂, in particular, Della Ventura et al. (2012) provided recently a reliable molar absorption coefficient based on a combination of SIMS + FTIR data on a well-characterized set of samples. However, at present, it is unknown whether the ε_{CO₂} coefficient calibrated for cordierite can be exported to beryl.

A second point to note is that, although the nominally dry experimental conditions, the maximum amount of water incorporated into the sample is however significantly higher than that of CO₂. As explained above, the absolute H₂O/CO₂ amounts can be affected by the use of wrong the ε_{H₂O} coefficients, however, it is indisputable that the FTIR spectra of Figure 4 show significant H₂O in the examined sample. Such relatively H₂O content is probably the result of the different pressure medium used in this experiment compared to those described in Chapter 5 and 7. Indeed, the beryl described in this chapter was treated in an externally heated vessel using H₂O as a pressure medium, while the experiments described in Chapter 5 and 7 were performed in a piston-cylinder apparatus, where pressure is transmitted by NaCl.

### 3.2 Polarized-light FPA imaging

The distribution of H₂O[II], H₂O[III] and CO₂ across the treated beryl was studied by using polarized SR-FTIR FPA imaging; in this work, polarized light was necessary to differentiate the absorptions related to H₂O[II] and H₂O[III] (e.g. Della Ventura et al., 2010). Contour maps were obtained by integrating the ν₃ antisymmetric stretching mode of H₂O[II] at 3699 cm⁻¹ (Fig. 5b) for E//c, the ν₁ symmetric stretching mode of H₂O[III] at 3602 cm⁻¹ (Fig. 5c) for E//c, and the ν₃ antisymmetric stretching mode of CO₂ at 2360 cm⁻¹ (Fig. 5d) for E⊥c.

Figure 5b shows that H₂O[II] is distributed rather homogeneously across the sample, except close to the core of the grain, where the H₂O[II] content is almost 70%. H₂O[III] is also distributed rather homogeneously (Fig. 5c), however along the hourglass boundary its content decreases also about 70%. CO₂ on the opposite is distributed exclusively close to the (001) basal edges of the crystal, as expected, and, surprisingly, along the hourglass boundaries.
Figure 5 – Polarized light FPA images of the treated beryl sample. (a) optical image, (b) E//c FTIR-FPA contour map of H$_2$O$^{[I]}$ and (c) H$_2$O$^{[II]}$ distribution, and (d) E⊥c FTIR-FPA contour map of CO$_2$ distribution. Chromatic scale is proportional to H$_2$O/CO$_2$ content. Data collected under conventional FTIR light.

Figure 6b shows the diffusion profile for H$_2$O$^{[I]}$ (open circles), H$_2$O$^{[II]}$ (open triangles) and CO$_2$ (solid squares) along the AA’ trace of Figure 6a. Single-spot SR-FTIR analyses were collected with a beam size of 20x20 µm and absorbance data were obtained by integrating the mode at 3699 cm$^{-1}$ for H$_2$O$^{[I]}$, the $\nu_1$ mode at 3602 cm$^{-1}$ for H$_2$O$^{[II]}$ and the $\nu_3$ mode at 2360 cm$^{-1}$ for CO$_2$. The intensity data for each band were scaled to its maximum intensity. The diffusion profiles confirm the observations from Figure 5: the H$_2$O$^{[I]}$ content (open circles) is almost constant until ~200 µm from the grain edge, then progressively decrease close to the core of the grain. The H$_2$O$^{[II]}$ content (open triangles), on the other hand, is almost constant from rim to core; it decrease in the vicinity of the hourglass boundary crossed by the profile (Fig. 6a) and then increases again. The CO$_2$ absorbance (solid squares) has a trend opposite to H$_2$O$^{[II]}$: starting from the edge of the grain it decrease progressively until it reaches a minimum around 130 µm from the edge. The CO$_2$ content in addition shows two relative maxima around 200 and 280 µm from the edge, and finally goes to zero at the core of the grain. The relative maxima in CO$_2$ content correspond to fractures present inside the treated grain as also shown by the XPL picture (Fig. 6a).
Figure 6 – (a) XPL image of the treated beryl. (b) Absorbance profiles along the AA’ trace in (a) for H$_2$O$^{\text{II}}$ (open circles), H$_2$O$^{\text{II}}$ (open triangles) and CO$_2$ (solid squares); intensity data are expressed as % of the maximum intensity for each target molecule. A fracture is present about 200 µm from the grain edge and a hole at about 280 µm. Spot size 15x15 µm, step 10 µm.

4. Discussion

4.1 Hourglass zoning and CO$_2$ diffusion

During the experiments of CO$_2$ diffusion in beryl and cordierite (this Thesis, chapter 5) it was observed, in particular by high-resolution FPA imaging, that carbon dioxide diffusion in beryl is faster along the structural channels parallel to [001], and eventually along fractures presents in the grain. This behavior is in agreement with the diffusion mechanism of H$_2$O in beryl (Fukuda et al., 2009). The spectroscopic image given in Figure 5d clearly demonstrates that the CO$_2$ diffusion proceeds from the (001) surface into the grain along the [001] direction. Single-spot, quantitative data collected on a traverse parallel to [001] (Figure 6b) in addition show that the CO$_2$ concentration profile follows the typical one dimensional diffusion trend (see for example Fukuda et al., 2009, Zhang and Cherniak, 2010, and this Thesis, chapter 5) up to about 130 µm from the crystal edge.
Figure 7 – Contour map of CO$_2$ distribution in the indicated (red broken-line box) portion of the beryl sample; spectra collected with synchrotron. The traces of the “hourglass” growth structure and the fractures are highlighted. The same image obtained using a Globar IR radiation is given for comparison. Chromatic scale is proportional to the CO$_2$ content, units are arbitrary.

However, Figure 5d shows a feature that has never been observed so far, i.e. a clear and significantly increased diffusion of CO$_2$ along the boundaries of the hourglass zoning of chromium. In other words, the FPA images show that the hourglass boundary acts as a preferential, fast pathway, for the CO$_2$ diffusion. Figure 7c displays a higher-resolution FPA image of the CO$_2$ distribution across the hourglass boundary. The image was collected using a synchrotron source, a spot size of 10 x 10 µm and a step of 5 µm, i.e. oversampling the analytical points by significant overlapping of the signal; accordingly, these conditions ensure both a very high spatial resolution and an excellent signal-to-noise ratio (Della Ventura et al., 2014). Figure 7b gives also, for comparison, the FPA image obtained on the same area when using a conventional IR source; the gain in resolution due to the use of SR radiation is evident. From Figure 7c it is possible to distinguish two main directions of CO$_2$ diffusion: one parallel to the hourglass boundary (solid line) and a second along a fracture inside the grain (dashed line) that is well visible in the optical image in Figure 6a. To get a better insight into this issue we tried to check whether or not a physical discontinuity, i.e. a crack, was formed during the heat/pressure treatment, thus implying that the hourglass structure simply acted like a fracture in enhancing the CO$_2$ diffusion (this Thesis, Chapter 5).
Figure 8 – FESEM pictures of the treated beryl sample in correspondence of the “hourglass” structure, in a fracture-free area (a and b) and in a fractured area (c, d, e and f). Note that in a, c and d the BSE compositional images of the investigated areas are given, while in b, e and f the morphological SE images are displayed. The red dashed line indicates the limit of the “hourglass” sector zoning and the yellow dashed line indicates a fracture in the grain.

Figure 8 shows high-resolution FESEM (Field-Emission SEM) images of selected areas of the studied sample. The areas were chosen across the hourglass boundary, both in a point optically clean and without fractures (Fig. 8a) and in a second point characterized the presence of a fracture (Fig. 8c). The BSE (back-scattered electron) pictures displayed in Figures 8a and 8b show how the higher magnification images given in Figures 8b, 8e and 8f were indeed collected across the hourglass boundary, i.e. across the compositional discontinuity due to the different Cr contents, and across a fracture (Fig. 8d) running semi-parallel to this boundary. High-resolution SE (secondary electrons) morphological images
collected in the area displayed in Figure 8a show a perfectly flat surface suggesting that no cracks are present along the hourglass boundary (Figure 8b, see red broken line), while in correspondence of the fracture optically visible in Figure 8c (yellow dashed line) a defined groove is clearly present (Figs. 8d to 8f). The FESEM images of Figure 8 thus allow the conclusion that, at least at the scale of tenths of nm, the hourglass structure is exclusively due to a compositional inhomogeneity, and that there is no physical discontinuity along the compositional boundary. This being the case, the diffusion path observed along this structure (Figs 5 and 6) cannot be explained on the basis of a fracture-enhanced diffusion mechanism, therefore the process responsible for the enrichment of CO$_2$ in specific directions of the sample (i.e. along the hourglass boundaries) is probably similar to a defect-enhanced mechanism.

Hollister (1970) showed that differences in growth rates of different crystal faces may causes a mismatch in the periodical structure, and concluded that this mechanism may be responsible for the formation of sector zoning in minerals. The mismatch is usually characterized by chemical zoning, which is controlled by the presence of particular ions in the supply material, by differences in local charge-balance and/or atomic geometrical conditions (Hollister, 1970, Bahat, 1974); for instance this process has been shown to be responsible for Pb zoning in synthetic cordierite (Wunder et al., 1991), Cr zoning in Be-indialites (Mikhailov et al., 2007) and can explain the Cr zoning in the crystals studied here (Fig. 5).

The images of Figure 7c suggest that the defects arising from the structural mismatch likely speed up the diffusion of CO$_2$, similarly to what observed along a fracture. Zhang et al. (2006) studied the oxygen diffusion in titanite under different experimental conditions and observed that planar defects may act as fast-path for diffusion inside the crystal lattice and that diffusion along these directions may be even 4 - 5 orders of magnitude faster than the lattice diffusion at the same PTt conditions. A similar mechanism could explain the penetration of CO$_2$ down to the core of the grain along the hourglass discontinuity. A consequence of this discussion is that, in experimentally treated samples, several diffusion mechanisms may locally act; for example, in the studied case, our spectroscopic data suggest the possible combination of (a) a fast-path defects diffusion, (b) a fracture-induced diffusion and (c) a structural-channel diffusion (this Thesis, Chapter 5). Therefore, in diffusion studies, a careful characterization of the possible inhomogeneous distribution of the target molecule
inside the matrix is mandatory because measurement of diffusion coefficients could be complicated by local effects.

### 4.2 The role alkali ions on the H$_2$O diffusion

The images displayed in Figures 5c and 5d suggest that the role of the hourglass zoning on the H$_2$O diffusion is extremely different to that so far discussed for CO$_2$. As a matter of fact, the FTIR-FPA data show that while type I H$_2$O diffusion is not affected by the chemical zoning (Fig. 5b), H$_2$O$^{[\text{II}]}$ incorporation/speciation is significantly decreased where CO$_2$ concentration is higher, and where Na has been locally replaced by K (compare Fig. 3c with Fig. 5c).

In Figure 1b we showed that both H$_2$O and CO$_2$ share the same crystallographic position (2a) in the channel, thus we would expect that areas with a higher concentration of CO$_2$ (like the hourglass traces) presented a lower global H$_2$O content. However, the FPA images show that only H$_2$O$^{[\text{II}]}$ is depleted along the hourglass traces, while H$_2$O$^{[\text{I}]}$ is unaffected. In the introduction we mentioned that H$_2$O$^{[\text{II}]}$ is strongly associated to the monovalent cations inside the channels (Wood and Nassau, 1968; Goldmann et al., 1977), and we also mentioned that in beryl K$^+$ and other larger cations are located in the larger 2a site (Hawthorne and Černý, 1977), where H$_2$O$^{[\text{II}]}$ is also located; in Figure 3 we observe that along the hourglass boundary there is an increase in K$^+$ and a decrease of Na$^+$. Considering that H$_2$O$^{[\text{II}]}$ may be associated preferentially, if not exclusively, to Na$^+$, we conclude that the H$_2$O$^{[\text{II}]}$ depletion along the hourglass discontinuity may be the combined result of a paucity of Na (which is preferentially bound to H$_2$O) and an increase K$^+$ content at the 2a site (Fig. 1). In other words, the presence of K filling the 2a sites would prevent the occurrence of H$_2$O at the same site (compare Fig. 3c and 3d with Fig. 5c). Aines and Rossman (1984) in their high-T study of water and CO$_2$ in cordierite and beryl concluded that CO$_2$ probably acts as a partial plug for the diffusion of H$_2$O along the cordierite channels. The same feature was also observed by Johannes and Schreier (1981) in their hydrothermal equilibration studies on cordierite. Additionally CO$_2$ may alter the local thermodynamic equilibrium of H$_2$O, affecting a particular speciation of water, similarly to the problem of diffusion and speciation of OH and H$_2$O in melt/glasses. Based on these considerations, we suggest that an additional reason for the depletion of H$_2$O$^{[\text{II}]}$ along the hourglass boundary could be simply connected with the increased amount of CO$_2$. As a final comment, Fukuda et al. (2008) observed in their
experiments that the dominant diffusive species along the beryl channels was type I H$_2$O relatively to type II H$_2$O, however the FTIR-FPA images of Figure 5 show that this is not the case in our samples, and clearly suggest that there is no major difference in the diffusivity of the two water types, which seems to be controlled only by the alkali content. We have no explanation at this moment for this discrepancy.
CHAPTER 7

SPECIATION AND DIFFUSION PROFILES OF H₂O IN WATER-POOR BERYL:
COMPARISON WITH CORDIERITE

Abstract

This chapter reports the polarized FTIR study of two beryl samples treated in CO₂-rich atmosphere, at 700°C and 800°C, 700 MPa, respectively. The infrared spectra, as expected, show the presence of CO₂ but also of minor H₂O due to moisture present in the starting products used for the synthesis. FPA-FTIR images show that H₂O diffuses into the beryl matrix along the structural channels oriented parallel to [001]. Spectra collected along profiles parallel to the c crystallographic axis show subtle changes as a function of the distance from the crystal edge; these changes can be correlated to a progressive change in the H₂O coordination environment in the channel, as a response to the varying H₂O/alkali ratio. In particular, the data show that when 2·H₂O > Na⁺ apfu, H₂O can assume both type I and type II orientation; in the latter case, each Na cation coordinates two H₂O[II] molecules (doubly coordinated H₂O). If 2·H₂O < Na⁺ apfu, then H₂O[II] molecules are singly coordinated to each Na cation. The same type of feature is observed and commented for the structurally related cordierite.
Chapter 7: Speciation and diffusion profiles of H$_2$O in water-poor beryl: comparison with cordierite

1. Introduction

Beryl, ideally Be$_3$Al$_2$Si$_6$O$_{18}$, is an accessory mineral typical of pegmatitic and granitic rocks (e.g. Deer et al., 2006). In the beryl structure, SiO$_4$ tetrahedra share common oxygens to form six-membered hexagonal rings with [Si$_6$O$_{18}$]$^{12-}$ composition (Fig. 1a); the stacking of these rings along the crystallographic $c$ direction give rise to cages which are connected into open channels parallel to [001] (Fig. 1b). The cages diameter is about 5.0 Å (Gibbs et al., 1968), while the bottle necks of the channels have a diameter of 2.8 Å (Fukuda and Shinoda, 2011). For this reason beryl, as well as the isostructural cordierite, are of interest as a model for microporous materials. It is known since the early work of Wood and Nassau (1967, 1968) that several atoms and molecular groups may be present in the structural voids of beryl.

![Figure 1 - Schematic representation of the crystal structures of beryl viewed down the crystallographic c axis (a) and parallel to the (100) plane (b). In blue the Si site, in orange the Al site and in gray the Be site. Mean distances in the crystal cages are reported. The position on CO$_2$ and H$_2$O molecules are shown (modified after Fukuda and Shinoda, 2011).](image)

In particular, water and carbon dioxide (Wood and Nassau, 1968, Aines and Rossman, 1984) which are both located in the wider parts of the channels (2a position, Fig. 1b). Possible OH groups (Wickersheim and Buchanan, 1959, Aurisicchio et al., 1994) and large ions such as Cs and K are almost exclusively located at the 2a position (Hawthorne and Černý, 1977) while smaller cations like Na$^+$ (Wood and Nassau, 1968) always occupy the
narrower 2b site (Fig. 1b). The linear CO$_2$ molecules are oriented orthogonally to the c axis (Wood and Nassau, 1968; Aines and Rossman, 1984). H$_2$O groups occur in the structural channels with the molecular plane parallel to (100) but with two different possible orientations (Fig. 1b): type I H$_2$O (hereafter H$_2$O$^{[I]}$) has with the H–H vector parallel to the c axis, while type II H$_2$O (H$_2$O$^{[II]}$) has the H–H vector perpendicular to the c axis (Wood and Nassau, 1968). H$_2$O molecules of the latter orientation are bonded locally to alkali cations at the 2b site in a 2:1 ratio (Goldmann et al., 1977; Hawthorne and Černý, 1977), however, Fukuda and Shinoda (2008, 2011) showed recently that in a low-H$_2$O environment H$_2$O$^{[II]}$ may be bound to only one alkaline cation.

In the present PhD work, several volatile-free beryl single-crystals were treated in CO$_2$-rich environment at different P$\text{Tt}$ conditions, in order to study CO$_2$ diffusion in the structural channel (see Chapter 5). After the experimental runs, FTIR spectroscopy showed systematically the presence of weak amounts of H$_2$O in the samples. Due to the absence of water as a pressure medium during the experiments (see below), the H$_2$O trapped in the beryl is inferred to originate from the moisture adsorbed by the used materials during the tube preparation; because of this, diffused H$_2$O contents are very low. For this reason, a detailed polarized FTIR spectroscopic study was carried out to study the local environment of such trace amounts of water into the beryl structure, such as to contribute to the knowledge of the coordination environment and the physical state of H$_2$O in beryl, after the extensive studies of Kolesov (2008), Fukuda and Shinoda (2008, 2011) and Fukuda et al. (2009).

2. Experimental methods and studied materials

Experiments were carried out using synthetic H$_2$O and CO$_2$-free beryls (Hautefeuille and Perrey, 1888, 1890; Bellatreccia et al., 2008, this Thesis, cap. 5) as starting materials. Single-crystals were packed into Pt tubes together with crushed Al$_2$O$_3$ powder as inert, and silver carbonate as a CO$_2$ source and treated at different P$\text{Tt}$ conditions. Two samples were selected for the present study, treated at the same $P = 700$ MPa and $T = 700$ °C (Pa_340 r) and 800 °C (Pa_340 o), respectively. Experiments were done using a non end-load piston-cylinder apparatus QUICKpress™ at the HP-HT Laboratory of Experimental Volcanology and
Geophysics of Instituto Nazionale di Geofisica e Vulcanologia (INGV, Rome, Italy). After the run, the recovered crystals were oriented along (hk0) using the external morphology.

FTIR spectra were acquired using a Bruker™ Hyperion 3000 microscope equipped with a conventional Globar IR source, a KBr broadband beamsplitter and a liquid nitrogen-cooled MCT detector, at Laboratori Nazionali di Frascati, Istituto Nazionale di Fisica Nucleare (LNF-INFN), in Frascati (Rome). The polarized spectra were collected using a gold-wire-grid polarizer. The nominal resolution was 4 cm$^{-1}$ and 128 scans were averaged for both spectrum and background. FTIR images were collected with a 64 x 64 pixel focal-plane array (FPA) of liquid nitrogen-cooled MCT detectors coupled with a 15x Schwarzschild objective. The nominal resolution was set at 4 cm$^{-1}$ and 64 scans were averaged for both spectrum and background; each image covers an area of 170 µm x 170 µm with a spatial resolution close to 5 µm (Della Ventura et al., 2010, 2014). Polarized FTIR profiles were performed with a spot size 25 X 80 µm, collecting the data at steps of 20 µm.

Selected polarized FTIR spectra, collected on the crystal edge (see below) are given in Figure 2. The spectra show a sharp and very intense peak at 2360 cm$^{-1}$ for $E \perp c$ which is assigned to the antisymmetric stretching mode of CO$_2$, and a group of sharp peaks in the H$_2$O stretching region (3750-3500 cm$^{-1}$).

![Figure 2. Polarized FTIR spectra of sample Pa 340_o collected on the crystal edge (see text for explanation).](image)
Peak areas were determined using the routine built into the spectrometer software; the spectra were decomposed using Origin 9™ by using a Lorentzian shapes for all components except for the broad absorption at 3665 cm\(^{-1}\) which was modeled as a Gaussian band (Kolesov, 2008). Peak positions and widths were constrained to be constant and the background was modeled as linear; an example is given in Figure 3.

Figure 3 - Decomposed single-crystal polarized FTIR spectra of beryl Pa 340_r in H\(_2\)O stretching region for (a) E⊥c and (b) E // c, and in H\(_2\)O bending region (c). Experimental spectrum = black line, fitted peaks = gray line, calculated pattern = dashed black curve; peak position are reported.
Chapter 7: Speciation and diffusion profiles of H$_2$O in water-poor beryl: comparison with cordierite

The maximum amount of water and CO$_2$ incorporated into the sample were quantified, via the Beer-Lambert relationship, see this Thesis, cap 6. Absorbance values (A) were obtained from polarized data collected on the edge of the grain (see below); the used mode, type of absorbance and molar absorption coefficients are summarized in Table 1.

Table 1 – Used mode, method, absorption coefficients and resulting H$_2$O and CO$_2$ contents (ppm) for the studied beryl samples. For explanation, see text.

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<th>Molecule</th>
<th>Mode, position and polarization</th>
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<th>Pa$_{340_r}$</th>
<th>Pa$_{340_o}$</th>
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<tr>
<td>Type I H$_2$O</td>
<td>$\nu_3$ at 3699 cm$^{-1}$, E//c</td>
<td>197</td>
<td>1215 ± 172</td>
<td>544 ± 77</td>
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<tr>
<td>Type II H$_2$O</td>
<td>$\nu_2$ at 3602 cm$^{-1}$, E//c</td>
<td>256</td>
<td>725 ± 102</td>
<td>611 ± 86</td>
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<td>Total H$_2$O</td>
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Integrated absorbance data; ε$_i$ values recalculated after Charoy et al. (1996), see also Chapter 5

<table>
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<th>Molecule</th>
<th>Mode, position and polarization</th>
<th>ε$_i$ (l·mol$^{-1}$·cm$^{-2}$)</th>
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<tr>
<td>CO$_2$</td>
<td>$\nu_3$ at 2360 cm$^{-1}$, E.Lc</td>
<td>70000±7000</td>
</tr>
</tbody>
</table>

3. FTIR-FPA imaging

![FTIR-FPA images](image)

Figure 4 – FTIR-FPA images of the H$_2$O distribution for (a) sample Pa$_{340_r}$ (107 µm thick section) treated at 700 MPa, 700 °C for 24 hrs and (b) sample Pa$_{340_o}$ (188 µm thick section) treated at 700 MPa, 800 °C for 10 hrs. Color scale is proportional to water concentration (integration range 3740-3565 cm$^{-1}$), units are cm$^{-1}$. The white arrows indicate the direction FTIR profile in Figure 5.
The FPA-FTIR maps of the H$_2$O distribution within the studied samples (Fig. 4) shows that the H$_2$O content is maximum at both edges of the crystal or in fractures along the sample (Fig. 4a, see also Chapter 5). Based on single-spot FTIR data Fukuda et al. (2009) inferred that the H$_2$O diffusion in beryl proceeds exclusively along the structural channels parallel to the c crystallographic axis, implying that the H$_2$O content must be maximum on the edge of the grain, then progressively decrease toward the crystal; this is what we actually observe using FPA imaging (Fig. 4), and, more generally, in all beryl and cordierite samples studied during this Thesis (chapters 5 and 6). The white arrows in Figure 4 indicate the profiles along which we collected FTIR single spot data used for the discussion presented below. Based on the FPA images, we thus assume that proceeding from the edge of the grain along the analytical profile, the H$_2$O content progressively decreases, providing the possibility to compare the FTIR patterns collected on points with different H$_2$O contents, in the same matrix. For each point, the H$_2$O content was quantified using the polarized data, as explained above.

4. Polarized FTIR measurements

Figures 3a and 3b show an enlargement of the fitted spectra of Figure 2 in the water stretching 3800-3500 cm$^{-1}$ region. For E$\perp$ c (Fig. 3a) a very broad and convolute absorption is observed, centered at 3665 cm$^{-1}$; relatively sharp and intense peaks are resolved at 3725, 3643, 3602 and 3586 cm$^{-1}$, and a minor peak is also visible at 3699 cm$^{-1}$. The 3665 cm$^{-1}$ band is assigned to the $v_3$ mode H$_2$O$^{[II]}$, while the 3602 cm$^{-1}$ component is assigned to the $v_1$ mode of type I H$_2$O (see Fukuda and Shinoda, 2008). The sharp peaks at 3725 and 3586 cm$^{-1}$ have never been observed in the water region for beryl when E$\perp$ c; based on the data for cordierite, these bands can be related to the $v_3 + v_1$ and $v_3 + 2v_2$ combination modes of CO$_2$, respectively (Della Ventura et al., 2009, 2012). This assignment is confirmed by their polarization behavior and by the excellent correlation between their intensity with that of the $v_3$ mode of CO$_2$ (see Chapter 5). Assignment of the sharp 3643 cm$^{-1}$ peak will be discussed in a later section. The E//c spectrum (Fig. 3b) shows a sharp and intense peak at 3699 cm$^{-1}$ which is assigned to the $v_3$ mode H$_2$O$^{[II]}$ (Wood and Nassau, 1967); this band occurs also in the E$\perp$ c spectrum with a very low intensity (Fig. 3a), possibly due to a slight
misalignment of the section. In Figure 3b two relatively intense peaks are resolved at 3600 and 3589 cm\(^{-1}\), respectively. The former band is assigned to the \(\nu_1\) mode of type I H\(_2\)O. The latter component can be assigned to the \(\nu_1\) mode of a new water configuration in beryl, i.e. to the "singly coordinated" type II water (Fukuda and Shinoda, 2008); this point will be discussed in more details below. The \(E//c\) spectrum in the H\(_2\)O bending region (Fig. 3c) shows two components centered at 1633 and 1620 cm\(^{-1}\). Based on the work of Fukuda and Shinoda (2008, 2011) these peaks can be correlated with the \(\nu_2\) bending motion of H\(_2\)O\(^{[\text{II}]}\).

Figure 5 - Polarized IR spectra collected for sample Pa 340_r in the H\(_2\)O stretching region with (a) \(E\perp c\) and (b) \(E//c\), and in the H\(_2\)O bending region (c) for \(E//c\). The distance from the grain rim is indicated on the right. Upward and downward arrows indicate increase or decrease in the peak intensity.

The evolution of the polarized FTIR patterns of sample Pa 340_r, as a function of the distance from the crystal rim, is given in Figure 5; it is evident that several variations occur in the spectra, and, as explained above, these variations are connected with the progressive decrease in the H\(_2\)O content. In particular, the intense band at 3699 cm\(^{-1}\) rapidly decreases while progressing within the crystal, and disappears at a distance > 120 \(\mu\)m from the rim (see spectra for \(E//c\) in Figure 5b). The broad band at 3665 cm\(^{-1}\) (for \(E\perp c\), Fig. 5a) and the sharp peak at 3600 cm\(^{-1}\) (for \(E//c\), Fig. 5b) also decrease progressively in the same range. By
contrast, the sharp peak at 3643 cm\(^{-1}\) (E\(\perp\)c, Fig. 5a) and the 3589 cm\(^{-1}\) component (E//c, Fig. 5b) initially grow in intensity and then eventually decrease, but persist up to 340 \(\mu\)m from the rim. In the bending region (spectra collected for E//c, Fig. 5c), the 1620 cm\(^{-1}\) component follows the same intensity variation of the 3665/3600 cm\(^{-1}\) pair, while the trend of the 1633 cm\(^{-1}\) component is similar to that of the 3589 cm\(^{-1}\) band. No absorptions related to the H\(_2\)O\(^{[l]}\) bending mode (1626, 1600, 1544 cm\(^{-1}\) after Charoy et al., 1996) were present in the spectra, probably because of the low H\(_2\)O contents.

Figure 6 clearly shows that the measured absorbance of the 3600/1620 and 3589/1633 cm\(^{-1}\) pair of bands are strongly correlated, and this feature, coupled with the fact that both sets of bands occur with E polarized in the same direction, allows their assignment to two different water molecules, but oriented in a similar way.

![Figure 6](image)

**Figure 6** – Absorbance relationship between for the 1620/3600 cm\(^{-1}\) and 1633/3589 cm\(^{-1}\) peaks, sample Pa 340_r.

As discussed by Fukuda and Shinoda (2008) considering that these water molecules have different vibrational frequency, their coordination state in the structural channel must also be different. The 3643 cm\(^{-1}\) component, observed above in Figures 3a and 5a for E\(\perp\)c is also compatible with this scenario. From the recent work of Fukuda and Shinoda (2008, 2011) it is now clear that type II water occurs in the beryl channels with two bonding environments, called "doubly-coordinated" type II water, and "singly-coordinated" type II water in Fukuda and Shinoda (2008). The former molecule is characterized by a \(v_3\) mode
around 3660 cm\(^{-1}\) polarized for \(E \perp c\), a \(v_1\) mode around 3600 cm\(^{-1}\) polarized for \(E//c\), and a \(v_2\) mode around 1620 cm\(^{-1}\) polarized for \(E//c\), while the latter molecule is characterized by a \(v_1\) mode around 3589 cm\(^{-1}\) polarized for \(E//c\) and a \(v_2\) mode around 1633 cm\(^{-1}\) polarized for \(E//c\). The polarization direction and its behavior as a function of varying water contents, described above, allows assignment of the 3643 cm\(^{-1}\) to the \(v_3\) motion of singly-coordinated type II water. The spectra given in Figure 3 show in fact that the 3643 cm\(^{-1}\) peak is totally polarized for \(E \perp c\), indicating that this peak is correlated with a water molecule having the H-H vector perpendicular to [001]. However, according to the extensive literature on the FTIR spectroscopy of beryl (e.g. Wood and Nassau 1967, 1968, Charoy et al., 1996), the \(v_3\) mode of doubly-coordinated H\(_2\)O\(^{[II]}\) is systematically observed at 3660 cm\(^{-1}\), and typically in the form of a rather broad absorption (e.g. Adamo et al., 2008; see also Fig. 3 and 5). Bellatreccia et al. (2008) described the spectrum of a synthetic beryl containing a very low (~ 30 ppm) water content showing a very sharp peak at 3643 cm\(^{-1}\) polarized for \(E \perp c\), paired with a less intense component at 3589 cm\(^{-1}\), polarized for \(E//c\).

Figure 7 - Correlation between the measured intensity of the 3643 cm\(^{-1}\) and 3589 cm\(^{-1}\) bands in sample Pa 340_o.

Their pattern thus provides a definitive proof of the correlation between these two components, since no any other band appears in their spectra, and allows definitive assignment of the 3643 cm\(^{-1}\) band to the \(v_3\) mode of singly-coordinated type II water. In
agreement with this assignment, the intensities between the 3643 and 3589 cm\(^{-1}\) bands as a function of varying H\(_2\)O contents are also correlated, although there is some discrepancy at the very low concentrations due to the difficulties in the fitting procedure. Final band assignment is schematically displayed in Figure 8.

![Proposed band assignments](image.png)

Figure 8 - schematic representation of the proposed band assignments (modified after Fukuda and Shinoda, 2008).

The integrated intensities of all bands in Figures 5 are plotted in Figure 9 as a function of the distance from the edge. Examination of Figure 9 shows that the H\(_2\)O\([\text{II}]\) peaks at 3665, 3600 and 1620 cm\(^{-1}\), all assigned to doubly-coordinated type II water are initially constant and then progressively decrease. The 3643, 3589, and 1633 cm\(^{-1}\) peaks, on the other hand, initially increase in intensity and then decrease progressively, but are still observed, although with a very low intensity, up to 340 \(\mu\)m from the rim. This behavior suggests that, while progressing within the crystal, because of the decreasing content in the channel H\(_2\)O\([\text{II}]\) molecules modify their coordination environment from doubly-coordinated molecules to singly-coordinated molecules, the change occurring when the H\(_2\)O : Na apfu ratio becomes < 2 : 1.
5. The coordination of H$_2$O in beryl and cordierite

According to several studies, type II H$_2$O and alkali cations are typically in the ratio 2:1 in both beryl (e.g. Charoy et al., 1996; Kolesov, 2008) and cordierite (e.g. Della Ventura et al., 2010), suggesting that in both minerals each alkali cation is normally associated with two water molecules in the channel. However, both Fukuda and Shinoda (2008, 2011) and this work, provides evidence that in H$_2$O poor samples this relationship is no longer valid, and each alkali cation may coordinate to a single H$_2$O$^{[ii]}$ molecule. The same point was also addressed by Kolesov (2008) in his analysis of Raman spectra collected on H$_2$O-poor beryl.

A theoretical approach to this feature has been provided by Bauschlicher et al. (1991) and Lee et al. (2004), who simulated the energy of M(H$_2$O)$_n^+$ clusters as a function of
increasing number of water molecules coordinating a metal cation (M). Accordingly, for increasing n, both the $\nu_3$ and $\nu_1$ stretching modes of H$_2$O shift to higher wavenumbers, while the frequency of the bending mode shifts to lower wavenumbers. The frequency shifts are related to changes in the geometry of the H$_2$O molecule, and can be explained by considering that changes in the electrostatic charge exchanged by the M cation (in the present case Na) and the hydroxyl oxygen in the M(H$_2$O)$_n^+$ cluster (Fig. 10), are translated into changes of the M-O bond distances. If n = 1, the fraction of the electrostatic charge of sodium exchanged with the hydroxyl oxygen ($^W$O) is maximum, the O-H bond is longer and the H-O-H angle decreases. When n = 2, the charge of Na is shared by two $^W$O and the O-H bond shortens to compensate for the resulting charge deficit; the H-O-H angle simultaneously increases (Fig. 10). The geometrical changes of the water molecule, due to the described different coordination environments are evidenced by the observed shifts in frequency of the stretching and bending modes.

![Diagram of H$_2$O geometry](image)

Figure 10 – Schematic representation of H$_2$O geometry around an alkaline cation for a singly coordinated (top) and a doubly coordinated (bottom) H$_2$O molecule. The symmetry of the cluster is reported on the side (after Bauschlicher et al., 1991).

Similar shifts in frequency in response to the modified electrostatic environment in the M(H$_2$O)$_n^+$ cluster can be modeled by the GF matrix method (Wilson et al., 1955); for type II H$_2$O in beryl the calculations are reported in Fukuda and Shinoda (2008, 2011).
Chapter 7: Speciation and diffusion profiles of H₂O in water-poor beryl: comparison with cordierite

Figure 11 – (a) FTIR polarized light spectra for E//b (black line) and E//c (red line) crystallographic directions, for different cordierites. The H₂O/Σch ratio is expressed as H₂O apfu over the total Na⁺ + K⁺ + Ca apfu. Compositional data for Crd_pr 40 are from Della Ventura et al. (2012), for BB3a from Della Ventura et al. (2012) and for HO33 from Della Ventura et al. (2009). (b) Frequency position of ν₃ antisymmetric stretching (black squares) ν₂ bending (red dots) and ν₁ symmetric stretching mode (blue triangles) as a function of H₂O/Σₕ ratio. Lines are only a guide for the eye.

The mechanism so far described can be extended to explain the peak shifts observed in the FTIR spectra of the structurally-related cordierite. In Figure 11a we compare the E//b and E//c FTIR spectra of four cordierites (BB3a, from Della Ventura et al., 2012; HO33, from Della Ventura et al., 2009; Crd_pr 40 and Crd_pr 8 from this Thesis, cap 5) having a different H₂O to alkali cation ratio (H₂O/Σ_ch = H₂O over Na⁺ + K⁺ + Ca⁺⁺ apfu). Dotted lines indicate the peak position of the ν₃ and the ν₁ modes for H₂O[II]. Examination of Figure 11a shows that both ν₃ and ν₁ peaks shift to lower energy as the H₂O/Σ_ch ratio decreases, similarly to what observed for beryl. Starting from sample Crd_pr 40 (H₂O/Σ_ch = 11.46) there is a progressive shift from the 3630/3575 cm⁻¹ (Della Ventura et al., 2012) to 3617/3568 cm⁻¹ in sample BB3a (H₂O/Σ_ch = 2.52). The broad band in cordierite BB3a sample shows two pronounced shoulders at ~ 3583 cm⁻¹ and 3542 cm⁻¹, respectively. These shoulders become the main peaks in the spectra with the lowest H₂O/Σ_ch ratio (Crd_pr 8 and HO33). In Figure 11b (top)
we plot the $\nu_3$ (squares) and $\nu_1$ (triangles) peak positions against the $\mathrm{H_2O/\Sigma_{ch}}$ ratio (data from Della Ventura et al., 2012). As expected from the above discussion, the $\nu_2$ bending mode (Fig. 11b, circles), shows an opposite trend for increasing $\mathrm{H_2O/\Sigma_{ch}}$ ratio, from $1634 \text{ cm}^{-1}$ to $1650 \text{ cm}^{-1}$. Figure 11b emphasizes that there is a sudden shift in peak position for compositions with $\mathrm{H_2O/\Sigma_{ch}} < 2$. This threshold value corresponds to the ratio of 2 $\mathrm{H_2O^{[II]}}$ for each alkali cation atom in the channel: when this ratio is below 2 the $3583 - 3542 - 1650 \text{ cm}^{-1}$ components prevail suggesting that $\mathrm{H_2O^{[II]}}$ is predominantly in a singly-coordinated state.

6. Conclusions

![Decreasing H$_2$O content](image)

Figure 12 – Top: schematic representation of the configuration of water molecules inside the structural channels of beryl, as the overall water content decreases. Bottom: concentration trends of selected peaks in the FTIR spectra. Peak intensities are scaled to the maximum intensity value.
Figure 12 displays schematically the summary of the discussion presented so far, providing a sketch of the water molecules within the beryl channels as H$_2$O concentration progressively decreases, correlated with the plots relating the intensity variation of the antisymmetric stretching modes for each H$_2$O configuration. From the plot it is apparent that for higher water contents on the crystal edge, H$_2$O can assume both type I and type II orientations (black squares and gray circles curves close to the edge in Fig. 12) and this implies that 2·H$_2$O > Na$^+$ apfu. Proceeding within the channel, all H$_2$O molecules tend to assume the type II configuration (doubly H$_2$O$^{[II]}$, gray circle curve) implying that the water content approaches 2·H$_2$O ≈ Na$^+$ apfu. Proceeding further within the channel, the water content reaches 2·H$_2$O < Na$^+$ apfu and singly coordinated H$_2$O$^{[II]}$ predominates (singly H$_2$O$^{[II]}$, black triangles curve).

The above FTIR data thus allow to conclude that H$_2$O diffuses across the structural channels as an unbounded molecule, then it changes its local bonding configurations as a function of the Na/H$_2$O ratio. The diffusion coefficients for H$_2$O$^{[I]}$ and H$_2$O$^{[II]}$ (considering for simplicity the doubly and the singly coordinated H$_2$O$^{[II]}$ as a single molecule) were evaluated for both samples, using the monodimensional plane diffusion formalism (Crank, 1975; Zhang and Cherniak, 2010) as discussed in chapter 5. Profile data were obtained by integrating the H$_2$O$^{[I]}$ $\nu_3$ anti-symmetric stretching mode at 3699 cm$^{-1}$ polarized for E//c and the sum of both H$_2$O$^{[II]}$ $\nu_1$ symmetric stretching modes at 3600 and 3589 cm$^{-1}$ also polarized for E//c. The results are reported in Table 2. The calculated mean activation energy for H$_2$O$^{[II]}$ ($E_a$) is 135 kJ/mol with a pre-exponential (-log$D_0$) factor of 10$^{-6.61}$ (m$^2$/s) or 10$^{-2.61}$ (cm$^2$/s), for H$_2$O$^{[II]}$ $E_a$ = 90 kJ/mol and -log$D_0$ = 10$^{-8.43}$ (m$^2$/s) or 10$^{-4.43}$ (cm$^2$/s). The combined result for total H$_2$O is $E_a$ = 111±54 kJ/mol and -log$D_0$ = 10$^{-7.5}$ (m$^2$/s) or 10$^{-3.5}$ (cm$^2$/s). It is to be noted that the results for H$_2$O$^{[I]}$ are in good agreement with those obtained by Fukuda et al. (2009), for the same molecular type.

<table>
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<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>D (m$^2$/sec)</th>
<th>1000/T (K)</th>
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<tr>
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<td>1.5±0.1·E-13</td>
<td>0.93</td>
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CHAPTER 8

THE PERMANENT STORAGE OF CO\textsubscript{2} IN MESOPOROUS MINERALS: EXPERIMENTS WITH BERYL

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Abstract

In this short note we describe the recent experimental mineralogy work at University of Roma Tre focused on the diffusion of carbon dioxide within the structural channels of microporous silicates. The results obtained in the last few years for cordierite and beryl are briefly reported, as well as the developments of novel spectroscopic methods to characterize the volatile distribution across the studied materials.

KEY WORDS: CO\textsubscript{2} diffusion, HT/HP experiments, cordierite, beryl, FTIR-FPA spectroscopy and imaging, optical properties.
Carbon dioxide (CO$_2$) generated by the combustion of fossil fuels is by far the most abundant greenhouse gas; its reduction in the atmosphere is therefore a primary environmental concern. Due to several reasons, it can be easily understood that fossil fuels will continue to play a significant role in the world’s economy at least in the following decades, thus emphasis must be placed on improving methods to decrease the amount of CO$_2$ dispersed in the environment. The reduction of CO$_2$ from the atmosphere can be achieved by efficiency improvements in power plants, use of alternative energy technologies, sequestration of CO$_2$, or some combination of these methods. Up to the present, several techniques have been considered, and these include: 1) forestation, where CO$_2$ is removed from the atmosphere by biological activity; 2) aquifer storage, in which CO2 is injected into terrestrial aquifers where it is trapped hydro-dynamically; 3) deep sea storage, where CO$_2$ is injected into the ocean at approximately 3,000 meter depths, where it is believed to remain stable; and 4) mineral carbonation, in which CO$_2$ is reacted with minerals to form solid carbonates. This final form of sequestration is the most permanent method, because the carbonates are stable over geologic time periods (millions of years), rather than the hundreds to thousands of years of stability expected for the first three forms of sequestration. This process is however highly expensive and energy consuming, therefore research in material science has focused in the last decade at developing technically feasible processes for mineral sequestration of carbon dioxide alternative to carbonation.

Actually, many minerals contain carbon as a major to trace constituent, however the carbon content analysed in naturally occurring silicates is traditionally assigned to CO$_3^{2-}$ groups in the structure, whereas the possible presence of molecular CO$_2$ in these phases is almost completely ignored. Up to the present, the only accepted CO$_2$-bearing minerals are beryl (Wood and Nassau, 1967) and cordierite (Armbruster and Bloss, 1980, Della Ventura et al., 2009, 2012) two (structurally) closely related silicates characterized by open channels running along [001]; in these channels carbon dioxide is located together with H$_2$O and extra framework cations such as Na, Li or Cs. Recent research have shown that other silicate materials are able to host molecular CO$_2$ in their structural pores; these materials include some clay-like minerals (Zhang et al., 2005), some particular type of hydrous silica (Kolesov and Geiger, 2003) and several microporous, zeolite-type, feldspathoids (Bellatreccia, 2009, 2012, Bonaccorsi et al., 2007, Della Ventura et al., 2005, 2007, 2008).
We devoted significant efforts in the last years to the problem of CO$_2$ diffusion in microporous minerals, and in particular in cordierite and beryl. Cordierite is an extremely interesting material because it represents the only known case of a microporous structure (pore size under 2 nm) stable under extreme geological conditions and able to trap significant amounts of molecular H$_2$O and CO$_2$ (Armbruster and Bloss 1980). As a matter of fact, its occurrence extends from the amphibolite facies to ultra-high temperature metamorphism to crustal anatexis (Carrington and Harley, 1996; Harley et al., 2002). Because of its thermal and mechanical properties cordierite is used in applications such as high-tech ceramics or as a catalyst in petroleum industry. Beryl is a pegmatitic mineral and has a lower thermal and baric stability; it is well known for providing some of the most notable gemstones, such as the varieties emerald (green), aquamarine (light-blue), heliodor (yellow) or bixbite (red). We used natural cordierite and synthetic emeralds (Fig. 1) as starting materials for CO$_2$ diffusion experiments under high P and T conditions; this research has been developed in the frame of two Master Thesis and a PhD project in collaboration with the INFN (Istituto Nazionale di Fisica Nucleare) and INGV (Istituto Nazionale di Geofisica e Vulcanologia).
Briefly, we equilibrated previously degassed cordierite fragments and synthetic volatile-free emeralds in CO₂ saturated atmosphere, at different T, P and time conditions. The research was aimed at studying the diffusion of gaseous CO₂ across the mineral matrix as a function of the above mentioned parameters. We stress that from a practical point of view nobody would ever use emeralds as starting materials for carbon dioxide sequestration, thus our study must be regarded as a fundamental science research; however, knowledge of the process by which a gas having important geological implications, like CO₂, diffuses throughout solids, may open new frontiers in future applied science. The experiments were conducted using a variety of facilities (HT/HP press, Fig. 2, and Tuttle-type cold seal pressure vessels) and in different laboratories, including the HP/HT laboratory of INGV (Rome) and the Institut für Mineralogie of Leibniz Universität Hannover (Germany). The starting materials were encapsulated in Pt tubes with Ag carbonate or Ca-oxalate as a source for CO₂; these compounds in fact decompose at relatively low T thus saturating the charge with carbon dioxide. The charge was equilibrated for T in the range 700-900°C and P in the range 200-700 MPa.
Chapter 8: the permanent storage of CO$_2$ in mesoporous minerals: experiments with beryl

Figure 3 - Left: selected FTIR-FPA image of the CO$_2$ distribution within the emerald samples equilibrated at 700°C, 500 MPa in carbon dioxide saturated atmosphere. The spectroscopic image is oriented over the crystal image. The color from red to blue is proportional to the amount of CO$_2$. Right: schematic model for the CO$_2$ diffusion within the structural channels.

This short note is not intended to describe all obtained results, however, from a general point of view we observed that temperature has a very small effect on the CO$_2$ solubility in the studied minerals, while pressure has a significant effect; the effect of time is also negligible. To characterize the run products we used a novel technique in mineral spectroscopy (Della Ventura et al., 2014), which takes advantage of the focal-plane-array of detectors (FPA) to produce bi-dimensional images of the distribution of an absorber within a matrix, a concept very similar to the CCD detectors typically used in X-ray based methods. The extreme interest of these techniques in experimental studies is the possibility to probe the distribution of the target molecule, a piece of information that is crucial in diffusion studies where the homogeneity of the run product is rarely attained. Figure 3 shows a selected FTIR-FPA image of a beryl slice after the experiment, where the color intensity, from blue to red, is proportional to the CO$_2$ amount within the sample; the FPA image has been oriented onto the emerald crystal. The image clearly shows that the carbon dioxide diffused only for a short distance from the basal (pinacoidal) faces of the emerald along the channels; a schematic interpretation of the process is given on the right side of Figure 3.
Chapter 8: the permanent storage of CO$_2$ in mesoporous minerals: experiments with beryl

Figure 4 - (a) above: optical image of the experimental emerald fragment glued on the glass capillary for the spindle stage analysis; below: FTIR-FPA image of the same grain showing the CO$_2$ distribution. (b) above: optical image of the emerald sample in immersion within the Cargille liquid: the Becke line is visible; (below) final measured refractive indexes.

The refractive indexes of the emerald were measured using the spindle stage and the double variation method, by means of immersion liquids (Cargille liquids) of known refractive index under monochromatic light. For this analysis also, a map of the CO$_2$ distribution across the grain (Fig. 4) was essential to measure the correct optical property in different part of the crystal. Emerald is optically uniaxial negative, with a very low birefringence (0.005 to 0.009). It was found that the introduction of carbon dioxide into the structure has a significant effect on the ordinary ray value ($\omega$), which increases one order of magnitude (Fig. 4), while the extraordinary ray value ($\varepsilon$) is unaffected. This is consistent with the alignment of the linear CO$_2$ molecule perpendicular to the c crystallographic axis. A point we would like to stress here is that almost no laboratories worldwide are equipped to measure optical properties of minerals and perform crystal-chemical studies (including non-ambient conditions studies) based on optical methods. Optical mineralogy is an extremely powerful technique in geology and also in material Science, because the macroscopic
property which is displayed by a change in refractive index (a measure of the speed of light across the mineral), or in birefringence, retardation, conoscopic figures or interference colors is a quick measure of structural properties which can be obtained only by using much more sophisticated methods. For more than a century, the use of optical methods has been one of the prerogatives of Earth Science but this knowledge is unfortunately going to be lost.

Figure 5 - Left: optical image of the studied emerald showing the evident hourglass texture. Right: FTIR-FPA image of the CO$_2$ distribution within the samples

A final, spectacular observation on the distribution of carbon dioxide within emeralds is shown in Figure 5 which displays the FPA image collected on a particular sample, characterized by a pronounced hourglass zoning of chromium (Cr is a dopant used during the emerald synthesis to give the beautiful green color to the gem). The spectroscopic image shows that the CO$_2$ diffusion during the HT/HP treatment is significantly controlled by the hourglass texture, and is greatly enhanced along the zone boundaries. The reasons for this behavior are still unclear and we are working to better constrain the phenomenon. It is however clear that experimental mineralogy is able to open promising frontiers in technology, most of which originate from researches driven just by the scientist’s curiosity.
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Thanks are due to S. Mollo, C. Freda and P. Scarlato (INGV, Rome) for providing both facilities and their personal expertise to solve most of the technical aspects of this research. The spectroscopic work has been done at DaΦne Laboratory of FTIR spectroscopy of INFN (Frascati, Rome), thanks to the scientific collaboration of Mariangela Cestelli Guidi and Augusto Marcelli.
This PhD Thesis was aimed at investigating the ability of cordierite and beryl, considered as a model for microporous materials, to diffuse and trap H₂O and CO₂ within their structural channels.

The work focused in particular on the CO₂ diffusion because of very few and controversial results so far available in the literature. In addition, CO₂ is considered one of the major cause of long-term climate change, thus knowledge of the conditions under which it diffuses into minerals may have interesting bearings for the design of new materials for the permanent storage of this gas. The study was done by combining different analytical techniques, however most data were based on micro-FTIR and FTIR-FPA imaging. Indeed, during this work novel applications of the FPA imaging were developed and tested for the first time in the study of Earth Science materials, in particular under polarized and synchrotron radiation.

The volatile-free crystals were treated at different pressure and temperatures in a CO₂ rich atmosphere using a non end-load piston–cylinder press, especially designed for short term experiments. The results showed that CO₂ diffusion inside beryl and cordierite proceeds exclusively along the structural channels running parallel to the c crystallographic axis (Chapter 5); the same mechanism occurs also during CO₂ expulsion from the matrix (Chapter 3). Thus the CO₂ loss from cordierite and beryl is strongly affected by both the particle size and shape of the crystal, i.e. the length of the escape path. To examine quantitatively this feature, in Chapter 3 we performed experiments with two different crystallographic orientations: a first (001), 77 µm thick slab, with a diffusion pathway of 34 µm to simulate the loss from small or tabular grains, and a second (010) slab to model the case of large or prismatic grains (typical growth habit of cordierite, Deer et al., 2004). In this case, in fact, the mean diffusion pathway was about 120 µm, corresponding to half the slab
Final Remarks

dimension along the c axis. In the (001) lamella or in thin and tabular cordierite grains both CO\textsubscript{2} and H\textsubscript{2}O desorption proceeds smoothly even when T increases with a very fast rate; on the other side, for thicker or prismatic cordierite grains, as simulated by the (010) lamella, both CO\textsubscript{2} desorption and dehydration occur at higher temperatures, at least 50/100 °C higher than in the former sample. In other words, the data suggest that the difference in diffusion path length has a significant effect on the temperatures of CO\textsubscript{2} and H\textsubscript{2}O desorption and longer heating time are necessary to extract all volatile molecules from the core of the grain (see also Chapter 4).

Fractures inside the grains also acted as additional pathways of inward and/or outward CO\textsubscript{2} diffusion, in accelerating the CO\textsubscript{2} diffusion across the grain (Chapter 3 and 5); this finding is in line with the general observation that grain-boundary diffusion and diffusion along interfaces, like cracks, can be several order of magnitude faster than lattice diffusion (Zhang and Cherniak, 2010). A third additional way of diffusion was observed in synthetic beryls (Chapter 6). The planar defect generated by the structural mismatch in correspondence of the hourglass zoning also acted as a fast-path for CO\textsubscript{2} diffusion (Zhang et al., 2006). A direct conclusion is that the simultaneous occurrence of different diffusion mechanisms, i.e. (I) channel/lattice diffusion, (II) fracture induced diffusion and (III) fast path diffusion, may complicate the evaluation of diffusion coefficients of a molecular species, thus inspection of the distribution of a molecule inside the mineral via 2D imaging is mandatory in experimental work.

Differently to CO\textsubscript{2}, which is always oriented normal to the c axis, H\textsubscript{2}O may be oriented in different ways (Chapters 1, 2 and 7): relatively unbound H\textsubscript{2}O	extsuperscript{[I]}, doubly coordinated H\textsubscript{2}O	extsuperscript{[II]} and singly coordinated H\textsubscript{2}O	extsuperscript{[II]}. It follows that H\textsubscript{2}O in different coordination environments may have different diffusion mechanisms and consequently diffusion coefficients. Based on the results discussed in Chapter 7, it is possible to infer that when the amount of H\textsubscript{2}O in the channels is 2·H\textsubscript{2}O > Na apfu, than water may be present both as H\textsubscript{2}O	extsuperscript{[I]} and doubly coordinated H\textsubscript{2}O	extsuperscript{[II]}; when 2·H\textsubscript{2}O < Na apfu, than water is present as doubly and/or singly coordinated H\textsubscript{2}O	extsuperscript{[II]}. Characterization of the coordination state of H\textsubscript{2}O in the structural channels is thus important for a proper interpretation of diffusion data in experimental studies.

A major result of the experiments described in chapter 5 is that pressure plays a major role in controlling the amount of CO\textsubscript{2} diffused in both cordierite and beryl, while
temperature and time have a minor effect, in line with data from natural occurrences (Thompson, *et al.*, 2001; Harley *et al.*, 2002). Surprisingly, however, the CO$_2$ contents introduced during the present study into cordierite were at least one order of magnitude lower than expected (Johannes and Schreyer, 1981; Armbruster and Bloss, 1982). One of the reasons for this discrepancy probably is related to the fact that the crystals used here as a starting material had significant amounts of alkali cations (Chapter 1). Vry *et al.* (1990) observed that in natural cordierite the total content of CO$_2$ + alkali may induce a volatile deficiency of both H$_2$O + CO$_2$ during equilibration with the surrounding fluid because of a plug effect hindering diffusion of the relatively large CO$_2$ molecule from the fluid into the mineral. A second, additional source of discrepancy may be looked for in the sample handling and preparation for the analyses; HT/HP treatment of the sample during the experiments were found to induce development of a series of micro-fractures close to the edges of the cordierite crystals. These micro-fractures may induce the formation of a CO$_2$-rich but fragile external layer which may be removed during sample slicing and polishing for FTIR analyses, thus distorting the final data relative to analyses done on bulk samples.

Cracks and fractures, produced during the thermal treatment, were found to enhance significantly the CO$_2$ diffusion across with contents up to 4 times higher than at the edge of the grain. This feature has a great relevance from a technological point of view, because it demonstrates that to trap faster and larger CO$_2$ amounts inside the material, the use of highly fractured or clusters of micron-sized grains is preferred over larger grains (Chapter 8).

Because of the well-developed hexagonal prismatic habitus, the beryl samples were excellent candidates to evaluate the inward diffusivity of CO$_2$ in microporous structures (Chapter 5); diffusion coefficients for cordierite, on the opposite, could be evaluated only for the outward diffusion (Chapter 3). Diffusion coefficients of volatile species in silicates are expected to be related to the dimension of the diffusing species and the diffusing structure. It is also widely accepted that for more compact silicate structures diffusing rates are smaller and activation energies larger. As we may observe from Figure 1 the diffusing rates calculated for CO$_2$ (Chapter 5) and H$_2$O (Fukuda *et al.*, 2009) in beryl are very close, even though CO$_2$ molecule are larger than the H$_2$O molecule. On the other hand, the inward CO$_2$ diffusion coefficients for beryl (see Figure 1 and Chapter 5) are greater than the diffusion coefficient calculated for the outward CO$_2$ diffusion in cordierite (see Figure 1 and Chapter 3).
even though the structures are very similar. Vry et al. (1990) observed that in cordierite inward diffusion is quicker than outward diffusion. These authors stated that the difference between inward and outward diffusion rates may be caused by alkali cations and CO$_2$ itself, that, acting as plugs in the channel, preferentially slows down outward volatile diffusions.

Figure 1 – Arrhenius diagram of various diffusion coefficients D for different silicates or silicate melts for H$_2$O and CO$_2$. D for beryl after diffusion profiles (Chapter 5), D for cordierite after isothermal heating experiments (Chapter 3).

Figure 1 gives selected examples of diffusion rates for the most common hydrous minerals. In Figure 18 we may observe that the diffusion coefficients measured for CO$_2$ in beryl are close to the OH$^-$ diffusion coefficients obtained in other ring silicates like tourmaline (Desbois and Ingrin, 2007), layer silicates like muscovite (Graham, 1981), amphiboles like kaersutite (Ingrin and Blanchard 2000), or in disilicates like epidote (Graham, 1981). However, it’s important to note that structural OH$^-$ probably diffuses inside these structures in the form of H$^+$ (Zhang et al., 2010) thus the diffusing species is much smaller compared to molecular CO$_2$ and H$_2$O.

Our data suggest that the structural channels of cordierite and beryl act more likely as fast paths for the mobility of large molecular groups compared to similar silicate
structures, and for this reason the diffusing behavior is more similar (in terms of diffusion coefficients, not in the mechanism) to the one typically observed for grain boundary diffusion, such as, for example, H$_2$O in quartzite (Farver and Yund, 1991) or to the behavior of CO$_2$ in non-crystalline materials, like silicate melts (Watson et al., 1982; Watson, 1991).
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