

Carbon-bearing cordierite from Allumiere (Tolfa volcanic center, Latium, Italy): occurrence, crystal-structure and FTIR microspectroscopy

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ABSTRACT. — This paper reports the crystal-chemical study of cordierite from a volcanic ejectum from the Tolfa volcanic center (Latium, Italy). The studied rock was sampled within the pyroclastic deposit ("tufo caotico") outcropping in a quarry at Colle dello Spizzicatore, Allumiere Community. The sample was studied by electron microprobe analysis (EMP), single-crystal structure refinement and Fourier-transform infrared microspectroscopy (FTIR). Combination of these techniques allowed detailed characterisation of the amount, location and coordination of cations and volatile molecules in the channels.

Cordierite from Allumiere is orthorhombic, space group *Ccm*; refined cell-parameters are (in Å): $a = 17.1580(6)$, $b = 9.7573(3)$ and $c = 9.3228(3)$. EMP analyses show an intermediate X_{Mg} [$Mg/(Mg+Fe) = 0.58$], and a very low alkali ($Na + K = 0.042$ apfu) content. Single-crystal FTIR spectra are strongly polarised; the absorptions observed in the H_2O -stretching region can be assigned to H_2O molecules oriented with the $H...H$ vector // a and the molecular plane // (001). The absorptions observed in the C-O stretching region can be assigned to both CO_2 and CO molecules oriented // a ; the spectra also show the presence of ^{13}C and ^{18}O in the sample. Using the molar

absorption coefficients available in the literature, $H_2O = 0.02$ wt% and $CO_2 = 0.22$ wt% are calculated from the measured band intensities. The observed mineral assemblage and the volatile composition of cordierite are coherent with a thermometamorphic overprint on an early metapelite, which occurred at low-P (≤ 2 Kbar), high-T ($> 700^\circ C$) and extremely reducing conditions.

KEY WORDS: *cordierite, Allumiere, X-ray structure refinement, EMP analysis, polarised FTIR spectroscopy, volatile composition.*

RIASSUNTO. — In questo lavoro viene descritto lo studio cristallografico della cordierite di un proietto vulcanico dell'apparato della Tolfa (Lazio, Italia). La roccia esaminata è stata campionata all'interno del deposito piroclastico ("tufo caotico") affiorante in una cava a Colle dello Spizzicatore, Comune di Allumiere. Il campione è stato esaminato attraverso analisi in microsonda elettronica (EMPA), raffinamento strutturale su cristallo singolo e microspettroscopia infrarossa in trasformata di Fourier (FTIR). Combinando queste tecniche è stato possibile caratterizzare la quantità, posizione e coordinazione dei cationi e degli elementi volatili presenti nei canali strutturali del minerale.

La cordierite di Allumiere è ortorombica, gruppo spaziale *Ccm*; i parametri di cella sono (in

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Å): $a = 17,1580(6)$, $b = 9,7573(3)$ e $c = 9,3228(3)$. Le analisi microchimiche mostrano un rapporto Mg/Fe [$X_{Mg} = \text{Mg}/(\text{Mg}+\text{Fe})$] = 0,58, e un basso contenuto in alcali ($\text{Na} + \text{K} = 0,042$ apfu). Gli spettri FTIR ottenuti su cristallo singolo sono fortemente polarizzati; gli assorbimenti osservabili nella regione di stiramento dell'H₂O possono essere attribuiti a molecole di acqua orientate con il vettore H...H // a ed il piano della molecola // (001). Gli assorbimenti presenti nella regione di stiramento dei legami C-O possono essere attribuiti a molecole di CO₂ e CO orientate entrambe // a ; gli spettri mostrano anche la presenza di ¹³C and ¹⁸O nel campione. Utilizzando i coefficienti di assorbimento molare disponibili in letteratura, è possibile calcolare un contenuto di H₂O di 0,02 wt% e di CO₂ di 0,22 wt%. La composizione mineralogica della roccia, e la composizione dei volatili nei canali della cordierite sono concordi nel suggerire un evento termometamorfico a bassa P (≤ 2 Kbar) ed alta T ($> 700^\circ\text{C}$) avvenuto in condizioni estremamente riducenti su una metapelite preesistente.

PAROLE CHIAVE: *cordierite, Allumiere, raffinamento strutturale, analisi microchimica, spettroscopia FTIR in luce polarizzata, contenuto in volatili.*

INTRODUCTION

Cordierite, $(\text{Mg,Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18} \cdot (n \text{ H}_2\text{O}, m \text{ CO}_2)$ is a powerful mineral probe to monitor the fluid conditions during high-grade metamorphism (Smith 1996, Harley *et al.* 2002). It is in fact a rare case of a microporous mineral stable under geological conditions spanning from the amphibolite facies to the crustal anatexis and is able to incorporate significant amounts of both H₂O and CO₂ within its structural channels, as well as other molecular species, such as hydrocarbons (Zimmermann 1981, Mottana *et al.* 1983, Khomenko and Langer 1999), Ar (Armbruster 1985, Schreyer 1985), N₂ (Armbruster, 1985) and CO (Khomenko and Langer, 2005). Provided these channel constituents are preserved during the mineral equilibration and its subsequent geological history, their content can be used to constrain the volatile composition (particularly with respect to H₂O and CO₂) of coexisting fluids or melts during crystallisation (e.g. Vry *et al.*, 1990, Harley *et al.*, 2002). The incorporation and orientation of H₂O and CO₂ in cordierite has been the object of a large number

of studies, using a large variety of techniques, including optics (Armbruster and Bloss, 1982), X-ray and neutron diffraction (Cohen *et al.* 1977, Armbruster and Bürgi 1982, Armbruster 1985), proton NMR spectroscopy (Carson *et al.* 1982), thermogravimetry (Sugiura, 1959), secondary ion mass spectrometry, SIMS (Harley *et al.* 2002), confocal micro-Raman spectroscopy (Kaindl *et al.* 2006) and ab-initio molecular calculations (Winkler *et al.* 1994). Most of these studies have been however done using infrared (IR) spectroscopy (Farrell and Newnham 1967, Goldman *et al.* 1977, Aines and Rossman 1984, Le Breton 1989, Kolesov and Geiger 2000a, Khomenko and Langer 2005). In fact, this technique, when coupled with Raman spectroscopy, is able to unambiguously locate the volatile molecules within the structural pores and to clarify their interaction with the silicate framework; if properly calibrated it is a rapid and relatively easy tool to characterise volatiles in cordierite. IR spectroscopy in fact requires only small amounts of material, namely few milligrams for powder analysis (Vry *et al.* 1990) and small (few tenths of μm across) grains for single-crystal analysis. Despite the numerous efforts, however, several problems still persist, especially regarding the location and behaviour of the H₂O molecules within the channels. This point is crucial when attempting to use spectroscopy as an analytical tool for cordierite in petrological studies, because any calibration for quantitative purposes must be based on unambiguous assignments of the measured absorptions.

In this paper we describe a new finding of cordierite in an unusual occurrence, and provide its complete characterisation combining microchemistry, single-crystal structure refinement, and FTIR analysis.

DESCRIPTION OF THE SAMPLE

The examined sample was collected by one of us (D. Di Domenico) within the explosive pyroclastic deposit known in literature as “tufi caotici” which is characteristically found at the base of the Mt. Sassetto ignimbritic formation (Negretti 1962). The sampled rock in particular outcrops in a quarry at Colle dello Spizzicatore, Allumiere Community, Tolfa volcanic center (Latium, Italy). The studied deposit of “tufi caotici” consists of accumulated

ejected blocks, from centimetric to metric in dimension, cemented by a fine-grained glassy ash. Several types of rocks occur in the deposit; there are fragments of ignimbrites which show, under the polarizing microscope, a glassy groundmass with K-feldspar, labradoritic plagioclase, biotite, ortho- and clino-pyroxene as main phenocrysts. Other holocrystalline tephra have a syenitic appearance and are constituted by dominant K-feldspar and plagioclase, with minor pyroxene and biotite; common accessories are rutile and zircon (Negretti 1962). The host rock where the studied cordierite occurs, is found as blocks with dimensions up to 1 meter and appears as very fine-grained holocrystalline type. Studied with a polarising microscope, the studied ejectum shows a fine-grained texture and consists of an aggregate of dominant quartz plus K-feldspar containing ~ 5% (visual estimation) gem-quality cordierite prisms with a typical bluish colour in plane-polarised reflected light (Fig. 1a). An early metamorphic paragenesis is recognized, which is characterised by garnet (almandine) + biotite + staurolite + alkali-feldspar + quartz (Fig. 1b), corresponding to middle crust metamorphic conditions (5-7 kbars); these early metamorphic phases are highly corroded and replaced by cordierite, aluminous spinel and abundant plagioclase. Cordierite crystal cores often enclose euhedral spinel, ilmenite and quartz (presumably the reaction products of an ancient biotite, Fig. 1a), often coexisting with monazite and pyrrhotite droplets. The fine-grained matrix is composed of euhedral and locally zoned plagioclase (100 μm across), abundant graphite flakes, accessory minerals (ilmenite) and numerous vugs and vesicles (fusion melts?) that are now decorated by smectitic minerals. Graphite preferentially precipitated inside these vugs and at triple junctions of plagioclase crystals, yet it may occasionally be observed as inclusions in cordierite crystal rims. The cordierite crystals used for X-ray and spectroscopic data collection occur as well-developed, euhedral prismatic dark-blue coloured crystals, up to 2 mm in length.

EXPERIMENTAL METHODS

Microprobe analyses were done using a CAMEBAX 50X WDS-microprobe, at Camparis,

Université Paris VI. Operating conditions were 15 kV accelerating voltage and 15 nA beam current, with a beam size of 5 μm ; counting time was 10 sec on both peak and background. Standards, spectral lines and crystals used were: diopside ($\text{SiK}\alpha$, TAP; $\text{MgK}\alpha$, TAP; $\text{CaK}\alpha$, PET), orthoclase ($\text{AlK}\alpha$, TAP; $\text{KK}\alpha$, PET), albite ($\text{NaK}\alpha$, TAP), Fe_2O_3 ($\text{FeK}\alpha$ LIF). Analytical errors are 1% rel. for major elements and 5% rel. for trace elements. Data reduction was done using the PAP method (Pouchou and Pichoir, 1985).

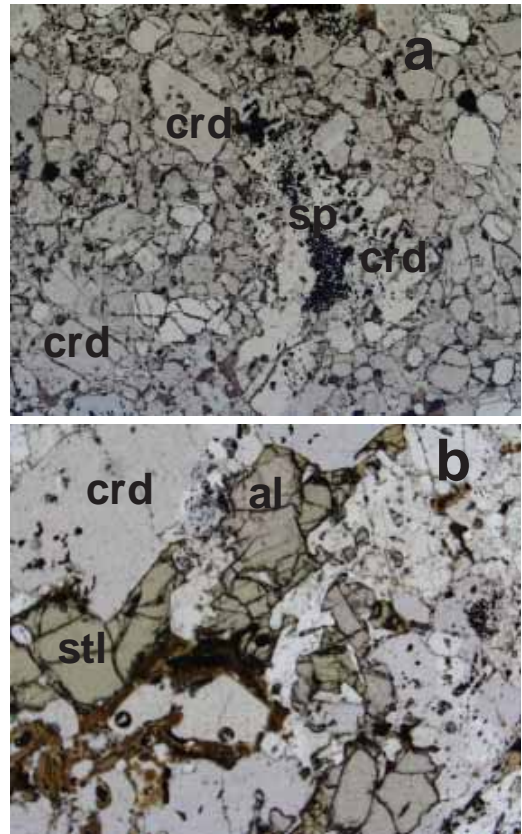


Fig. 1 – Thin section microphotograph of the studied sample, fieldwidth 5 mm. (a) a general view showing the large cordierite (crd) crystals in a quartz-feldspar groundmass. Near the center there is a concentration of spinel (sp) and cordierite, a typical assemblage after early biotite; the black spots are graphite. (b) the assemblage staurolite (stl) + almandine (al) + cordierite.

A crystal of $0.275 \times 0.150 \times 0.120$ mm was examined with a Bruker AXS SMART Apex single-crystal diffractometer with a 4 cm crystal-to-detector distance and graphite-monochromatised $\text{MoK}\alpha$ X-radiation at 50 kV and 35 mA. Three-dimensional data were integrated and corrected for Lorentz, polarisation and background effects using the SAINT+ software version 6.45a (© Bruker AXS). Unit-cell dimensions (Table 1) were calculated from least-squares refinement of the position of all collected reflections. Frame widths of 0.2° in ω were used to collect 840 frames per batch in four batches at different ϕ values (0° , 90° , 180° and 270°) collected at $2\theta = -40^\circ$. Counting time per image was 5 s. A total of 12537 reflections was collected in the θ range 2.4 – 38.0° , corresponding to 2231 unique reflections ($R_{\text{int}} = 2.4\%$). Raw intensity data were corrected for absorption using the SADABS v. 2.03 program (Sheldrick 1996).

Single-crystal, polarized-light FTIR spectra were collected using a Nicolet Magna 760 spectrophotometer equipped with a NicPlan microscope, a KBr beamsplitter, a liquid nitrogen-cooled MCT detector. Nominal resolution was 4 cm^{-1} , and 128 scans were averaged for each spectrum. Single slabs of cordierite were cut from crystals oriented using the external morphology as a guide and checking the orientation using a polarising microscope. Two sections, one // $[001]$ and a second $\perp [001]$ were ground and doubly polished to a thickness of 110 and 150 μm , respectively. Thickness was determined with a micrometer and checked with the optical microscope using standard slabs with known thickness as reference. Polarised spectra were collected using a gold-wire grid polariser on a ZnSe substrate. The α , β and γ spectra were collected orienting the slices by optical microscopy. The optic orientation of cordierite is well known (e.g. Armbruster *et al.* 1982) and is $a = \gamma$, $b = \beta$ and $c = \alpha$, therefore the optical directions could be unambiguously transformed into crystallographic directions. Hence we will use throughout the text the crystallographic notation to discuss the orientation of the H_2O and CO_2 molecules obtained from the polarisation behaviour of the absorbers.

CHEMICAL COMPOSITION

The average of 12 point analyses and the mineral formula calculated on the basis of 18 oxygen atoms are reported in Table 2. The examined cordierite from Allumiere has an intermediate Mg/Fe composition [$X_{\text{Mg}} = \text{Mg}/(\text{Mg}+\text{Fe}) = 0.58$] and is very low in alkali ($\text{Na} + \text{K} = 0.042$ apfu), with $\text{K} > \text{Na}$ (Table 2). Enrichment in K in cordierites is considered a signal for high-T and low-P crystallisation conditions (Schreyer 1985), in agreement with the provenance of the sample under investigation (see below). Whereas the Al content is exactly 4.0 apfu, the Si content is 4.95 apfu, suggesting partial solid solution with Fe^{2+} in the tetrahedra. The remaining Fe^{2+} content (0.024 apfu) is assigned to the channels; however, the refined site-scattering within the channels is lower than that corresponding to excess Fe^{2+} , suggesting that the latter may be an analytical artefact. Another possible model is to consider some Fe

TABLE 1 – Crystal data and selected refinement results for the studied crystal of cordierite from Allumiere.

Wavelength	0.71073 Å
Space group	Cccm
a (Å)	17.1580(6)
b (Å)	9.7573(3)
c (Å)	9.3228(3)
Volume (Å ³)	1560.78(9)
Crystal size (mm ³)	$0.275 \times 0.150 \times 0.120$
θ range	2.4 to 38.0° .
Index ranges	$-17 \leq h \leq 29$ $-14 \leq k \leq 16$ $-15 \leq l \leq 16$
Reflections collected	15080
Independent reflections	2231
R_{int} (%)	2.4
Completeness	99.9%
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2231 / 1 / 84
Goodness-of-fit on F^2	1.134
R indices [$I > 2\sigma(I)$] $R1$ (%)	2.1
$wR2$ (%)	6.1
R indices (all data) $R1$ (%)	2.2
$wR2$ (%)	6.3
Extinction coefficient	0.0042(3)
Largest diff. peak and hole (e.Å ⁻³)	0.54 -0.36

TABLE 2 – EMP analyses (average of 12 point analyses) and chemical formula on the basis of 18 oxygen atoms for the studied crystal of cordierite from Allumiere.

SiO ₂	48.56	Si	4.951
Al ₂ O ₃	33.29	Fe ²⁺	0.048
FeO	10.18	Al	4.001
MgO	7.92	Σ T	9.000
CaO	0.03	Fe ²⁺	0.796
Na ₂ O	0.05	Mg	1.204
K ₂ O	0.25	Σ M	2.000
TOTAL	100.28	Na	0.009
XMg	0.58	Ca	0.003
s.s. M _o	34.98	Fe ²⁺	0.024
s.s. M _c	35.14	Σ Ch	0.069

NOTE: s.s. = calculated site scattering at the M sites in electrons per formula unit (epfu), o = observed (XRD) c = calculated (from chemical formula).

as Fe³⁺, coherently with the strong pleochroism observed in the sample under investigation. We have no spectroscopic evidence on the oxidation state of iron, but previous work has shown that Fe³⁺ is rather uncommon in natural cordierites (Geiger *et al.* 2000, Malcherek *et al.* 2001), and thus we considered all Fe to be in the divalent state.

The rather high analytical total is in agreement with the fact that the mineral is virtually H₂O-free (0.02 apfu) and contains 0.22 apfu CO₂ (see below).

STRUCTURE REFINEMENT AND DESCRIPTION

The structure of cordierite from Allumiere was refined in space group *Cccm* starting from the atom coordinates of the Fe-rich cordierite crystal 8 of Malcherek *et al.* (2001) and using SHELXS 97 (Sheldrick 1997). Isotropic displacement factors were used in the first cycles with a model free of any cation or molecule within the structural channels. Two electron density maxima were identified in the difference-Fourier maps. One maximum at $z = 0.156$ was interpreted as the K atom [considering the chemical composition from the EMP analyses and in agreement with the findings of Daniels (1992) for potassium-rich cordierite]. Another maximum was found within the channels at $z = 0.25$, a position compatible with

CO₂ and H₂O molecules, but also with the excess Fe²⁺ located within the cages. These maxima were added to the model; their coordinates were allowed to vary in the following cycles, but their displacement parameters were kept fixed. At this point, a [001] projection of the difference-Fourier maps at $z = 0.25$ revealed a rod-like shape with two weak maxima at ca. 1 Å from the maximum at (0,0,0.25) and oriented along [100]. These features are compatible with the two oxygen atoms of a CO₂ group. The coordinates of these maxima were added to the model and kept fixed during the last cycles of structure refinement. Their occupancy and displacement parameters were constrained to be equal to those of the C atom. The atomic displacement parameters were converted to the anisotropic form in the last cycles for all atoms but those within the channel. The refinement converged to $R_{\text{all}} = 2.1\%$ and $wR2 = 6.1\%$. Final coordinates and displacement parameters are reported in Table 3, selected bond distances are reported in Table 4 and observed and calculated structure factors are reported in Table 5 (which can be obtained upon request from the authors).

Cordierite from Allumiere has the low-cordierite structure, with Al and Si ordered to obey the Löwenstein's rule (Löwenstein 1954). The observed <Al1-O> and <M-O> distances (1.753 Å and 2.126 Å, respectively; Table 4) agree well with the value expected from the correlations derived by Malcherek *et al.* (2001) as a function of the Mg content. The Al content is exactly 4.0 apfu, and the Si contents is slightly < 5 apfu. Thus some Fe²⁺ (0.05 apfu) is present at the tetrahedral sites. In principle, also Mg could be hosted at the tetrahedral sites; however, this model would worsen the agreement between the site-scattering values refined at the M site and those calculated from the chemical formulae reported in Table 2.

Malcherek *et al.* (2001) showed that natural cordierites show a nearly constant <Si16-O> values, around 1.628 Å, and have some Al excess, which is likely ordered at the Si16 site. The cordierite from Allumiere has the same <Si16-O> value (1.628 Å), but the Al content is stoichiometric; we thus suggest that tetrahedral Fe²⁺ is ordered at the Si16 site. Accordingly, this site has the higher distortion parameters in Table 4.

TABLE 3a – Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for cordierite from Allumiere. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
M	3375(1)	0	2500	8(1)
Al11	2500	2500	2501(1)	8(1)
Si16	0	5000	2500	7(1)
Si21	1915(1)	782(1)	0	6(1)
Si23	1349(1)	-2363(1)	0	7(1)
Al26	503(1)	3072(1)	0	7(1)
O11	2460(1)	-1033(1)	3584(1)	10(1)
O16	617(1)	-4156(1)	3489(1)	10(1)
O13	-1733(1)	-3085(1)	3581(1)	10(1)
O26	435(1)	-2490(1)	0	14(1)
O21	1217(1)	1847(1)	0	14(1)
O23	1637(1)	-787(1)	0	14(1)
KCh	0	0	1550(50)	30
OCh	619	0	2500	90(30)
CCh	0	0	2500	90(30)

TABLE 3b – Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for cordierite from Allumiere.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
M	7(1)	7(1)	10(1)	0(1)	0	0
Al11	9(1)	7(1)	7(1)	0	0	1(1)
Si16	7(1)	8(1)	7(1)	0	0	0
Si21	7(1)	6(1)	7(1)	0	0	0(1)
Si23	6(1)	7(1)	7(1)	0	0	-1(1)
Al26	6(1)	7(1)	7(1)	0	0	1(1)
O11	13(1)	9(1)	9(1)	-1(1)	3(1)	-1(1)
O16	9(1)	12(1)	10(1)	-4(1)	0(1)	-2(1)
O13	10(1)	11(1)	9(1)	-2(1)	-2(1)	2(1)
O26	7(1)	17(1)	18(1)	0	0	-2(1)
O21	11(1)	12(1)	18(1)	0	0	5(1)
O23	15(1)	7(1)	19(1)	0	0	-3(1)

NOTE: the exponent of the anisotropic displacement factor has the form: $-2\pi^2[h^2a^2U^{11} + \dots + 2hkab^*U^{12}]$.

The z coordinate of the K atom within the channel was refined to 0.156(4), yielding a six-fold coordination within 3.26 Å (Figure 2).

A projection onto (001) of the difference $[F_o - F_c]$ Fourier map drawn at $z = 0.25$, obtained after removing from the model all the atoms in the channel, shows significant cation disorder. The low occupancies of (Na, K) and molecules (H_2O and CO_2) within the channels do not allow a reliable interpretation of the Fourier maps. The refined

site-scattering value is compatible with 0.03(2) CO_2 pfu (corresponding to ~0.20 wt%); although considering the high error associated to site occupancy this estimate is in very good agreement with the spectroscopic data (see below).

In the examined sample, the distortion index (Selkregg and Bloss 1980) calculated for the channels is high ($\Delta = 0.282$). This parameter depends on the degree of Al-Si order and the chemical composition; considering the high Fe-content and the low Na and H_2O contents (which raises and lower the distortion index, respectively), and taking into account the X_{Mg} ratio, the observed value implies some degree of Al-Si-Fe²⁺ disorder.

SINGLE-CRYSTAL POLARIZED-LIGHT FTIR SPECTROSCOPY

Figure 3 shows the polarised spectra of the studied sample, collected along the three optical directions, where the regions due to the absorption of H_2O molecules and C-O species within the structural channels are indicated. All the bands observed in these regions show a clear and strong polarisation, which will be discussed in details below. The immediate information from Figure 3 is, however, that in the examined cordierite from Allumiere CO_2 is by far dominant over H_2O as channel occupant. Note the periodic noise (interference fringes: Shinoda and Aikawa 1993) which is superimposed to the spectra and which is due to the reduced crystal thickness.

The H_2O region (3900-3400 cm^{-1})

The polarised spectra collected in the H_2O region (Figure 4) show a very sharp and intense band at 3708 cm^{-1} which is strongly polarised for $\mathbf{E} // a$; along this direction it has maximum integral absorption $A_{\text{max}} = 0.514 \text{ cm}^{-1}$. For $\mathbf{E} // b$ its intensity is extremely reduced ($A = 0.067 \text{ cm}^{-1}$), and for $\mathbf{E} // c$ the band disappears completely (Figure 4). A second broad, possibly composite absorption, is observed at around 3595 cm^{-1} . This absorption has maximum intensity ($A_{\text{max}} = 0.998 \text{ cm}^{-1}$) for $\mathbf{E} // b$, and reduced intensity for $\mathbf{E} // a$ ($A = 0.213 \text{ cm}^{-1}$); it almost disappears for $\mathbf{E} // c$. Finally, a broad bands is observed at 3545 cm^{-1} which appear to be completely polarised for $\mathbf{E} // c$.

TABLE 4 – Selected bond distances and geometrical parameters for the studied crystal of cordierite from Allumiere.

M-O11 ×2	2.122	(1)	Al11-O11 ×2	1.754	(1)	Al26-O16 ×2	1.772	(1)
O16 ×2	2.126	(1)	O13 ×2	1.753	(1)	O26	1.707	(1)
O13 ×2	2.131	(1)	<Al11-O>	1.753		O21	1.712	(1)
<M-O>	2.126		V(Å ³)	2.59		<Al26-O>	1.741	
V(Å ³)	12.00		TAV*	170.15		V(Å ³)	2.69	
OAV*	139.70		TQE*	1.046		TAV*	14.18	
OQE*	1.045					TQE*	1.003	
Si16-O16 ×4	1.628	(1)	Si21-O11 ×2	1.636	(1)	Si23-O13 ×2	1.637	(1)
V(Å ³)	2.14		O21	1.586	(1)	O26	1.573	(1)
TAV*	83.96		O23	1.604	(1)	O23	1.615	(1)
TQE*	1.021		<Si21-O>	1.615		<Si23-O>	1.616	
			V(Å ³)	2.16		V(Å ³)	2.16	
K-O26 ×2	2.92	(2)	TAV*	4.81		TAV*	7.10	
O21 ×2	3.11	(2)	TQE*	1.001		TQE*	1.002	
O23 ×2	3.25	(2)						
<K-O>	3.096		CCh-OCh	1.06				

* Conventional distortion parameters from tetrahedral and octahedral geometry from Robinson *et al.* (1971).

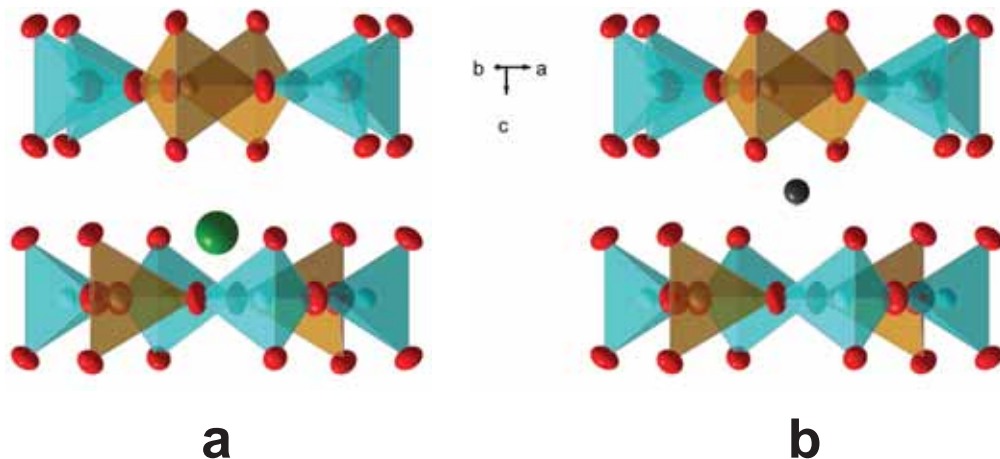


Fig. 2 – Detail of the coordination of the cations occurring within the channels: (a) K, (b) CO₂. Orange tetrahedra = Al; sky blue tetrahedra = Si; green sphere = K; black sphere = C.

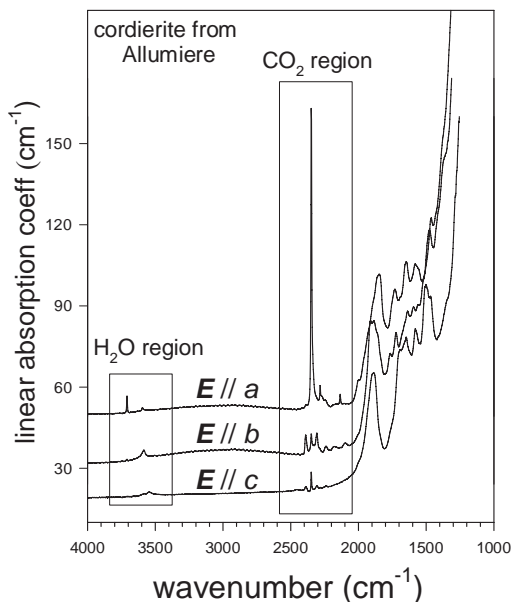


Fig. 3 – Single-crystal FTIR spectra for the studied cordierite from Allumiere, collected with the electric vector (E) along the three optical directions. The $E // a$ and $E // b$ spectra were collected on oriented (001) doubly-polished section, 110 μm thick, while the $E // c$ spectrum was collected on a (hk0) section, 152 μm thick. The spectra are plotted with the same absorbance scale, normalised to the thickness. The linear absorption coefficient is defined as a/t , in cm^{-1} , where a = absorbance and t = thickness (Libowitzky and Rossman, 1996). The principal absorption regions for H_2O and CO_2 , respectively, are indicated.

The spectroscopic literature on the orientation of the H_2O molecules within the structural channels of cordierite is extensive but rather contradictory. Farrell and Newnham (1967) found that the H_2O molecules in cordierite lie in the (010) crystal plane with the H...H vector parallel to the channel axis [001]. Goldman *et al.* (1977), on the basis of the close similarities with beryl, recognised the existence of two types of H_2O molecules in cordierite, which they labelled type I and type II, following the nomenclature of Wood and Nassau (1967) for beryl. In their model, the molecular plane of both types of H_2O is located in the (100) plane, but the orientation of their H...H vector is different, being parallel to [001] for type I and perpendicular to [001] for type II H_2O . It is worth to be noted that this interpretation has remained

unchallenged until the last years, and that in all petrological works where the infrared spectra are used to quantify H_2O and CO_2 in the sample (Vry *et al.* 1990, Visser *et al.* 1994, Kalt 2000) the spectra are systematically assigned on the basis of this model. Kolesov and Geiger (2000a), studied a set of samples with different volatile compositions and showed that the H_2O orientation in cordierite is much more complex than previously believed. By combining single-crystal polarised Raman and FTIR spectroscopy measurements they concluded that the several bands observed in cordierite can be assigned to two groups of H_2O molecules, labelled class I (three types) and class II (five or more types)

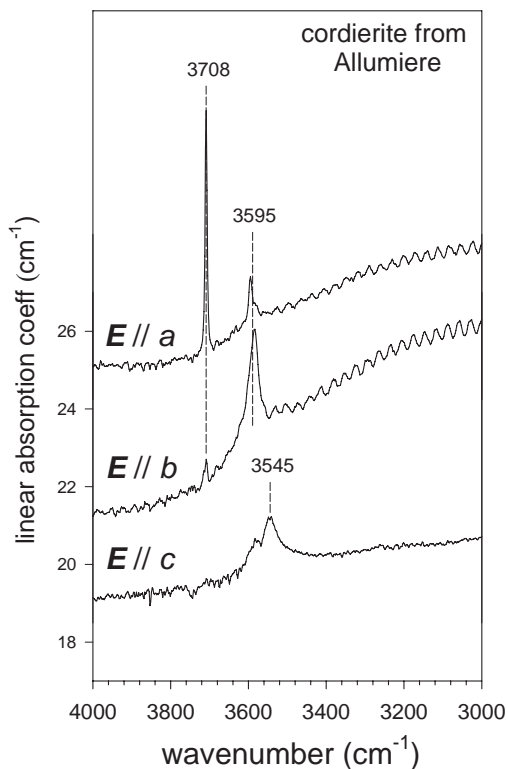


Fig. 4 – Single-crystal FTIR spectra in the OH-stretching region for the studied cordierite from Allumiere, collected with the electric vector (E) along the three optical directions; (001), 110 μm thick, and (hk0), 152 μm thick, doubly-polished, sections. The spectra are plotted with the same absorbance scale. Note the periodic noise which is superimposed to the spectra (interference fringes, Shinoda and Aikawa, 1993).

H₂O. Class I H₂O molecules have no interactions with alkali cations located at 0,0,0. The H...H vector for two of them lies parallel to [001] and their molecular plane is parallel to (010) and (100), respectively. The third type has its H...H vector parallel to [100] and its molecular plane is parallel to (010). Class II H₂O molecules have interactions with the alkali cations located at 0,0,0; their H...H vector is always perpendicular to [001] but their molecular plane may have different orientations around the channel axis. Raman measurements at low T suggest significant dynamical disorder of Class I H₂O molecules with possible hopping between different orientations, in line with the NMR study of Carson *et al.* (1982) which indicates that the H₂O molecules in cordierite hops back and forth with a frequency which is however slow enough to be sampled by infrared radiation.

In the infrared, all internal H₂O vibrations are active; the antisymmetric ν_3 mode is the most intense, whereas the ν_1 symmetric stretching mode is expected to be weak, with an ideal intensity ratio $\nu_3 : \nu_1 \sim 20 : 1$ (Clough *et al.* 1973, Kolesov and Geiger 2000b). The polarisation of the antisymmetric stretching ν_3 gives the direction of the H...H vector directly, whereas the polarisation of the symmetric stretching ν_1 gives the orientation of the molecular plane.

This being the case, the sharp and intense band at 3708 cm⁻¹ (Fig. 4) is assigned to the ν_3 antisymmetric stretching motion of a H₂O molecule in the analysed sample. The polarisation behaviour of this band (Fig. 4) indicates that this H₂O molecule has its H...H vector // *a*. The second band at 3595 cm⁻¹ is assigned to the ν_1 symmetric stretching of this H₂O molecule, as suggested by the intensity ratio $I_{3708} : I_{3595}$. This assignment is also supported by the fact that the difference in wavenumber between the ν_3 and ν_1 modes ($\Delta\nu$) for H₂O in solid inert matrixes is close to 100 cm⁻¹ (e.g. Kolesov and Geiger 2000b), and for the examined sample $\Delta\nu = 113$ cm⁻¹. Such a $\Delta\nu$ value also indicates that the H₂O molecule has very little interaction with the silicate framework, as suggested in previous studies (Langer and Schreyer 1976, Winkler *et al.* 1994). The 3595 cm⁻¹ band is strongly polarised along *b*; therefore the molecular plane of this H₂O molecule is parallel to (001). We cannot complete these information with the polarisation behaviour of the ν_2 bending

motion and the ($\nu_2 + \nu_3$) combination absorptions in the 5500-5000 cm⁻¹ region (also indicative of the orientation of the molecular plane) because due to the low amount of H₂O in the sample these absorptions are too weak (ν_2 bending) or absent ($\nu_2 + \nu_3$ combination).

The above data (ν_3 at 3708 and ν_1 at 3595 cm⁻¹) closely correspond to what Kolesov and Geiger (2000a) classify as "class I, type III" H₂O; except for the orientation of the molecular plane which, in the sample examined here is // (001). In their model, this type of H₂O is not associated with extra-framework cations, but in our case this point is rather ambiguous. Our sample contains small but significant amounts of alkalis (Na + K = 0.04 apfu), hence it seems logical to expect the low amount of H₂O molecules present in the channels to be associated with them. However, given the well-known relationship alkali-cations : H₂O = 1:2 apfu (e.g. Vry *et al.* 1990), 0.04 apfu alkalis would require at least 0.08 apfu H₂O in the sample, and this is not the case (see below). This observation seems to support the conclusion of Kolesov and Geiger (2000a) that "class I, type III" H₂O is not associated with alkali cations within the structural channels. The band at 3545 cm⁻¹ is rather enigmatic at present. Its frequency is lower than any other band assigned so far to water molecules within cordierite; a possible explanation could involve O-H groups hydrogen-bonded to the water molecules and strongly aligned along the *c*-axis, however this interpretation is not confirmed by other evidences.

The C-O region (2500-2000 cm⁻¹)

The location and role of H₂O in the cordierite structure (as well as in the closely related beryl, e.g. Kolesov and Geiger 2000b) are still under debate. In contrast, there is general consensus that the linear CO₂ molecule is preferentially aligned along [100] (a-position) (Armbruster and Bloss 1982, Aines and Rossman 1984, Le Breton 1898, Kolesov and Geiger 2000a, Khomenko and Langer 2005). This orientation is energetically favourable because the width of the cage is longer along the *a* than along the *b* direction (Armbruster 1985). Armbruster and Bloss (1982) also proposed that the cations situated in the channels, as well as a low degree of channel filling, may favour

an orientation of the CO₂ molecule along [001] (c-position); however, this interpretation has been questioned by Mirwald *et al.* (1983).

The **E // a** spectrum in Figure 5 shows a very sharp and intense absorption at 2348 cm⁻¹, with a resolved shoulder at 2330 cm⁻¹ on the low-frequency side. Two minor but significant bands are also observed at 2282 and 2135 cm⁻¹, respectively. The **E // c** spectrum is featureless, and shows also a very minor band at 2348 cm⁻¹, while the **E // b** spectrum shows a minor band at 2348 cm⁻¹ with two side bands at 2389 and 2307 cm⁻¹, respectively. Following the vast spectroscopic literature on cordierite, the most intense band at 2348 cm⁻¹ can be assigned to the ν₃ antisymmetric stretching of the ¹²C¹⁶O₂ molecule (e.g. Khomenko and Langer 2005). The minor bands at 2282 and 2135 cm⁻¹, which are systematically observed in single-crystal and powder spectra of cordierites (e.g. Le Breton 1989), have the same polarisation behaviour as the main band at 2348 cm⁻¹, and should thus be assigned to the same molecular type. This point has been reviewed 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 [100] direction in the crystal. 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 2389 and 2307 cm⁻¹ observed in the **E // b** spectrum is still obscure; 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. The final band assignment is indicated in Figure 5.

QUANTITATIVE ASPECTS AND ANALYTICAL DETERMINATION OF H₂O AND CO₂ IN CORDIERITE

The channel volatile content of cordierite affects significantly its stability and may have profound effects on the mineral reactions and the topology of reaction grids involving cordierite. Therefore, a quantitative evaluation of the H₂O and CO₂ content

of the sample is crucial in petrologic studies where the mineral is used as a P-T tracer. For instance, Schreyer (1985) showed that the stability field of Mg-cordierite is expanded by 3 Kbar due to incorporation of H₂O. In addition, several studies showed that H₂O and CO₂ strongly affect the physical properties of cordierite (Schreyer and Yoder 1964, Medenbach *et al.* 1980, Armbruster and Bloss 1980). To make the plot thicker, there are evidences that the orientation of H₂O into the channels affects the mineral structure: type II H₂O, for instance, drastically decreases the distortion index Δ (Schreyer *et al.* 1979).

The spectroscopic quantitative determination of an absorber in minerals is based on the Beer-Lambert law: $c = a_i / \varepsilon_i$, where a_i = integrated absorption coefficient (defined as absorbance / thickness in cm, A_i/t ; Libowitzky and Rossman 1996), ε_i = matrix specific integrated molar absorption coefficient [$\text{mol}^{-1} \text{cm}^{-2}$], and c = concentration of the absorber (mol l^{-1}). A_i is measured from the FTIR spectrum,

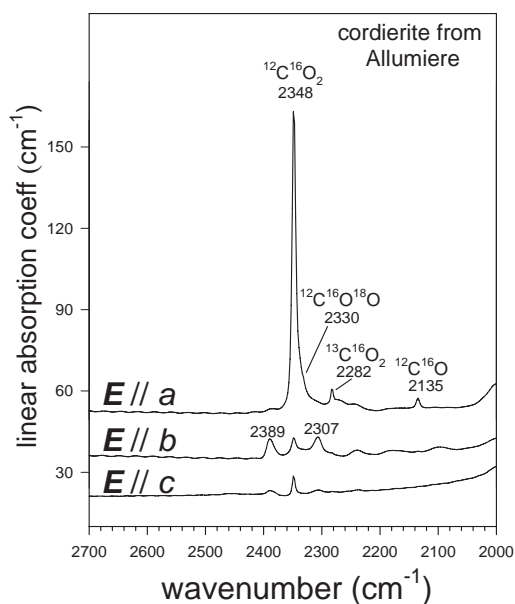


Fig. 5 – Single-crystal FTIR spectra in the principal C-O stretching region for the studied cordierite from Allumiere, collected with the electric vector (**E**) along the three optical directions; (001), 110 μm thick, and (hk0), 152 μm thick, doubly-polished, sections. The spectra are plotted with the same absorbance scale.

but ϵ_i must be calibrated for any type of absorber and for any mineral family. In the case of OH, it can be extracted from working curves such as those of Paterson (1982) or Libowitzky and Rossman (1997). Libowitzky and Rossman (1996) definitely showed that accurate measurement of absorbance in anisotropic materials requires polarised data collection either on three orthogonal sections of a crystal or along two orthogonal sections parallel to the indicatrix axes. The total integrated absorbance A_{tot} is then obtained summing-up the integrated absorbances along the three principal directions. For a trimetric crystal $A_{\text{tot}} = A_x + A_y + A_z$, and for a dimetric crystal $A_{\text{tot}} = 2A_x + A_z$.

Infrared spectroscopy has been widely used in the latest years to quantify H₂O and CO₂ in cordierite for petrological purposes (Vry *et al.* 1990, Visser *et al.* 1994, Kalt 2000), but most of these studies have been based on calibration curves established on powdered samples. However, from the above discussion it turns out that any calibration based on powdered samples (which has a relative internal consistency for sets of samples examined with the same instrumentation and under a fully standardised sample preparation procedure), cannot be extrapolated for other studies. With this respect, the case of cordierite is particularly complex because, as discussed previously, the H₂O region is still not completely understood, and suitable molar absorption coefficients for H₂O and CO₂ are still lacking. Examination of previous studies in fact shows extremely variable ϵ coefficients for both H₂O and CO₂ (see for example Vry *et al.* 1990).

For H₂O, the only available molar absorption coefficient for single-crystal measurements has been calibrated by Goldman and Rossman (1977) using linear (peak height, not peak area) intensity data. They found two very similar values for type I ($\epsilon = 204 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and type II ($\epsilon = 269 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) H₂O, and concluded that, considering the analytical error, both types of H₂O molecules have the same molar absorption coefficient.

For the sample studied here, the H₂O content can be estimated from the spectra of Figure 4, using the equation

$$c(\text{H}_2\text{O}) = a_{3708} \cdot 1.8 / (D \cdot \epsilon) \quad (1)$$

where $c = \text{H}_2\text{O}$ concentration (wt%), $a =$ linear absorbance of the band at 3708 cm^{-1} assigned to

the antisymmetric ν_3 mode of H₂O, $D =$ sample density (g/cm^3) and $\epsilon = 230 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ (average of the two ϵ values from Goldman and Rossman 1977); the factor 1.8 results from the conversion of the H₂O concentration from mol l^{-1} to wt% (Beran *et al.* 1993). The calculated H₂O content in the sample is thus H₂O = 0.02 wt%. Note that if we introduce the intensity of the 3595 cm^{-1} in the calculation, i.e. if we assign part of this composite absorption to the antisymmetric ν_3 mode of an additional H₂O molecule, the error in the bulk H₂O calculation is $< 0.01 \text{ wt}\%$.

The estimation of CO₂ can be done from the spectra of Figure 3 using the equation

$$c(\text{CO}_2 \text{ wt}\%) = a \cdot 4.401 / (D \cdot \epsilon) \quad (2)$$

where 4.401 is the factor needed to convert the concentration of CO₂ from mol l^{-1} to wt%. No ϵ_{CO_2} data are available in the literature for cordierite (and for minerals in general), thus we were forced to use the ϵ_{CO_2} calibrated for aluminosilicate glasses (Fine and Stolper 1985); we tried in equation (2) both the linear $\epsilon = 945 \text{ (litres}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$, and the integrated $\epsilon_i = 25200 \text{ (litres}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2})$ coefficient and obtained CO₂ = 0.22 wt% and 0.09 wt%, respectively. These results are surprisingly different; however the one obtained using the linear absorbance measurements is in excellent agreement with the X-ray diffraction results (see above), suggesting the former procedure to be the more appropriate in the present case. It must be finally noted that if we use the ϵ_{CO_2} coefficient calibrated for powders ($\epsilon_{\text{CO}_2} = 630 \text{ litres}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, Vry *et al.* 1990) we obtain CO₂ = 0.32 wt% in our sample, which is significantly higher when compared to the results obtained above on single-crystals.

CONCLUSIONS

Several experimental studies show that H₂O and CO₂ contents in cordierite are directly correlated with pressure (and Na), and inversely correlated with temperature (Schreyer and Yoder 1964, Johannes and Schreyer 1981, Schreyer 1985) but are independent of the Mg/Fe ratio of the mineral (Boberski and Schreyer 1990). Johannes and Schreyer (1981) equilibrated Mg-cordierite

with a mixed CO₂/H₂O fluid, at 600 °C, 0.5 GPa, and showed that for given bulk CO₂/H₂O ratios, H₂O is strongly partitioned into cordierite, while CO₂ is enriched in the fluid. Thus CO₂-dominant cordierites [the examined sample has $X_{\text{CO}_2} = \text{CO}_2 / (\text{H}_2\text{O} + \text{CO}_2) \sim 0.9$] can only be formed in the presence of extremely CO₂-rich fluids, and this is in line with the occurrence of abundant graphite in the studied rock assemblage. In addition, the absolute values of CO₂ and H₂O in cordierite may allow a rough estimation of the metamorphic conditions; in the present case, despite analytical uncertainties due to lack of suitable calibrations (see discussion above), the volatile content of the examined sample is certainly indicative of high-temperature and low-pressure metamorphic conditions (e.g. Johannes and Schreyer 1981, Harley *et al.* 2002). The observed mineral assemblage points to thermometamorphic effects on a parent metapelite, according to the reaction Mg-Ti biotite = cordierite + hercynite + quartz + ilmenite + H₂O, which occurs for T > 700°C and P ≤ 2 Kbar (Frost 1991). At these conditions the widespread presence of graphite imposes a very low oxygen fugacity, since the assemblage graphite + pyrrhotite + ilmenite is stable for log f_{O₂} = IW + 1-2 log units (Frost 1991). This inference is also in agreement with the presence of carbon-monoxide in the cordierite channels, which is possible only under extremely low oxidising conditions (Schreyer 1985). These conclusions are also coherent with the general genetic model for the particular host rocks where the studied cordierite occur (Di Sabatino and Della Ventura 1982, van Bergen 1983), according to which the studied rock represent fragments of a thermometamorphosed basement underlying the volcanic area at relatively shallow depths.

A final point which is worth to be stressed here is the significant difference in final results which is obtained when quantifying the volatile content in cordierite by spectroscopic methods using molar absorption coefficients calibrated using unsuitable procedures, such as those based on powdered samples. This conclusion definitively suggests that there is the need for properly calibrated ε values for volatiles in cordierite to be used as standard inter-laboratory values, especially when the resulting data are used for petrologic studies or in thermodynamic calculations.

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