

# IR SPECTROSCOPY AND IMAGING AS A TOOL FOR EARTH SCIENCE MATERIALS



**G. Della Ventura**

Dipartimento di Scienze, Università Roma Tre, Roma

INFN-LNF, Via E. Fermi, Frascati, Roma

INGV, Sezione di Roma 1, Via di Vigna Murata 605, Roma

[giancarlo.dellaventura@uniroma3.it](mailto:giancarlo.dellaventura@uniroma3.it)

Laboratorio di Spettroscopia Infrarossa



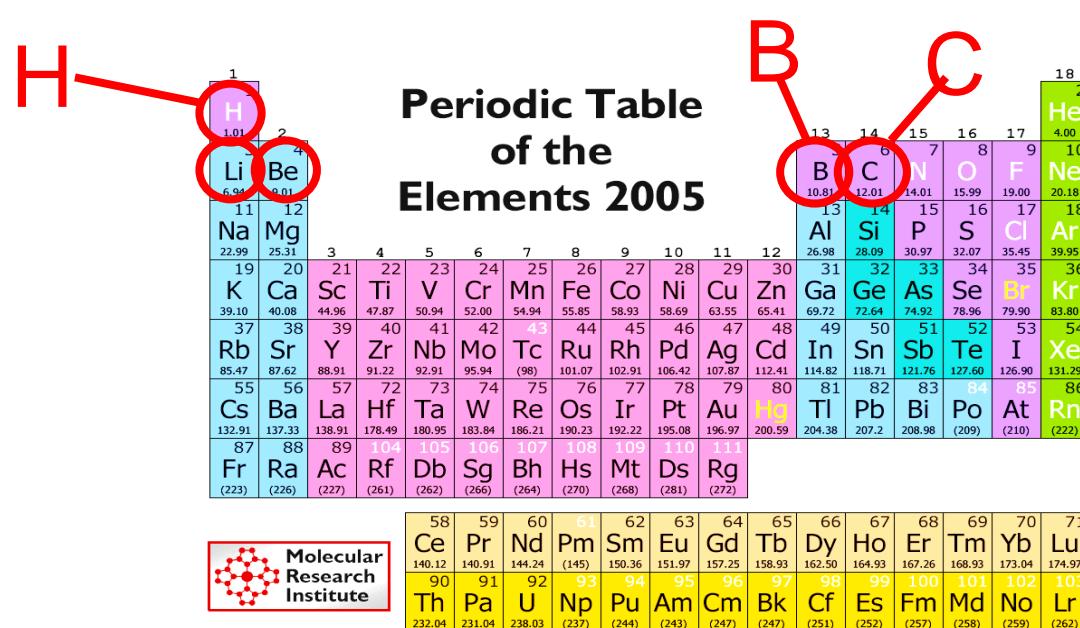
Istituto Nazionale di  
Geofisica e Vulcanologia



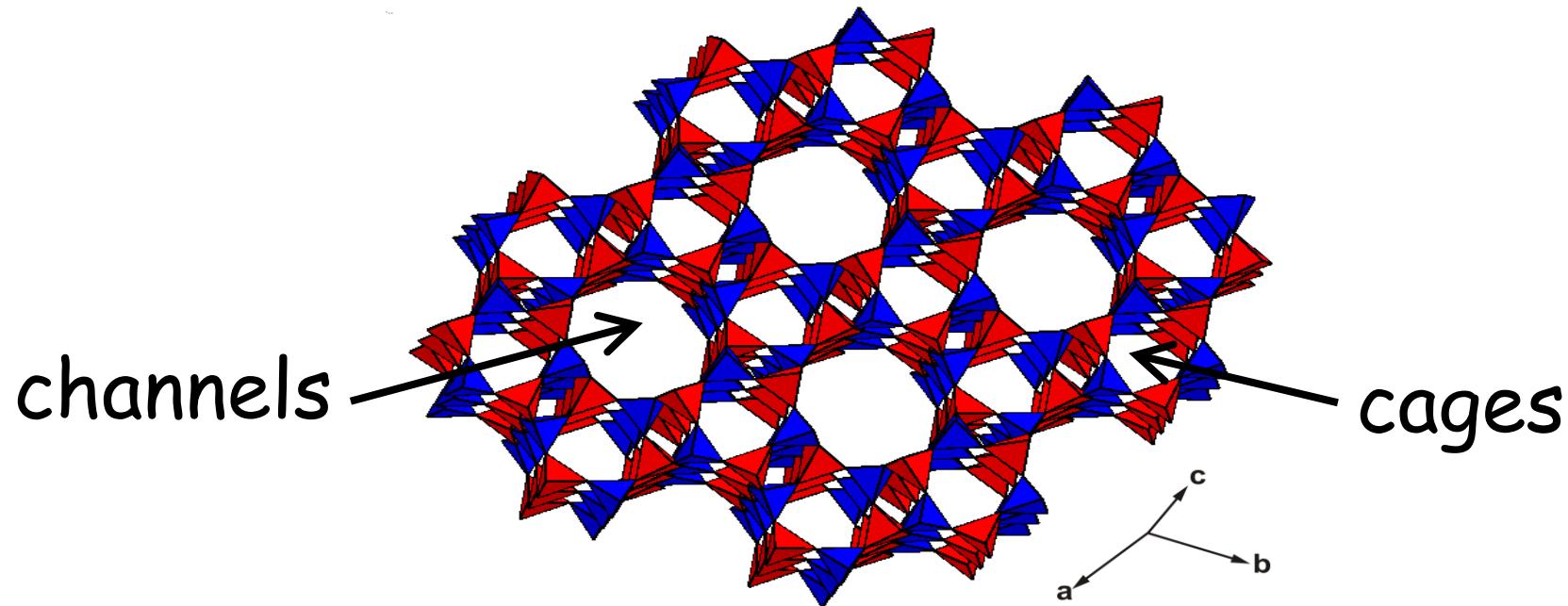
- Spettroscopia FTIR
- Spettroscopia FTIR in luce polarizzata
- Analisi di H e C in minerali, materia organica
- Spettroscopia in HT
- Imaging
- Beni culturali
  - Raggi X (XLAB)
  - Magnetismo

- **Tesi – Tesi di Dottorato**
  - Progetto Vinci, fibre/cellule
  - CO<sub>2</sub> in silicati mesoporosi
  - μCT-X con policapillari
  - Diffusione di H e ossidazione del Fe in silicati fibrosi
- **Progetti PRIN**
  - Cosmic DUST
  - Interazioni biologiche fibre/cellule
- **Progetti vari** (PM10, cementi, nano materiali)
- **Collaborazioni con varie facilities SR:** Diamond (UK), Bessy (D), Hefei + Pechino (Cina), SSRL (USA), ESRF (EU), Trieste (EU)

For earth-science materials, FTIR spectroscopy involves primarily the analysis of light elements



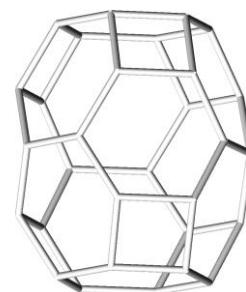
# THE CHANNEL CONSTITUENTS OF CANCRINITE-GROUP MINERALS



The different stacking sequences also give rise to several types of cages and channels which host extra-framework anions and cations



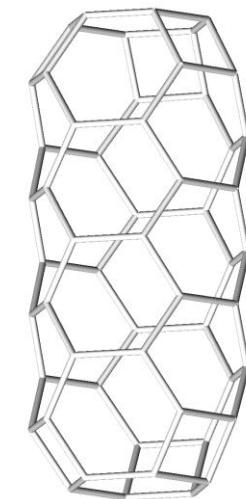
cancrinite cage



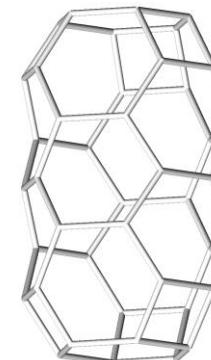
losod cage



sodalite cage

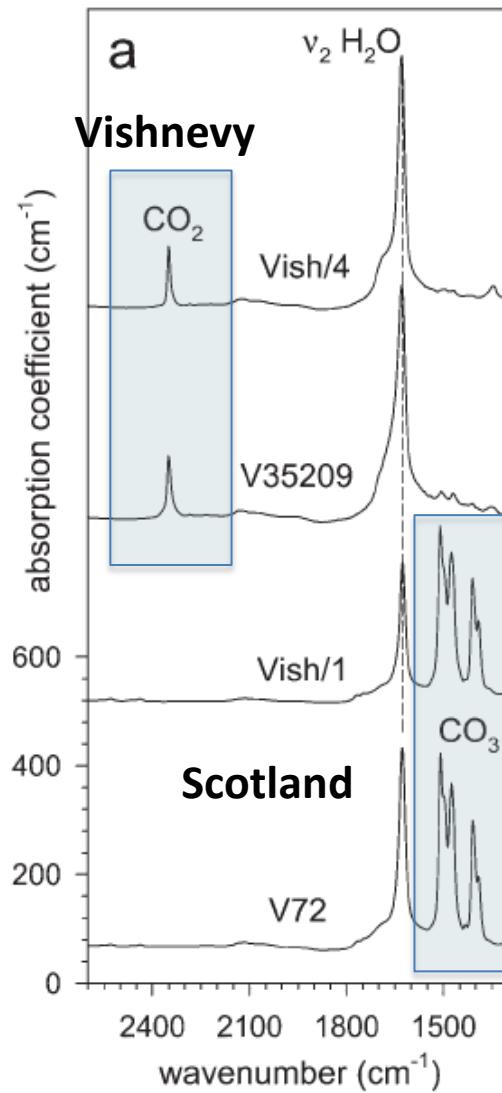


Giuseppettite  
cage

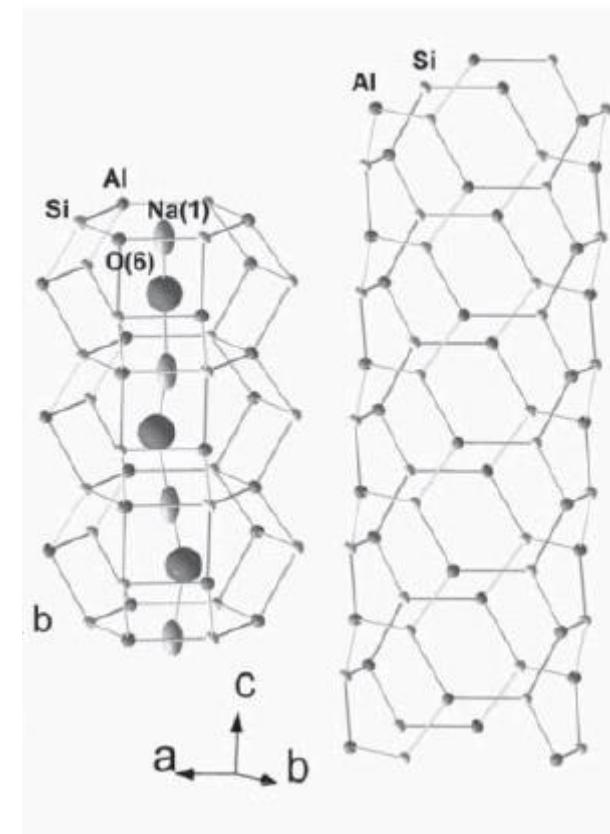


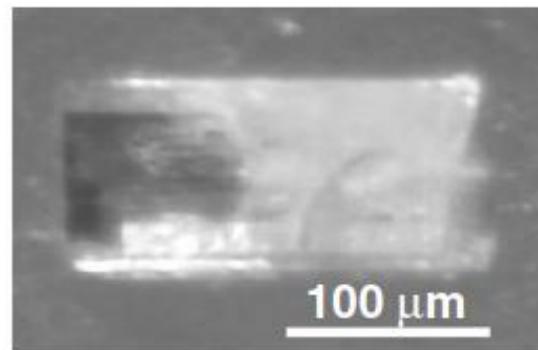
liottite cage

Common anions within the structural channels are  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{O}/\text{OH}$ . The identity of the prevailing anion has been also used for classification purposes (e.g. Hogarth, 1979; Leoni et al., 1979)

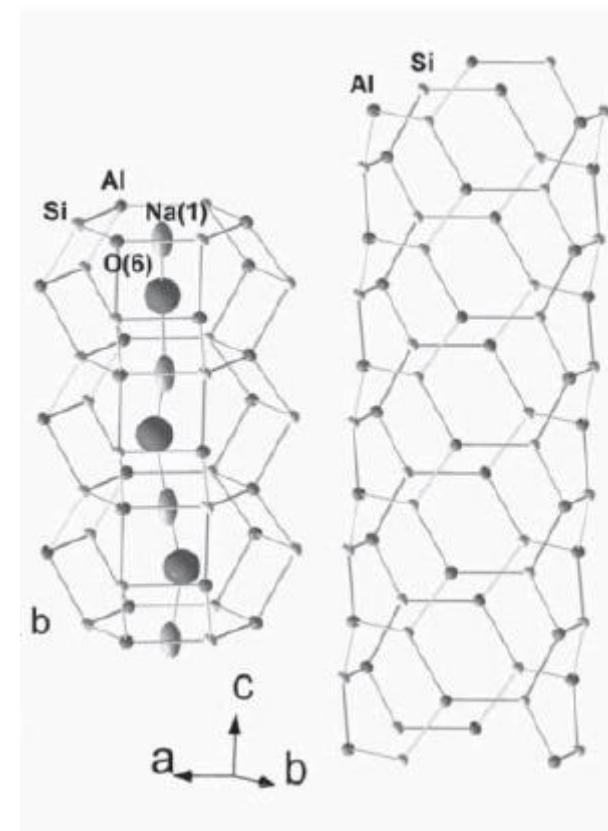
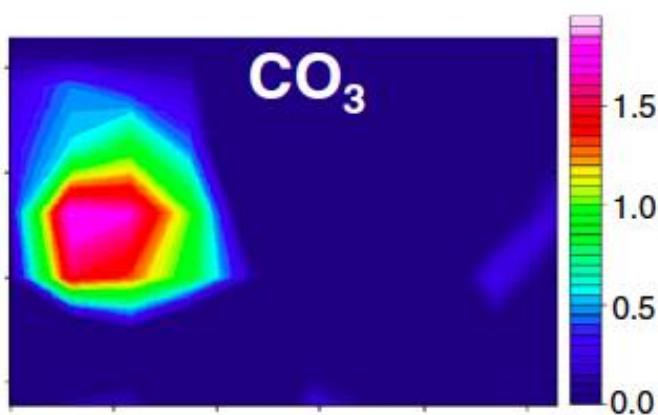
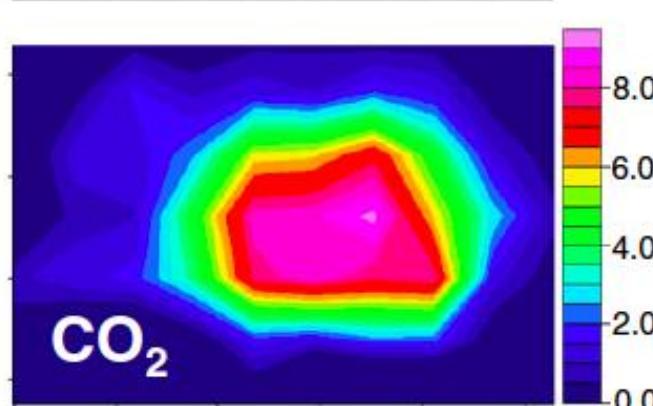


## carbon in cancrinites: vishnevite





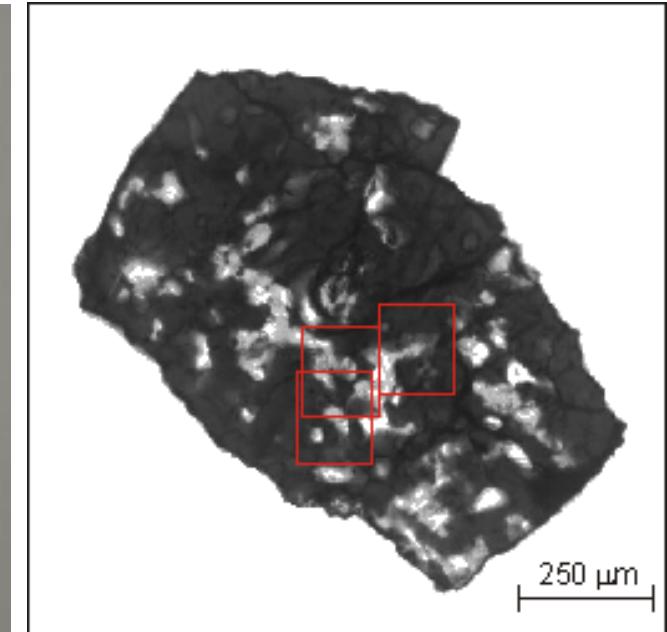
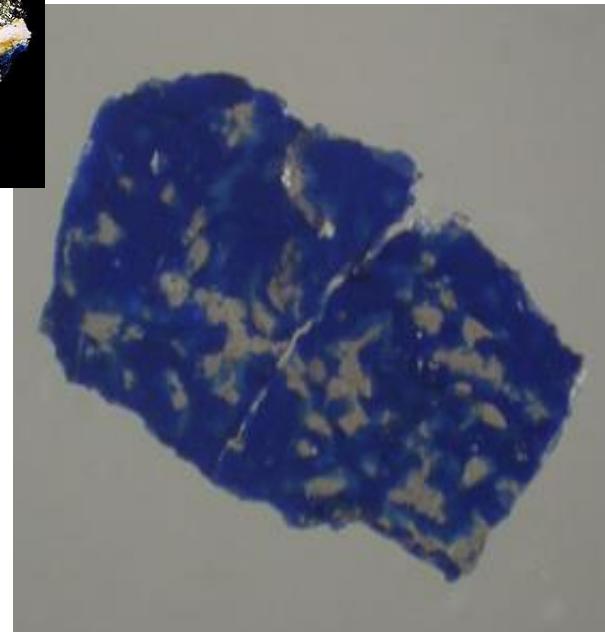
## Mapping of C in vishnevite from Latium

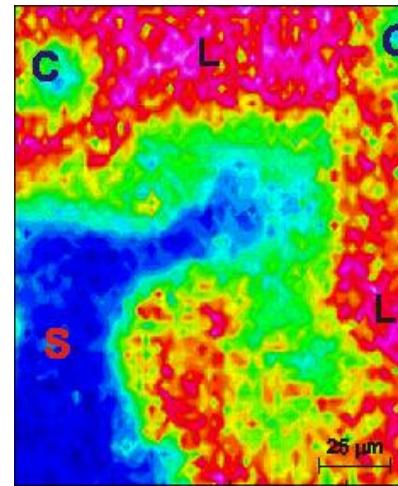
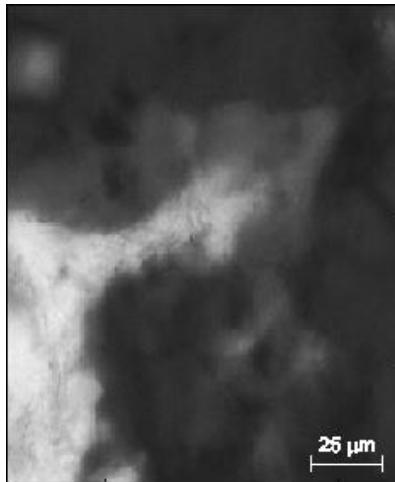




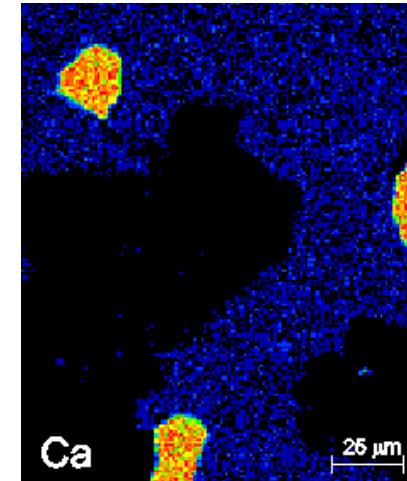
## Imaging of $CO_2$ across lazurite from Sar-e-Sang

XRD + EMPA:  
Lazurite  
Sodalite  
Albite  
Calcite  
dolomite



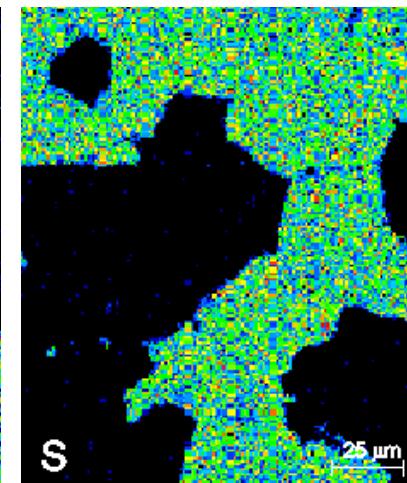
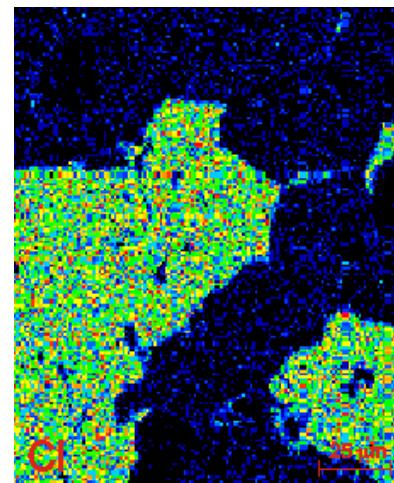


**C = calcite  
L = lazurite  
S = sodalite**



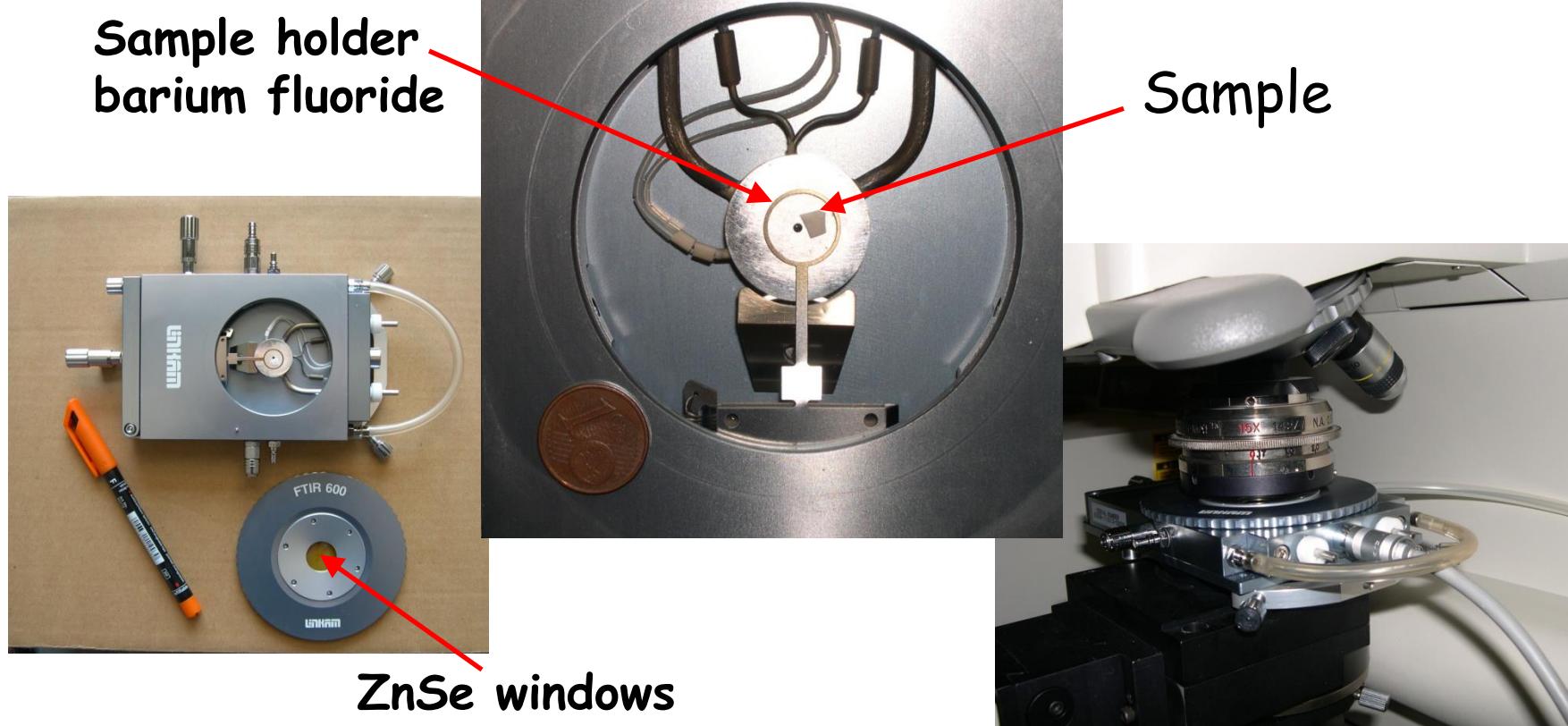
## FTIR maps

## XRF maps



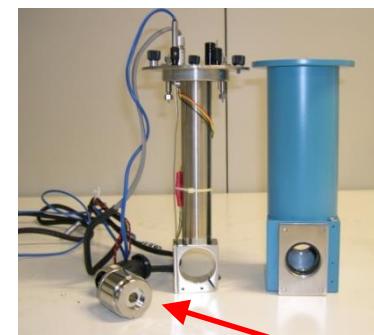
# High-T experiments on single-crystals

Linkam FTIR600 heating stage, range -190 to +600 ° C

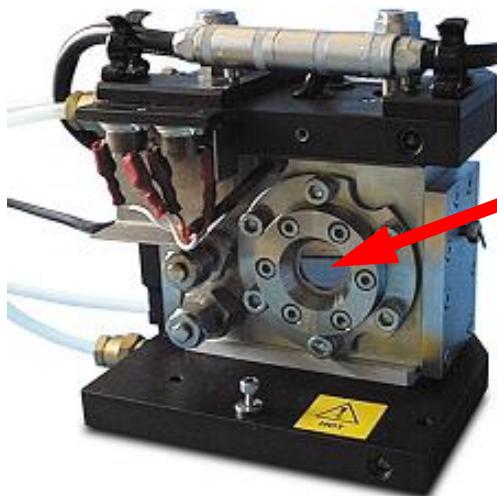


# High-T experiments in the bench

Range from -190 to  
+250 ° C Specac  
microfurnace



microfurnace

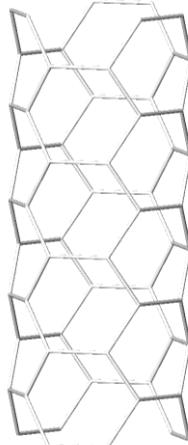
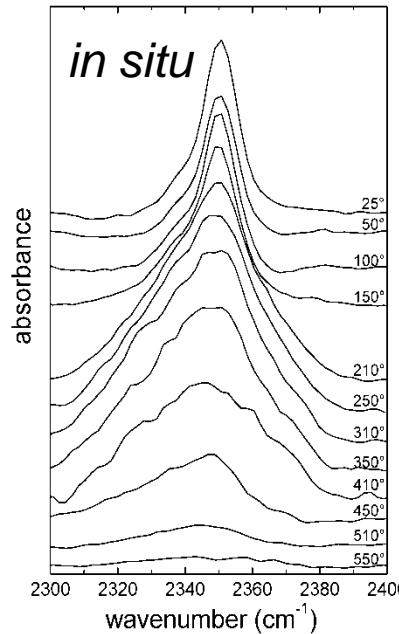
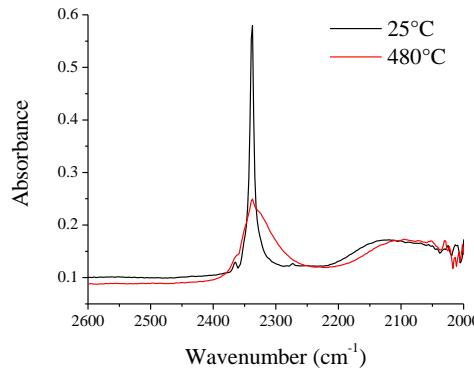


ZnSe windows

Range 25-800 ° C  
high-T/P cell  
Gas pressure to 66 bars

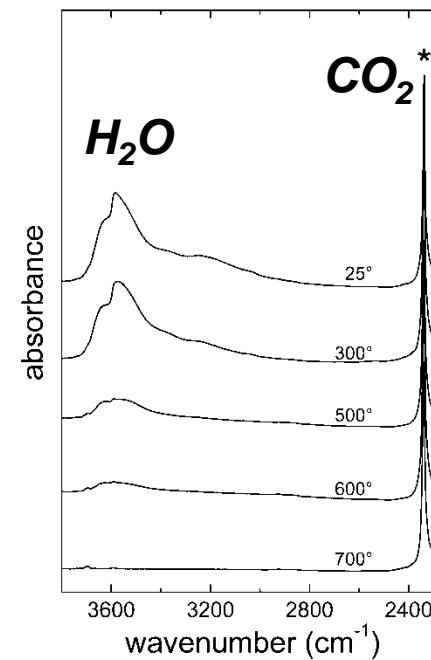


## *in situ* heating FTIR data

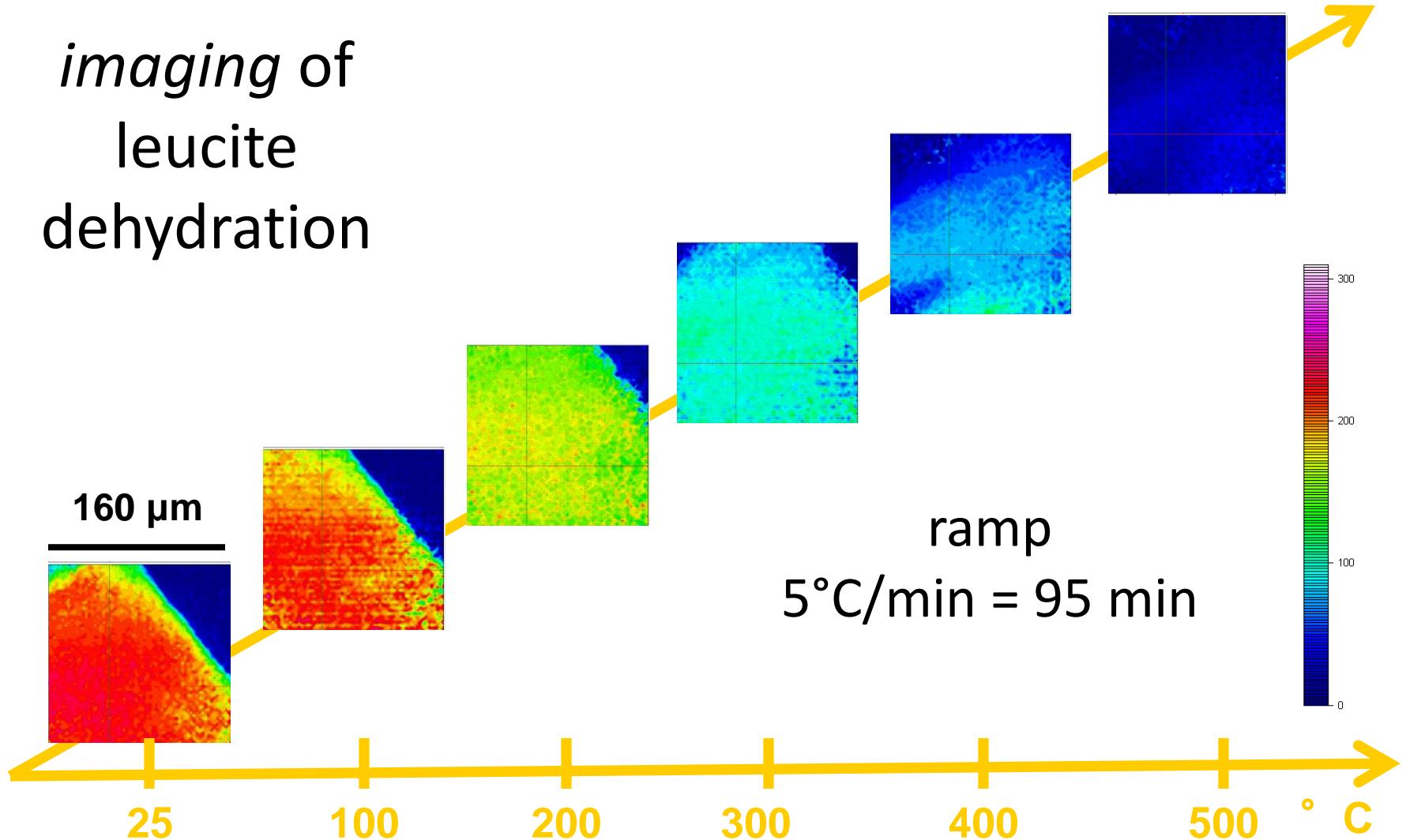


cancrinites:  $\text{CO}_2$  in  
connected pores (channels)

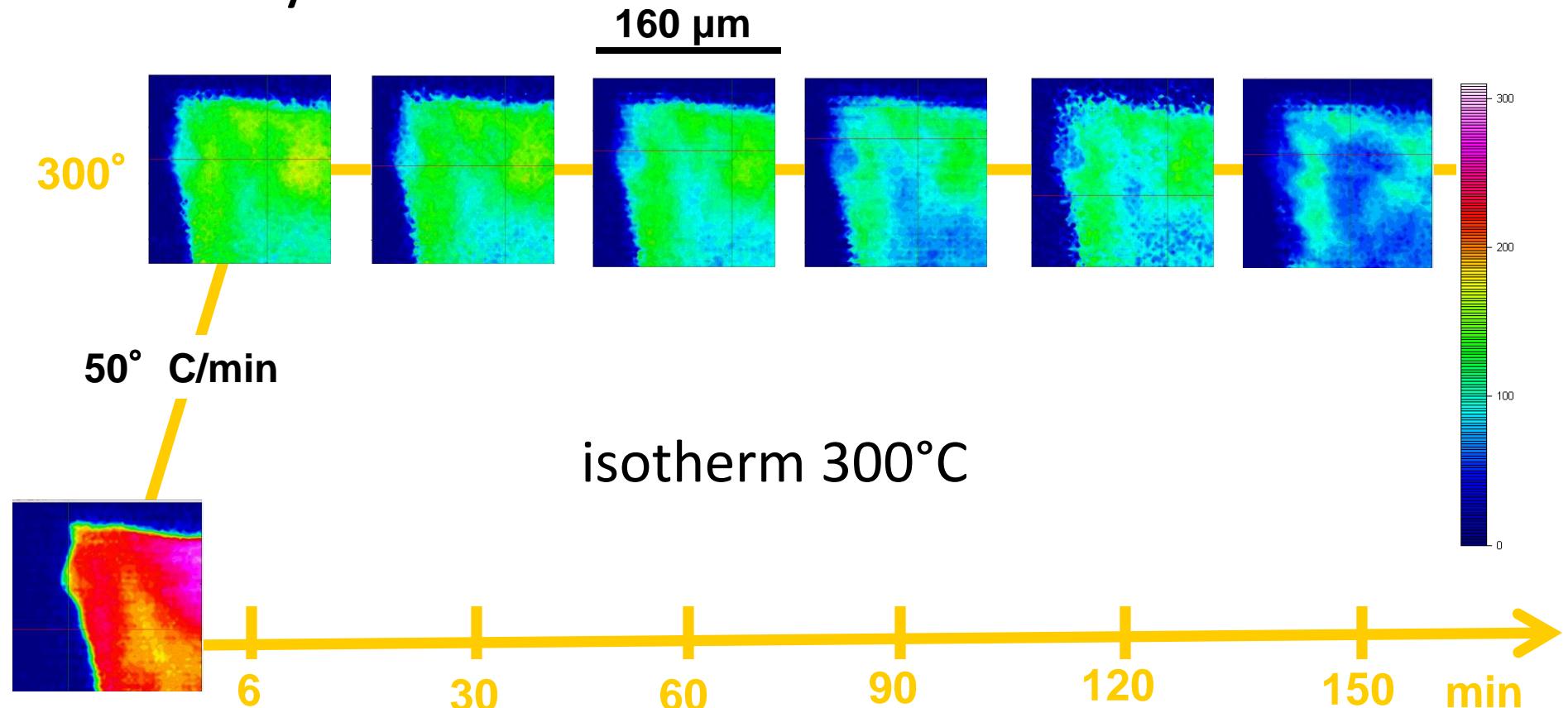
sodalite-type:  
non-connected  
pores (cages)



# *imaging of leucite dehydration*

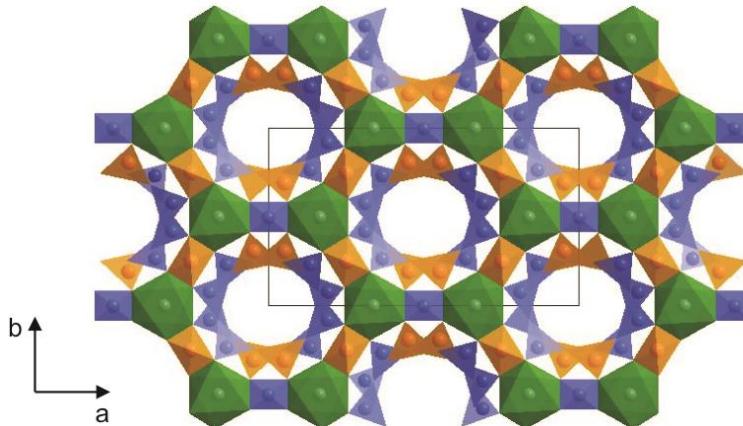


# kinetic of leucite dehydration

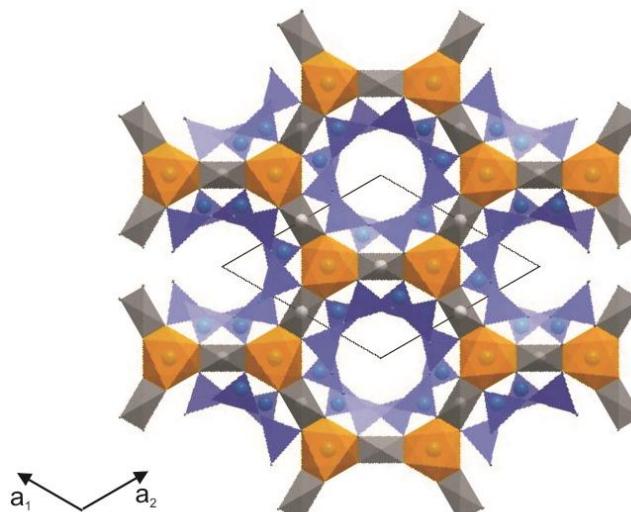


# Experimental diffusion of CO<sub>2</sub> in cordierite and beryl

### Cordierite - $(\text{Mg},\text{Fe})_2[\text{Si}_5\text{Al}_4\text{O}_{18}]$



### Berillo - $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$



Vista (001) nella cordierite (sopra) e berillo (sotto)

## Minerali microporosi di grande rilevanza geologica e tecnologica

Canali formati da gabbie  
intercomunicanti con  
diametro massimo da 5 a 5.8  
Å (Gibbs 1966, 1968)

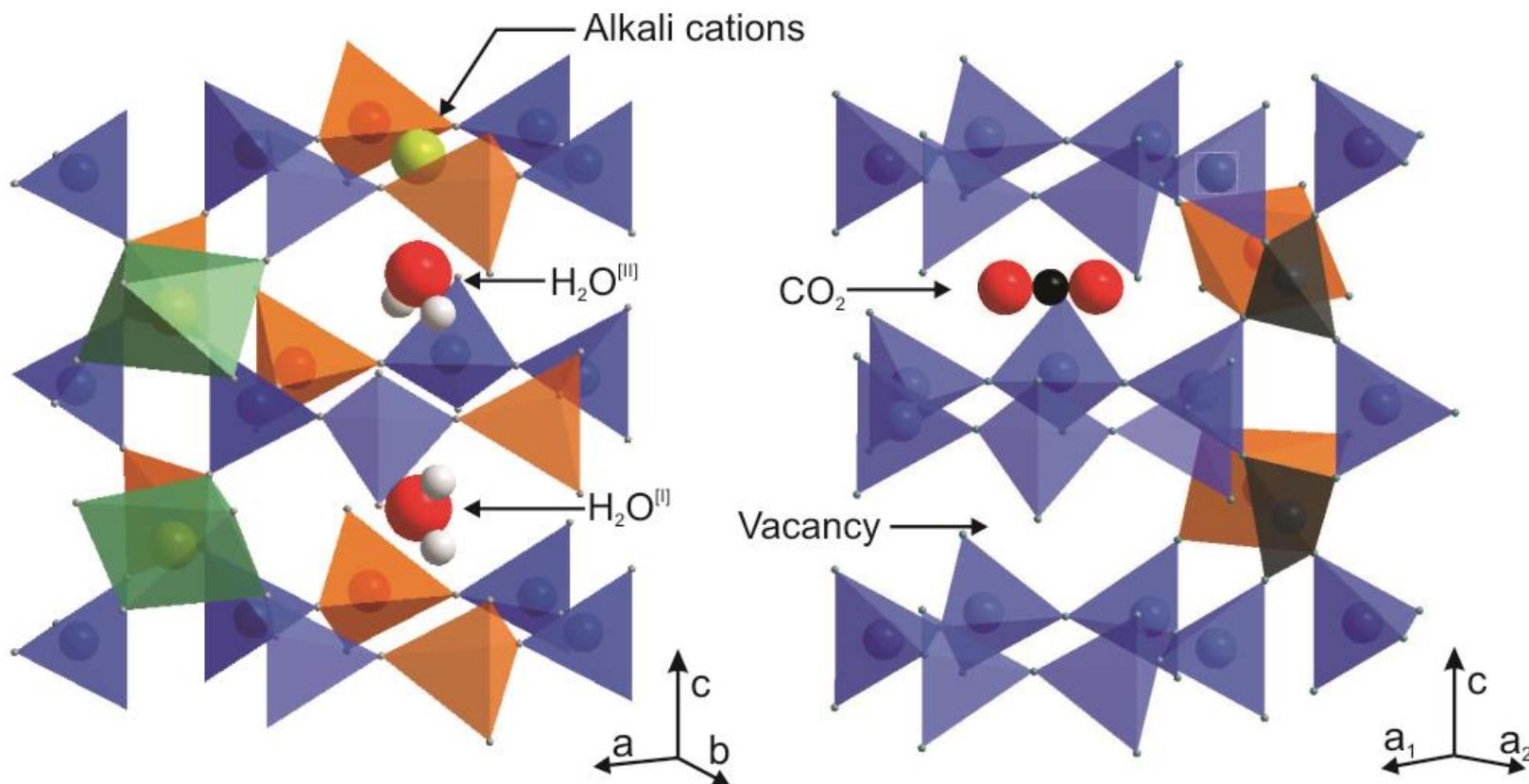
**Blue** – Si tetrahedra

**Gray** – Be tetrahedra

**Orange** – Al octahedra/tetrahedra

**Green** – Mg/Fe octahedra

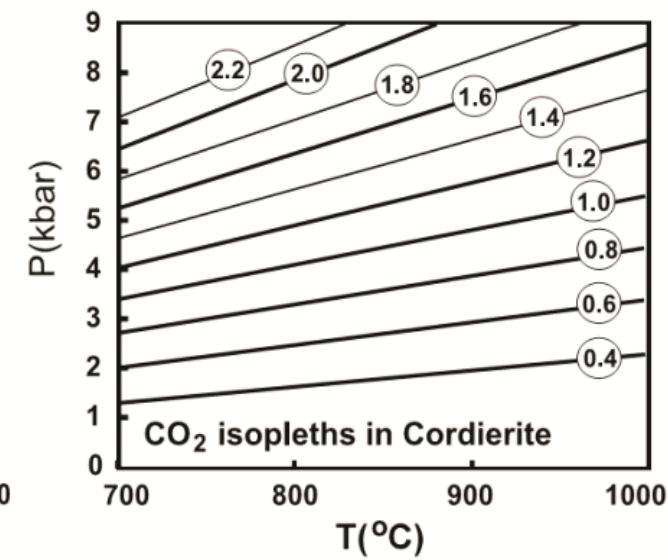
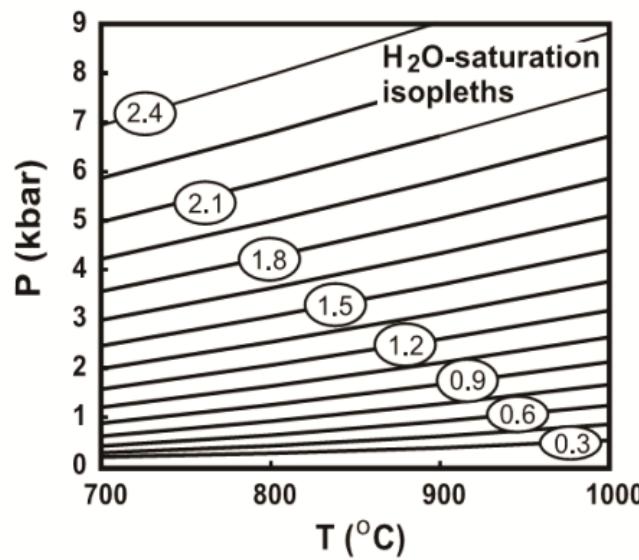
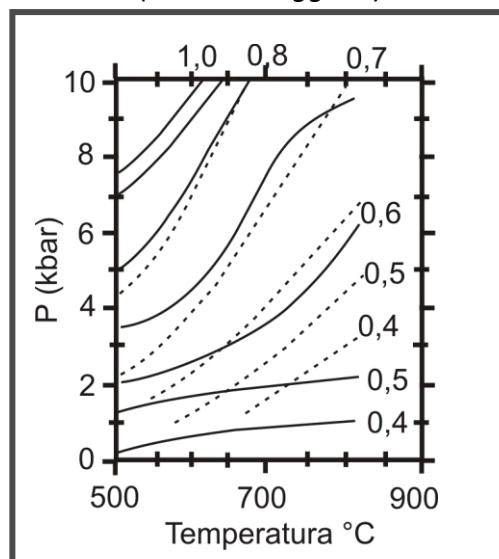
I canali strutturali possono ospitare cationi alcalini ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ) ma soprattutto  $\text{H}_2\text{O}$  (fino al 2.5 wt.%) e  $\text{CO}_2$  (fino al 7 wt.%) stabili ad altissime pressioni e temperature, dalla facies anfibolitica al metamorfismo di altissima temperatura fino all'anatessi crostale



Vista  $(hkl)$  in **cordierite** (sinistra) e **berillo** (destra)

Diversi studi sulla riequilibrazione tra fluido e minerale in differenti condizioni termobariche su fasi naturali e sintetiche.

Molecole di  $H_2O$  per unità di formula in assenza di  $CO_2$  per Mirwald et al. 1979 (linee continue) e Hegelson et al. 1978 (linee tratteggiate)



Sinistra, isoplete dell' $H_2O$  (in wt.%) nella cordierite in equilibrio con un fluido composto da sola  $H_2O$  (Harley and Carrington, 2001); a destra isoplete della  $CO_2$  nella cordierite in equilibrio con un fluido composto da sola  $CO_2$  (Thompson et al., 2001); mod. da Harley and Thompson, 2004

A causa delle basse velocità di diffusione della  $CO_2$  nei canali i lavori sperimentali sull'interazione FLUIDO-MINERALE presentano numerose **difficoltà analitiche**

Gas CO<sub>2</sub>

Strutture tipo-cordierite



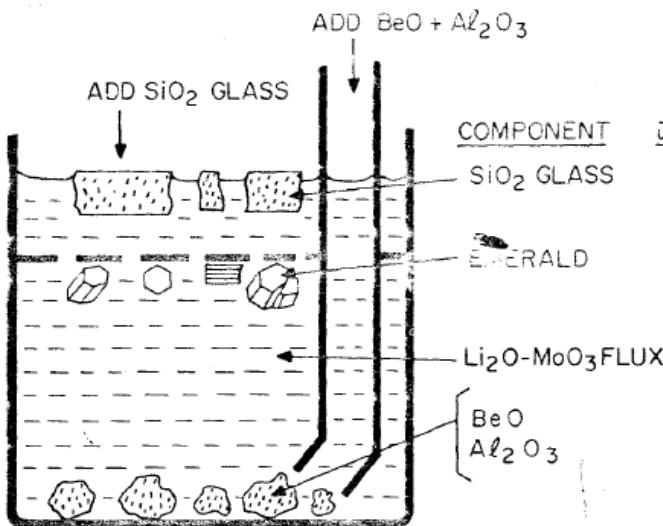
Non end-load Piston-cylinder Press,  
presso INGV (Roma)



Linkam TS 1400 Heating stage,  
modificato per microscopio IR

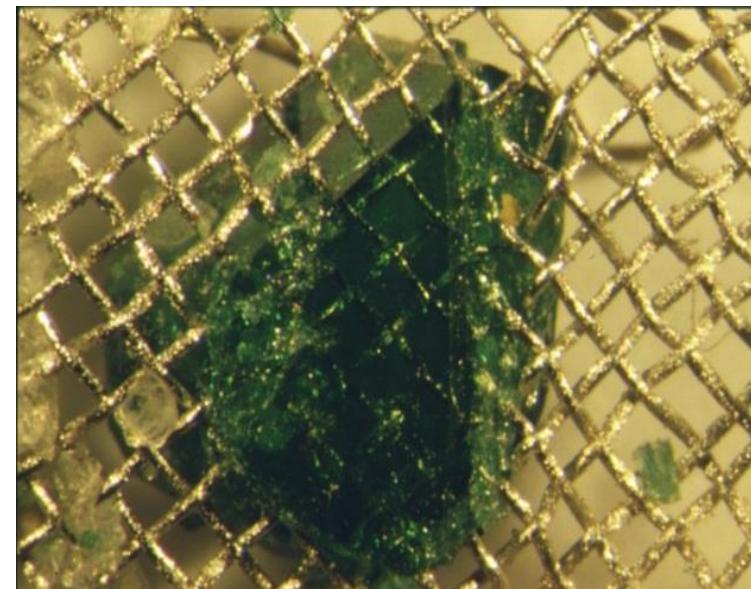
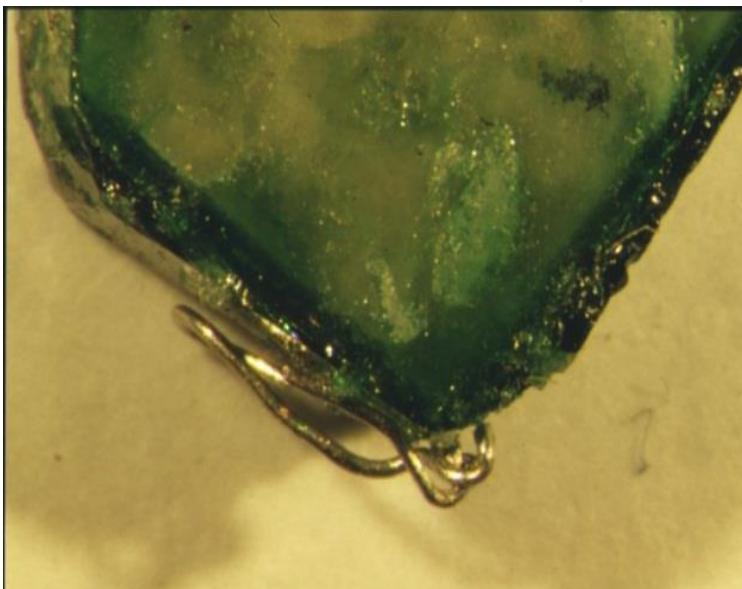


Microscopio FTIR con detector FPA, presso INFN (Frascati)

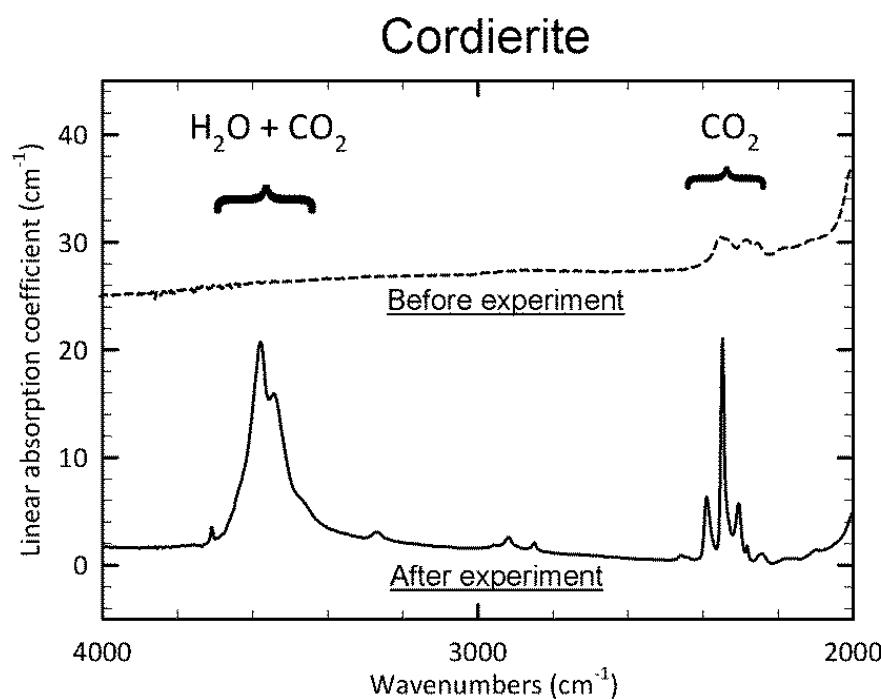


## Synthesis

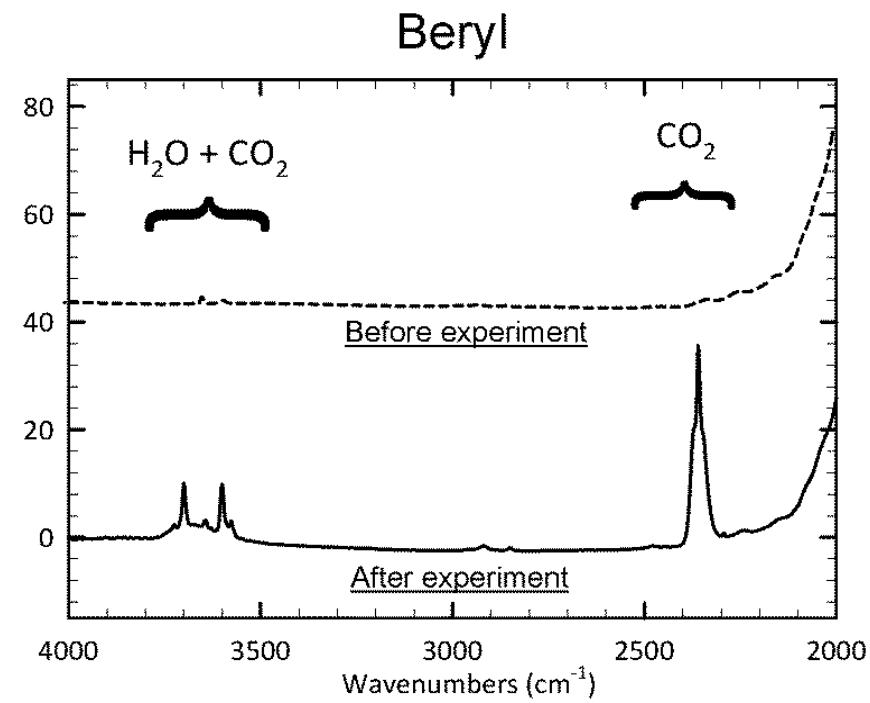
- Flux method
- flux: LiMoO<sub>4</sub>
- 24h - 800°C
- 15 days



cortesia del Dott. B. Rondeau, Università di Nantes

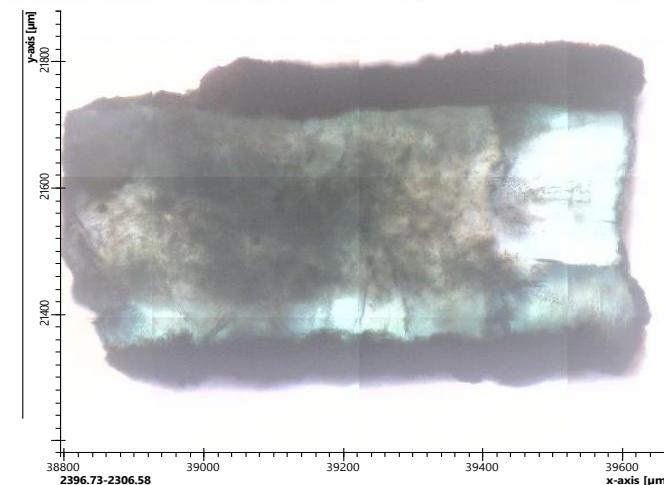
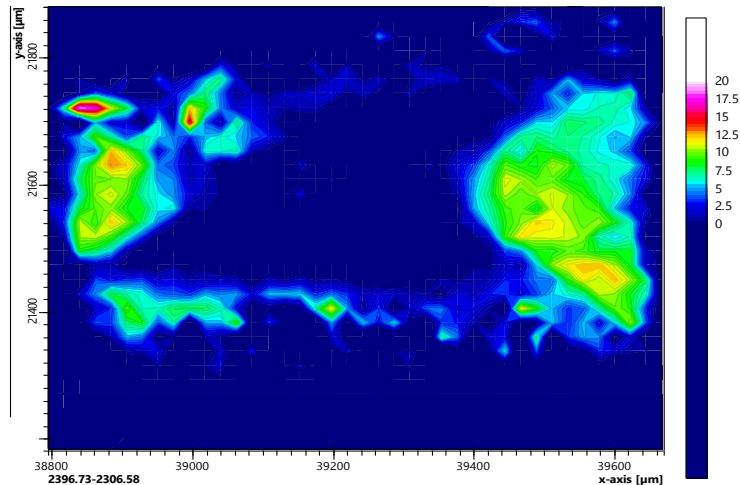


Spettro a luce non polarizzata di un cristallo singolo di cordierite  
CRD\_Pr 15 prima e dopo il trattamento a 900 °C e 500 MPa per 1 ora

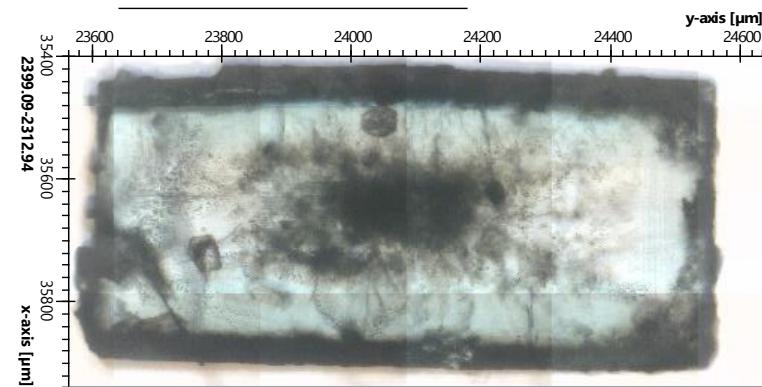
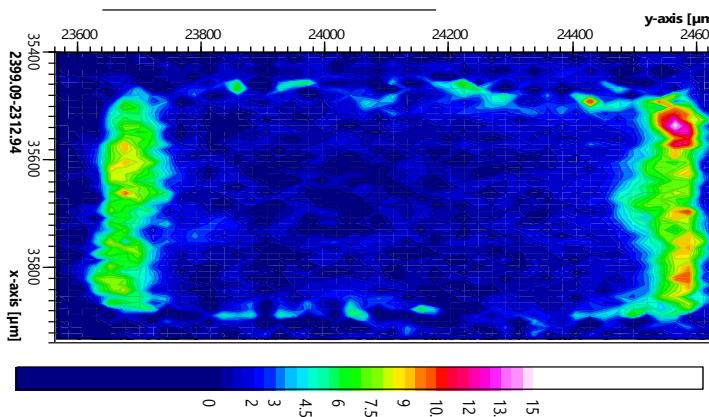


Spettro a luce non polarizzata di un cristallo singolo di berillo Pa\_340  
t prima e dopo il trattamento a 800 °C e 500 MPa per 10 ore

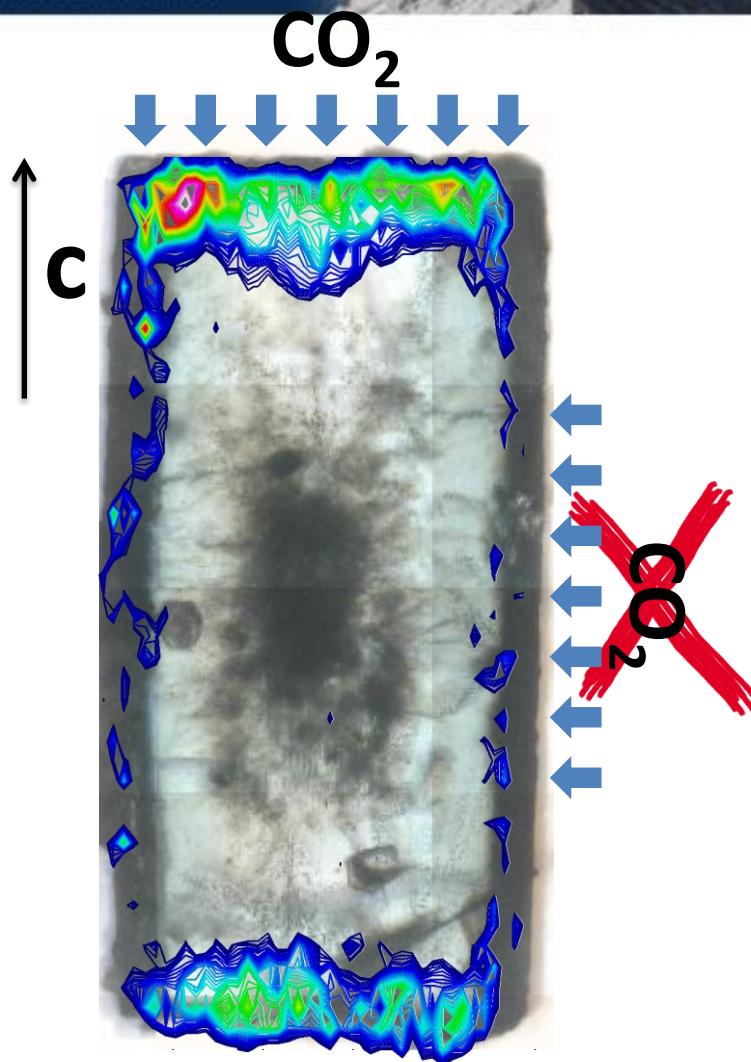
L'acquisizione di diversi punti di analisi sul il campione ha rivelato una **distribuzione estremamente disomogenea**  
di  $\text{H}_2\text{O}$  e  $\text{CO}_2$



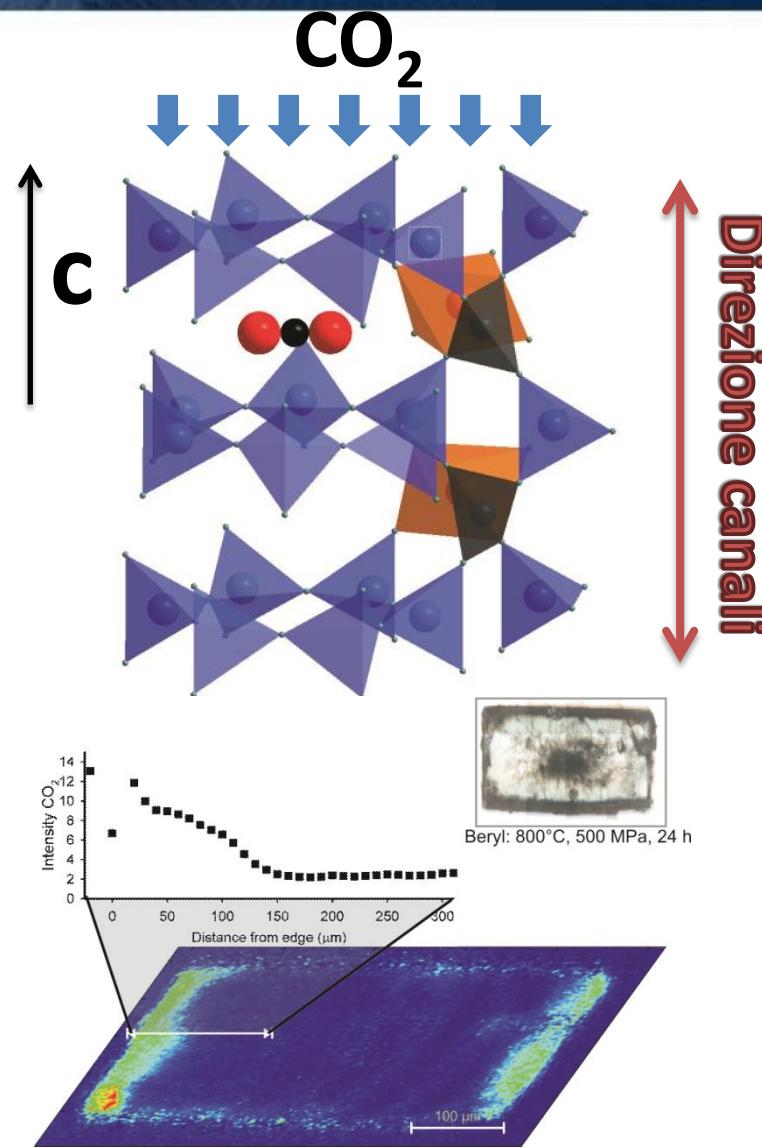
sample Pa 340 j



sample Pa 340 d bis

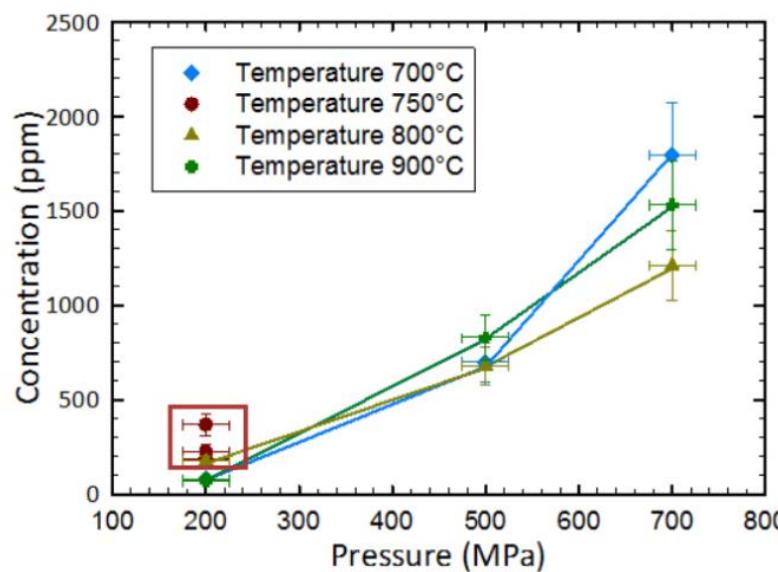
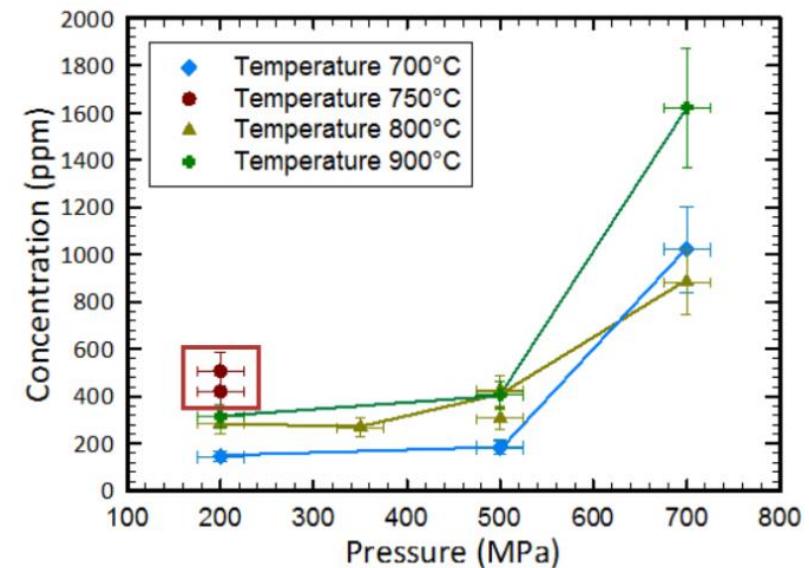


*Pa\_340 d: 500 MPa, 700 °C 24 h*

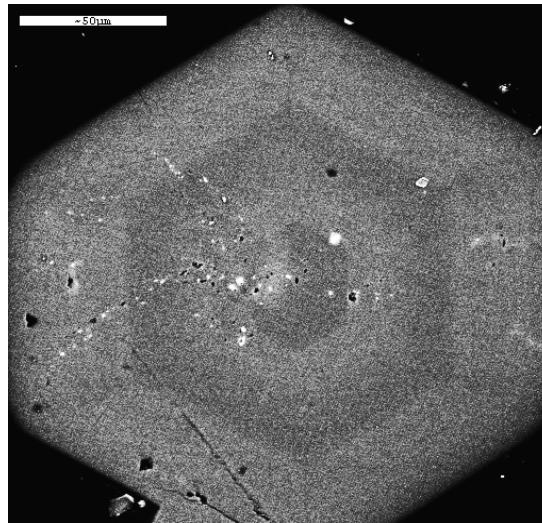


*Immagine FPA e transetto IR in un berillo sintetico trattato a 700°C e 500 MPa per 24 ore*

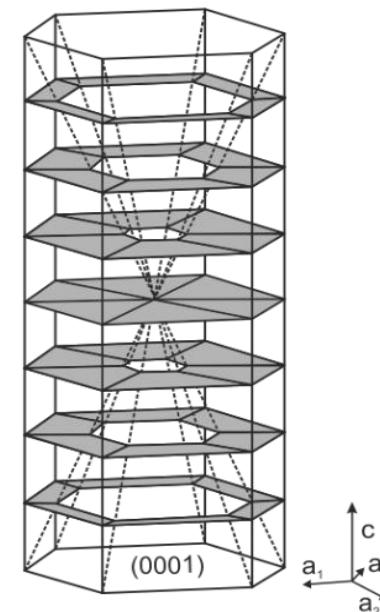
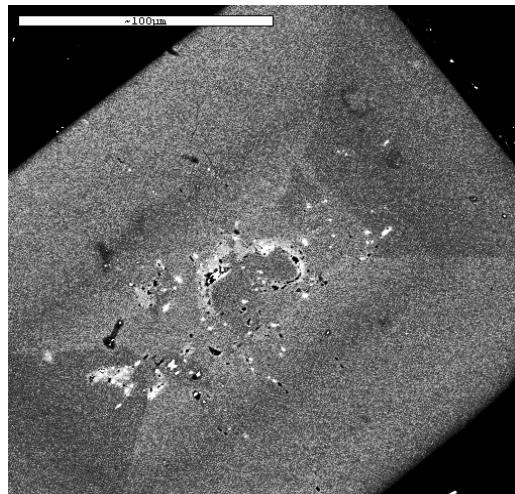
- La pressione ha un effetto significativo
- La temperatura ha un effetto trascurabile
- Il tempo ha un effetto poco significativo

**Berillo**

**Cordierite**


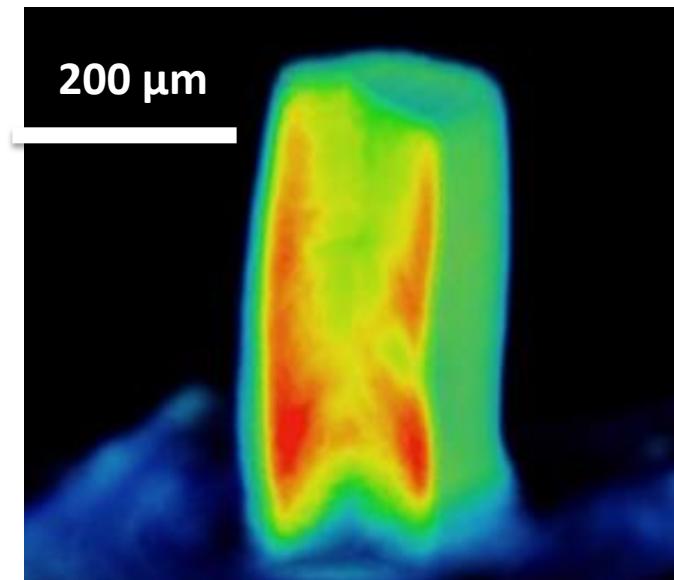
Concentrazione della  $\text{CO}_2$  misurata negli esperimenti di 24 ore di durata per il berillo (sinistra) e cordierite (destra) in funzione della pressione. I campioni corsi nella **CSPV** sono evidenziati nei riquadri

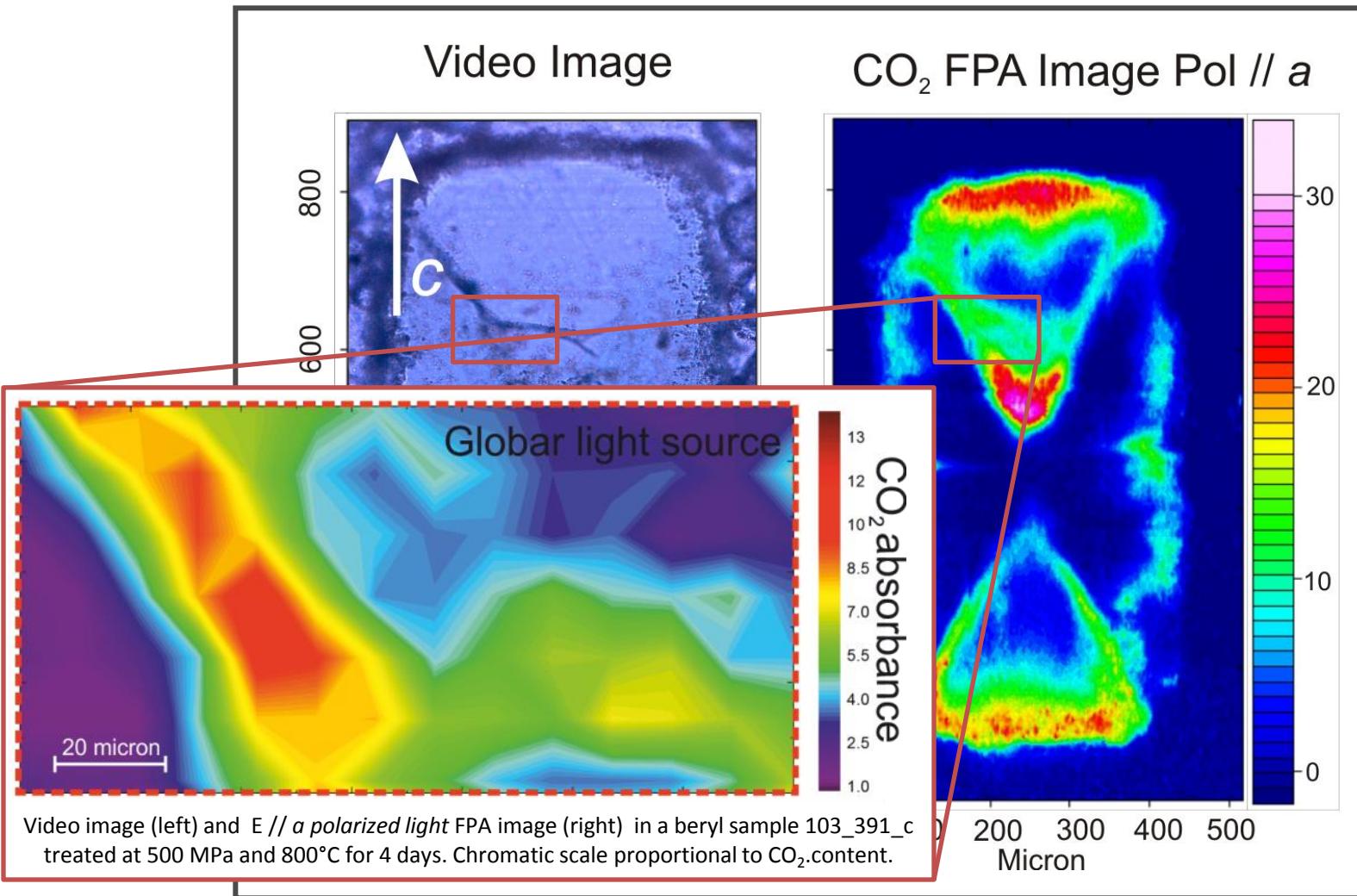


SEM-BSE

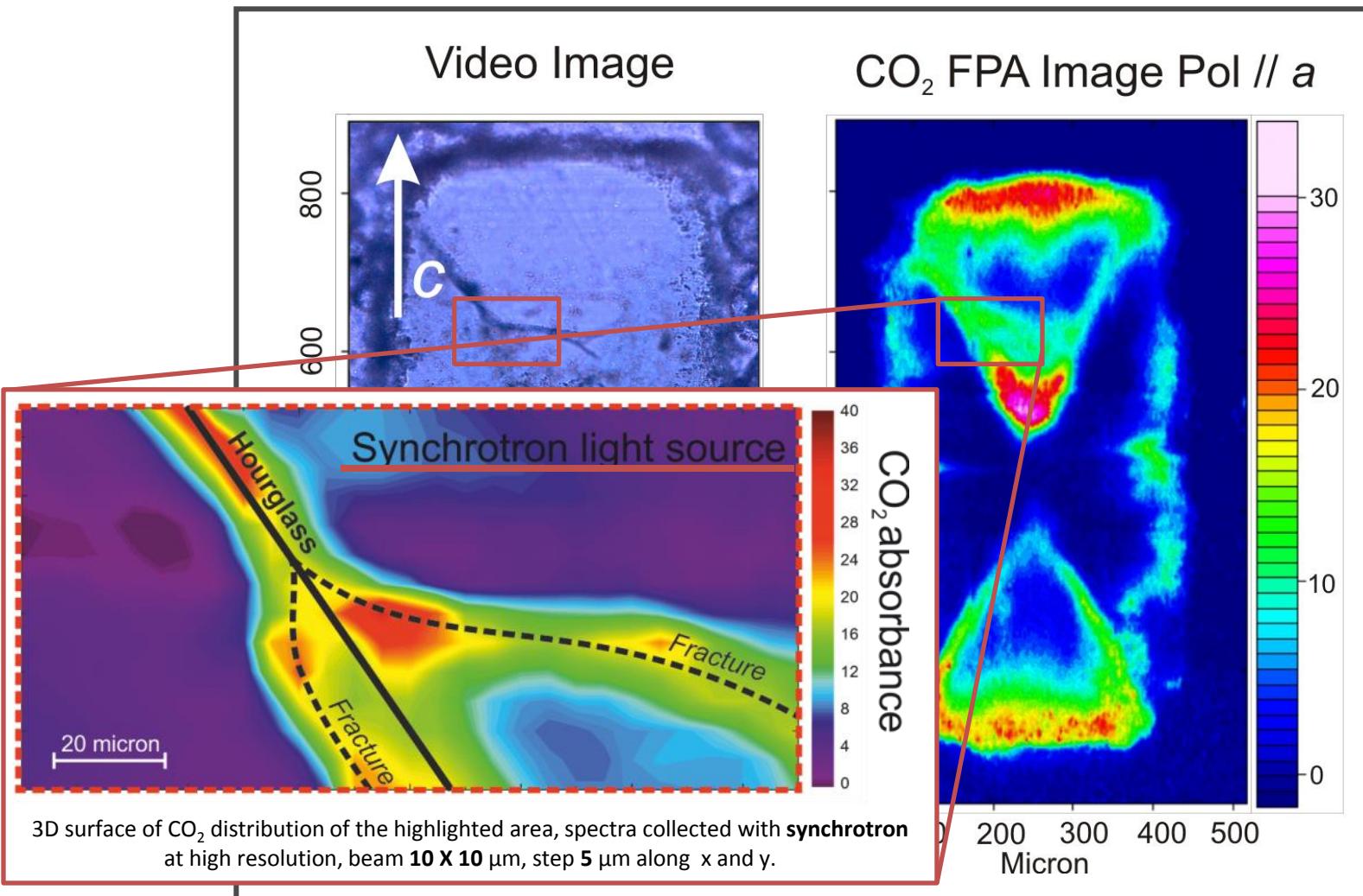


XRF polyCO images

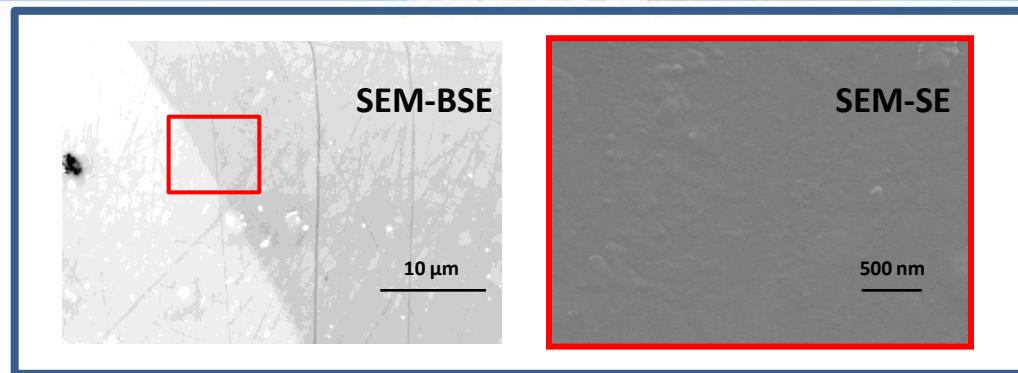




Video image (left) and  $E // a$  polarized light FPA image (right) in a beryl sample 103\_391\_c treated at 500 MPa and 800°C for 4 days. Chromatic scale proportional to  $\text{CO}_2$ .content.

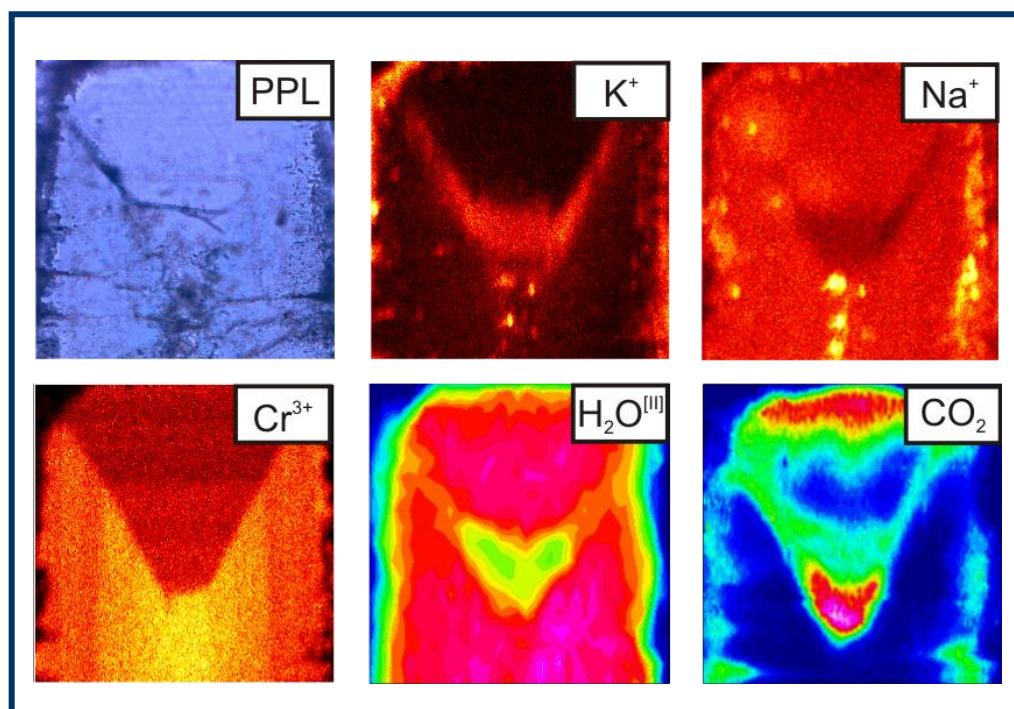


Video image (left) and E // a polarized light FPA image (right) in a beryl sample 103\_391\_c treated at 500 MPa and 800°C for 4 days. Chromatic scale proportional to CO<sub>2</sub>.content.

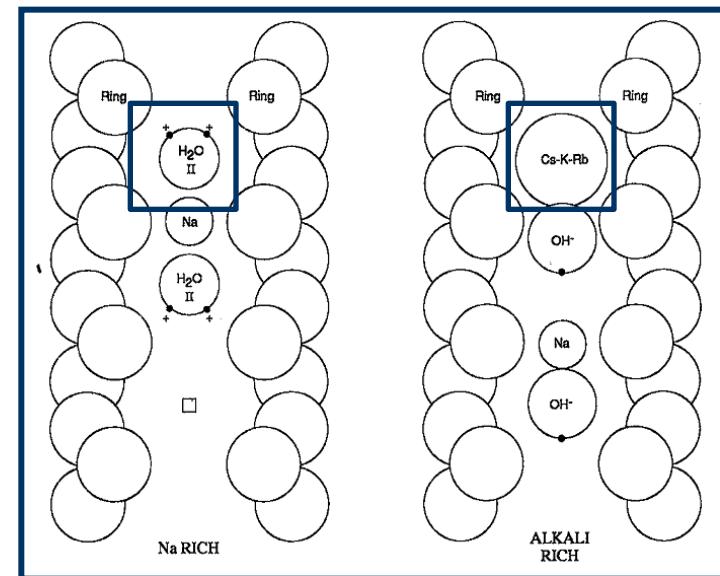


SEM-BSE (compositional) and SEM-SE (topographic) image of an "hourglass" branch

- No topographic discontinuity
- Strong  $\text{Cr}^{3+}$  zoning
- $\text{K}^+$  and  $\text{Na}^+$  are anti-correlated
- $\text{H}_2\text{O}^{[II]}$  depleted in  $\text{K}^+$  and/or  $\text{CO}_2$  rich areas



Parallel polarizers optical microscope view (PPL), TOF-SIMS chemical maps of  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Cr}^{3+}$ , FTIR-FPA images of  $\text{CO}_2$  and  $\text{H}_2\text{O}^{[II]}$  distribution in the 103\_391\_d beryl sample

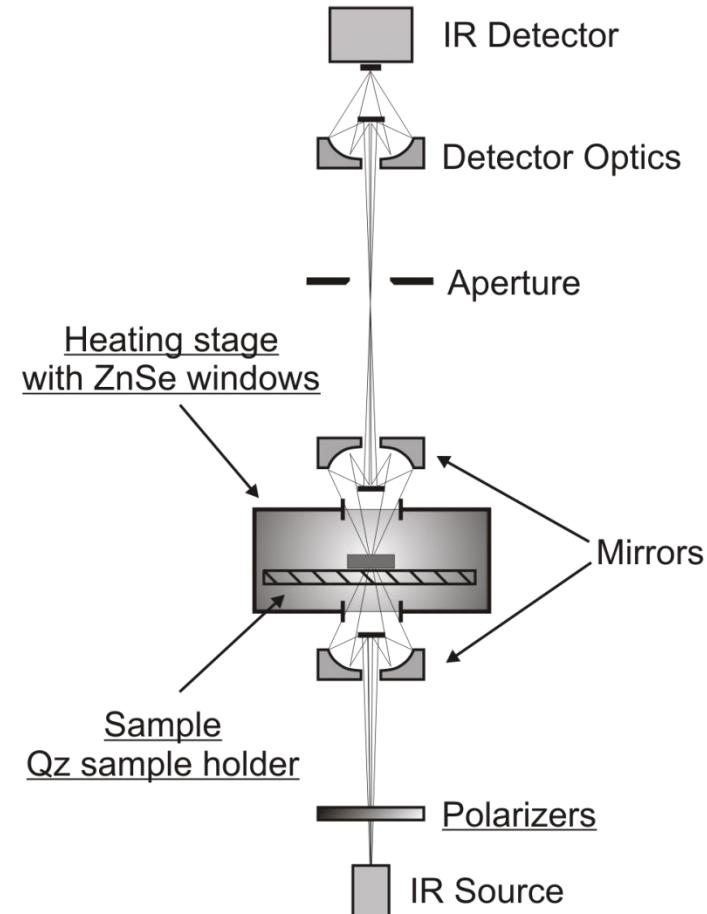


Schematic representation of  $\text{Na}^+$   $\text{K}^+$  and  $\text{H}_2\text{O}^{[II]}$  site occupancy inside beryl structural channels (Aurisicchio et al., 1994)

- Goal: investigate CO<sub>2</sub> loss rate in oriented cordierite sections
- Equipment: Linkam TS 1400xy™ Heating Stage modified to work up to 1200 °C in FTIR microscopes. Microscope quipped with **polarisers** and **2D FPA detector**



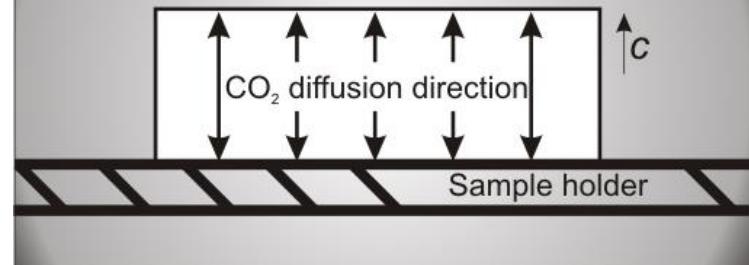
IR microscope equipped with heating stage



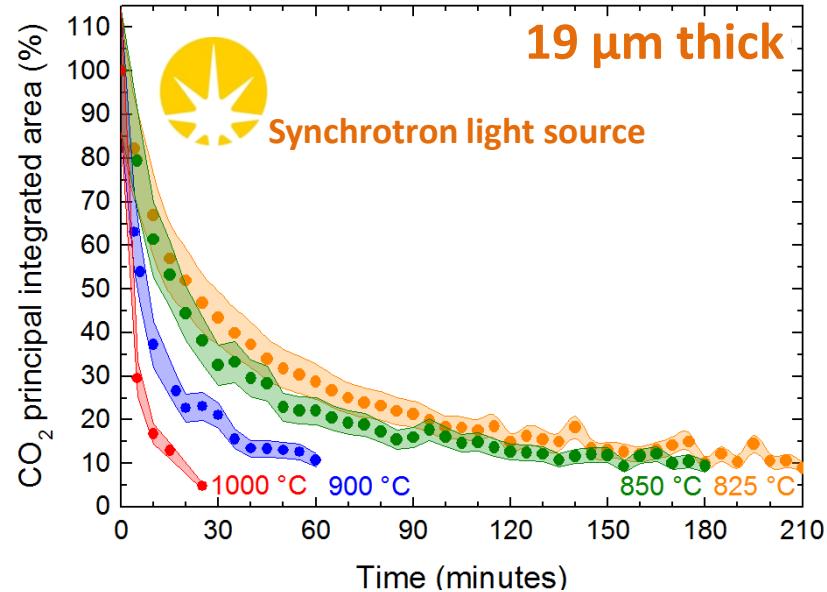
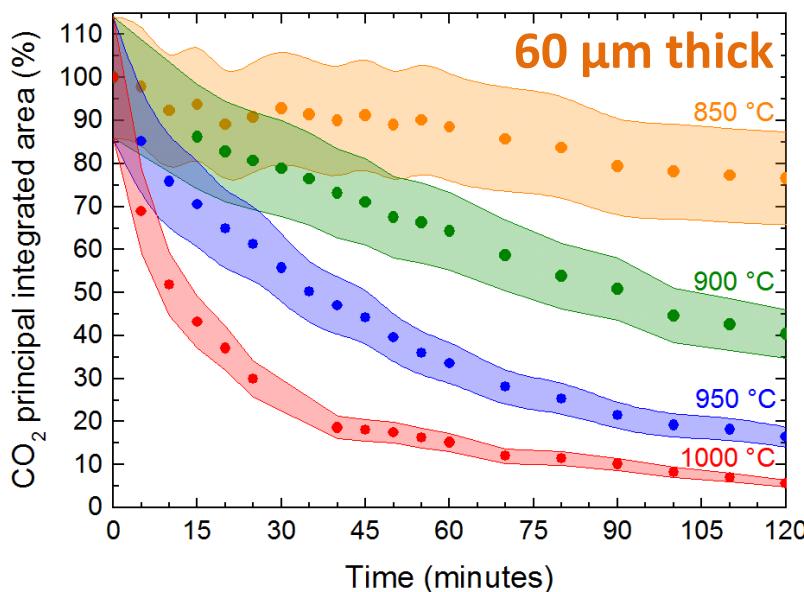
*Schematic layout of an IR microscope equipped with an heating stage*

- Structural channels oriented **normal** to slab surface
- Two sets of lamellae 60 and 19  $\mu\text{m}$  thick

### Isotropic heating



Schematic set up of the  $\text{CO}_2$  diffusion across the sample (white) inside the heating stage. Heat distribution is homogeneous inside the crucible



Isothermal plots of residual  $\text{CO}_2$  within the cordierite channels as a function of time; sample BM96512, (001) section with E//a.  
Shaded areas represent the estimated error on the absorption. (left) 60  $\mu\text{m}$  thick section, (right) 19  $\mu\text{m}$  thick section

## Avrami Rate equations

Avrami (1939,1940,1941)

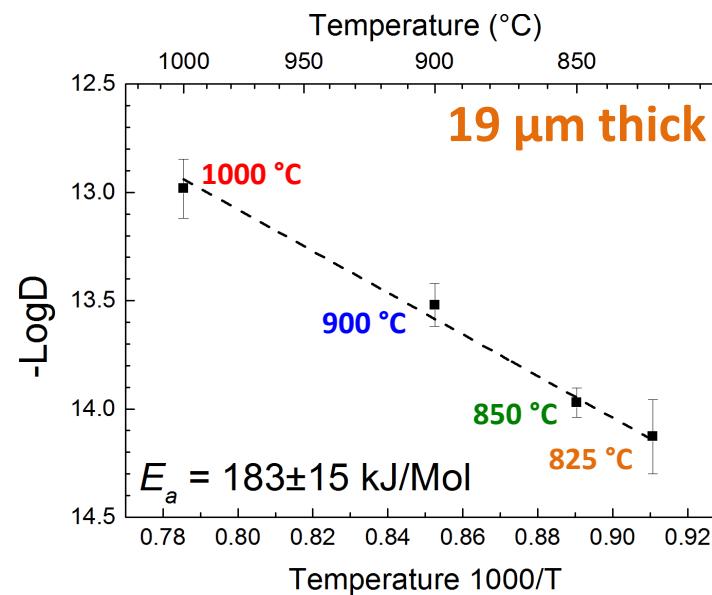
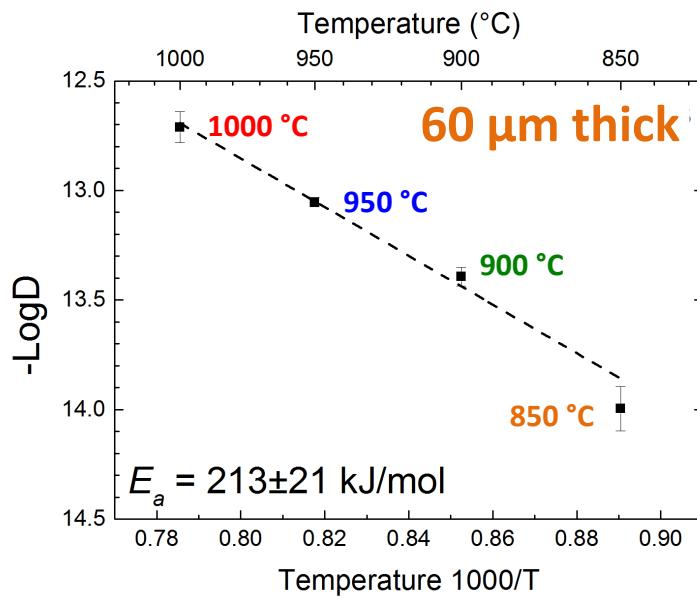
$$A_t = A_0 \cdot \exp(-f(t)) \longrightarrow k = A \times \exp\left(-\frac{E_a}{RT}\right)$$

Calculated activation energies are rate and thickness dependent

## 1D plane sheet diffusion

Ingrin et al., (1995)

$$A_t = A_0 \cdot \sum_{n=0}^{\infty} \left\{ \frac{8}{(2n+1)^2 \pi^2} \right\} \cdot \exp\left\{ -\frac{D(2n+1)^2 \pi^2 t}{L^2} \right\} \longrightarrow D = D_0 \times \exp\left(-\frac{E_a}{RT}\right)$$



Arrhenius plot using values of the diffusion coefficient  $D$  obtained fitting the mono-dimensional plane sheet diffusion equation for the **60  $\mu\text{m}$  thick** experimental set (left) and for the **19  $\mu\text{m}$  thick** experimental set (right)

# Analisi quantitativa di decarbonatazione e deprotonazione per T variabile

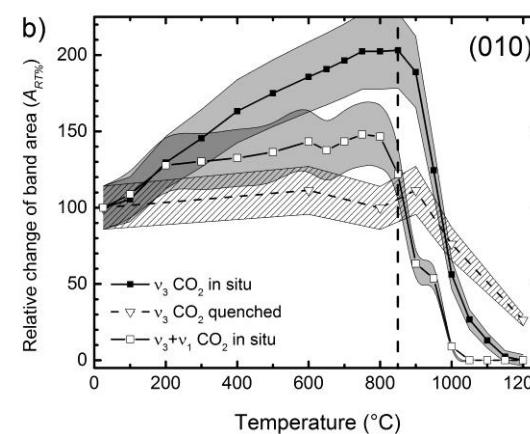
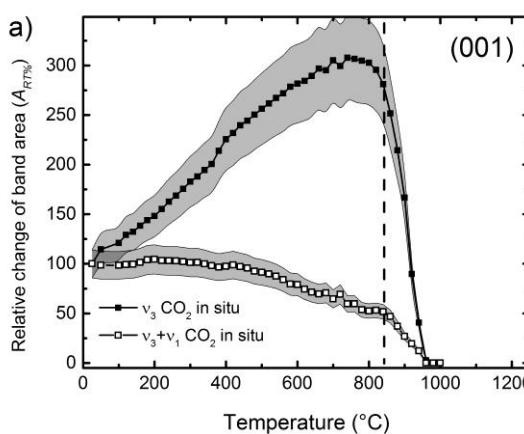


figure 7

CO<sub>2</sub>

H<sub>2</sub>O

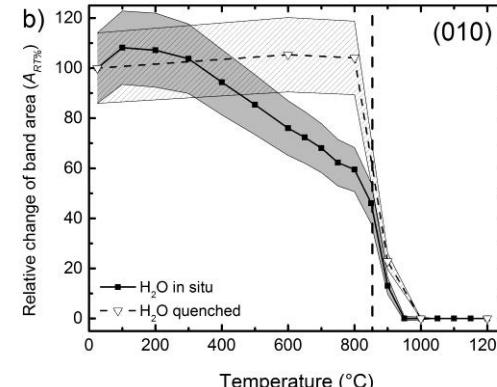
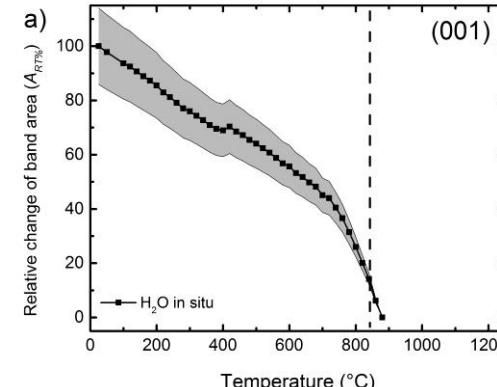
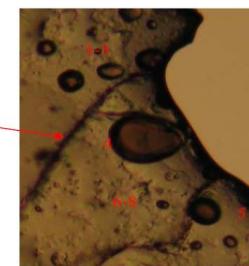
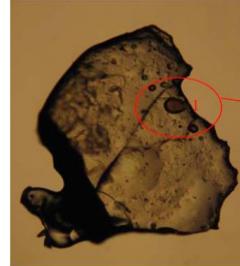


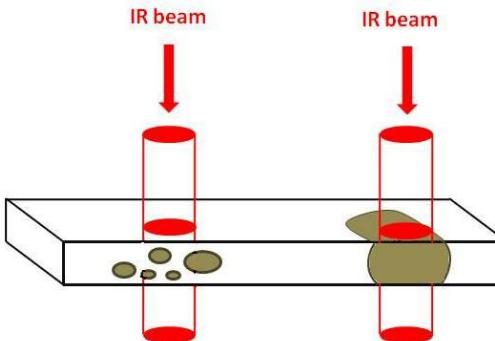
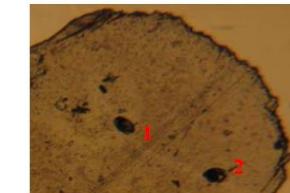
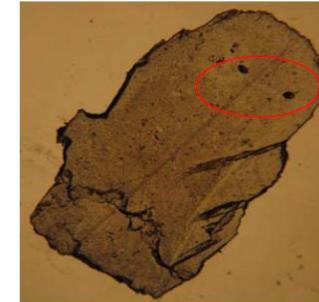
figure 8

# Melt inclusions in olivine from Stromboli (Sicily, Italy)

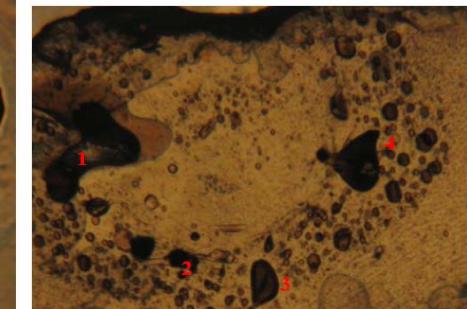
STR2007 Pomici Bionde OL 12a



STR 2007 Pom. Bionde CxPx 11

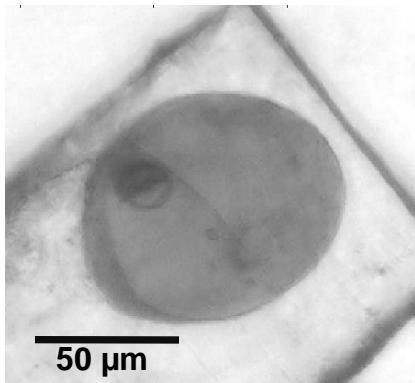


STR 2009 scoria OL12b

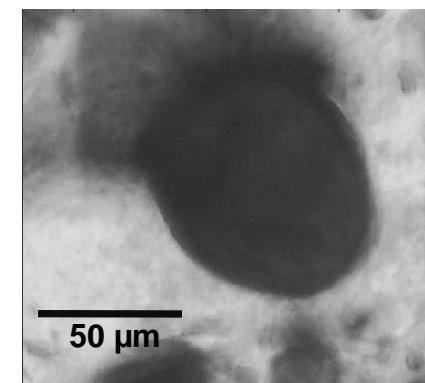


## Images of water in melt inclusions within olivine

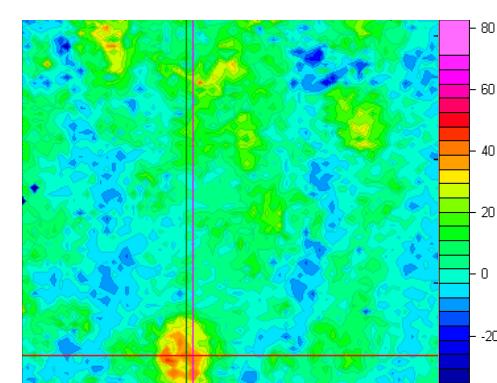
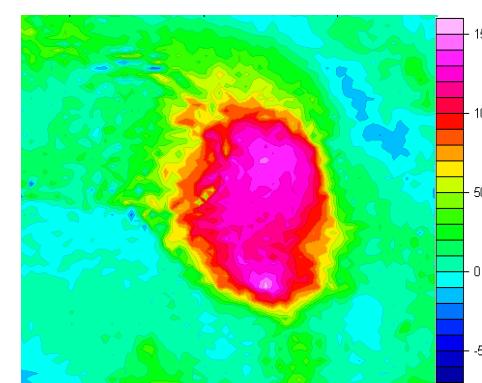
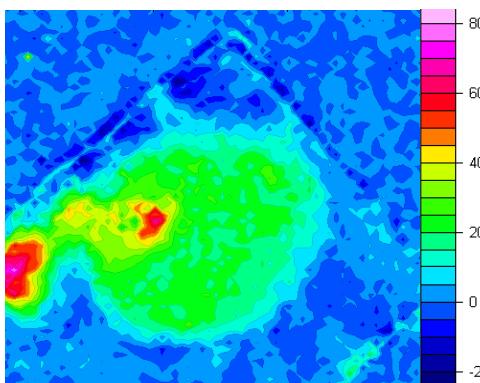
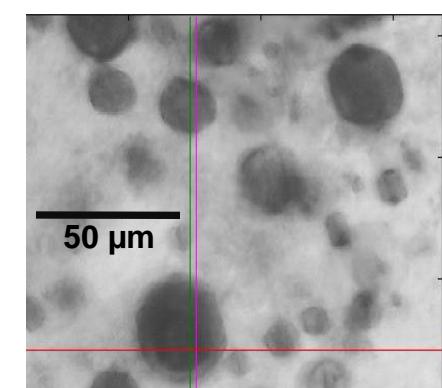
Olivine 3b



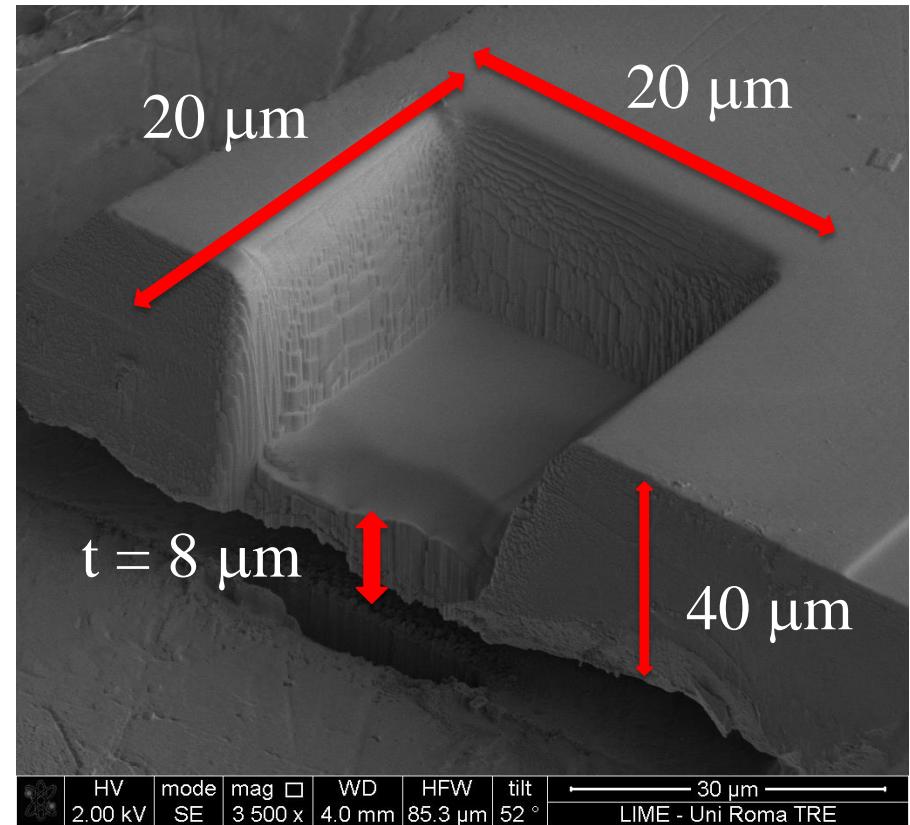
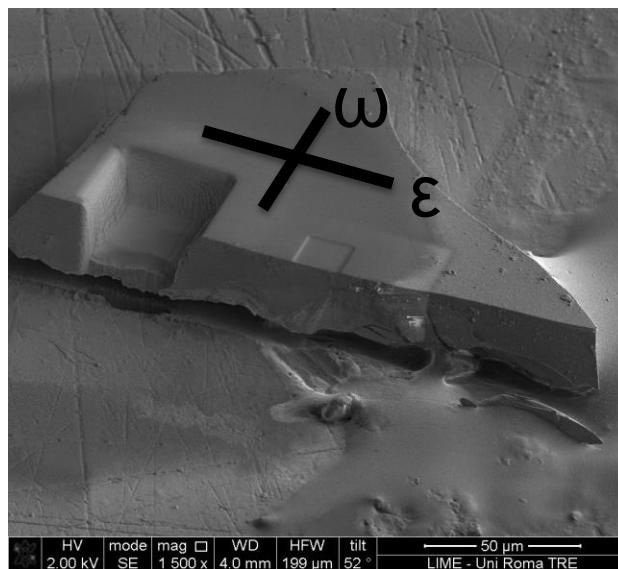
Olivine 12b

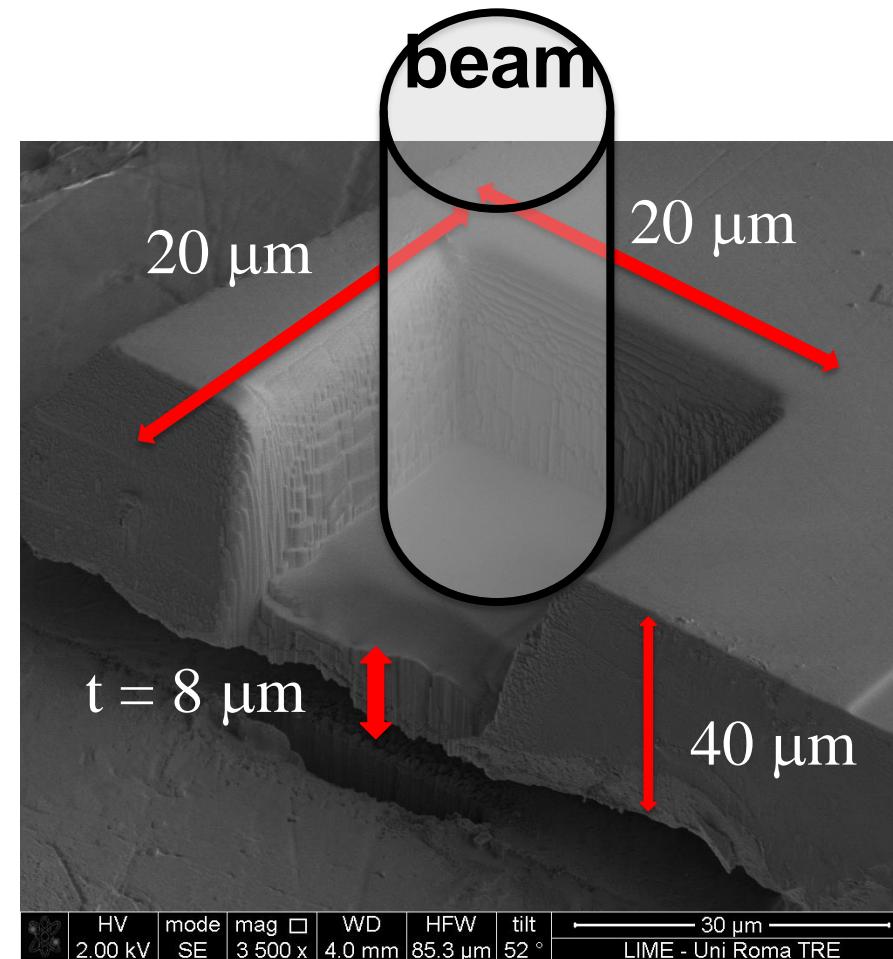


Olivine 12b



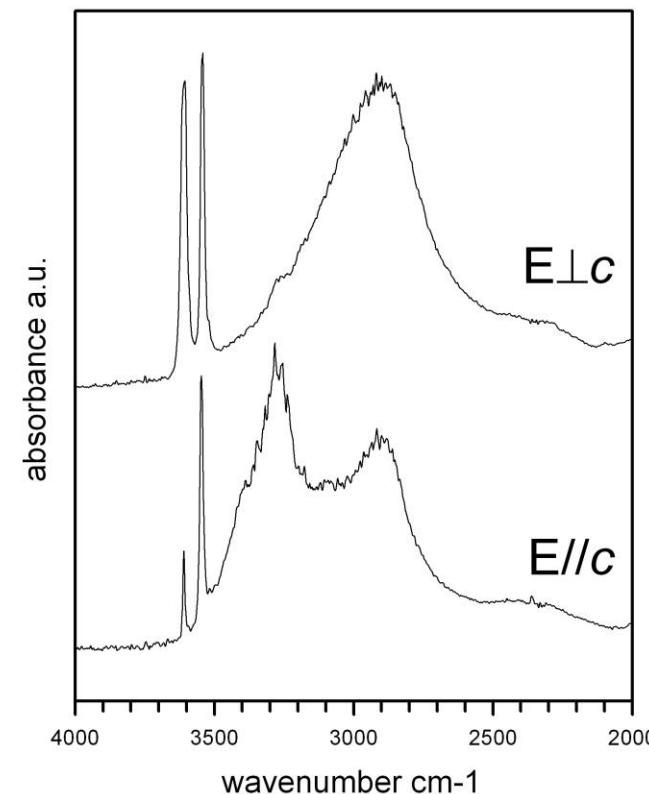
# Single-crystal SR-FTIR spectroscopy of wardite: $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2(\text{H}_2\text{O})$



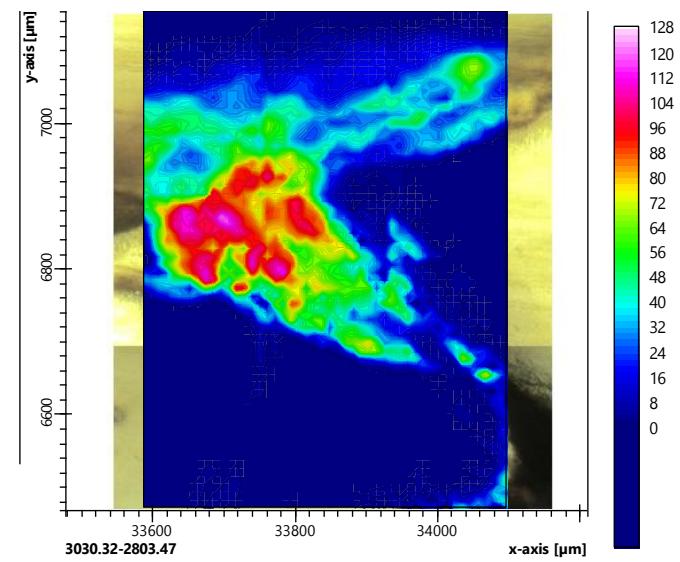
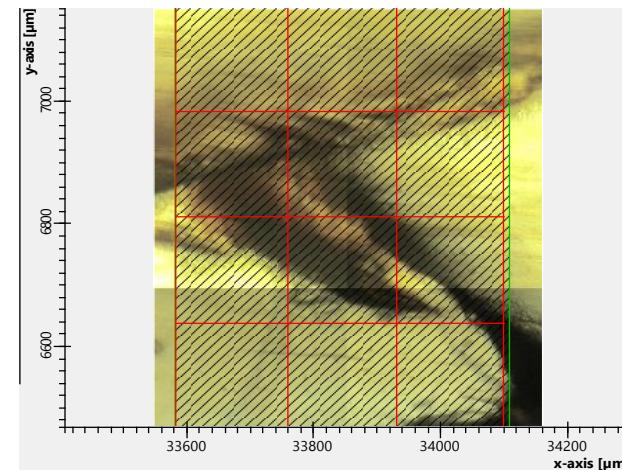
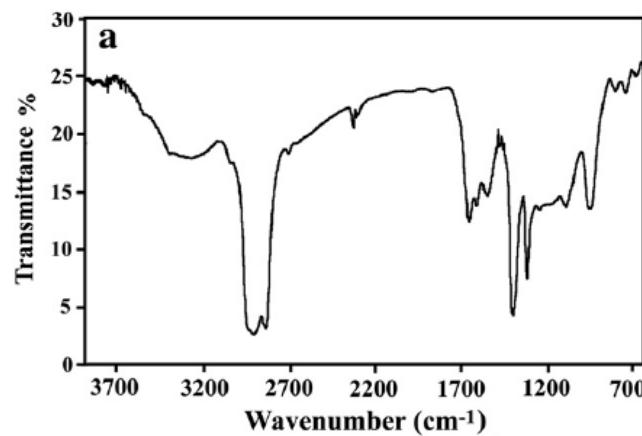
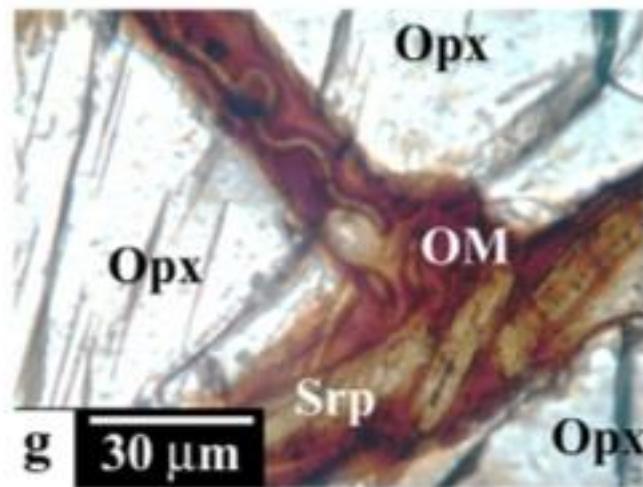


# Polarized spectrum of wardite

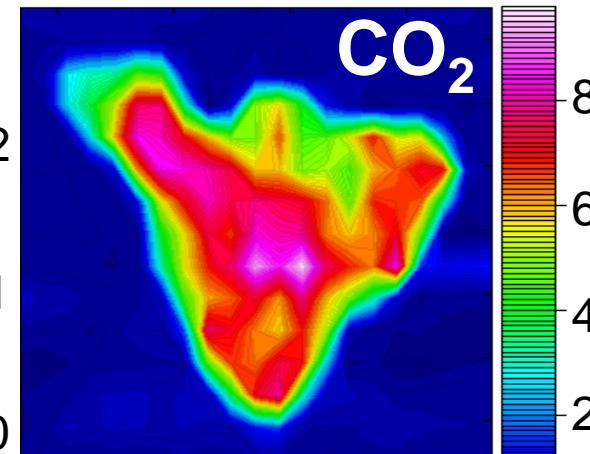
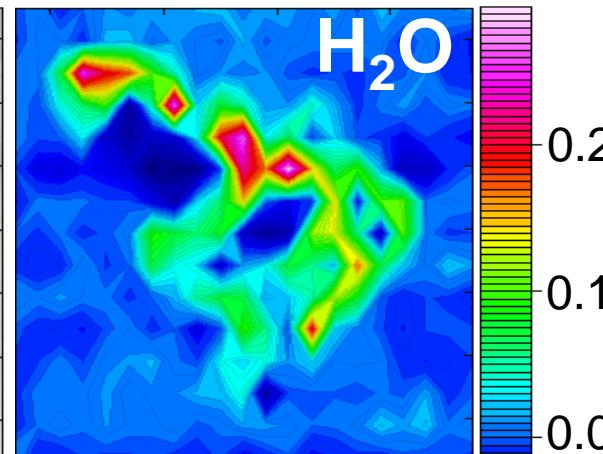
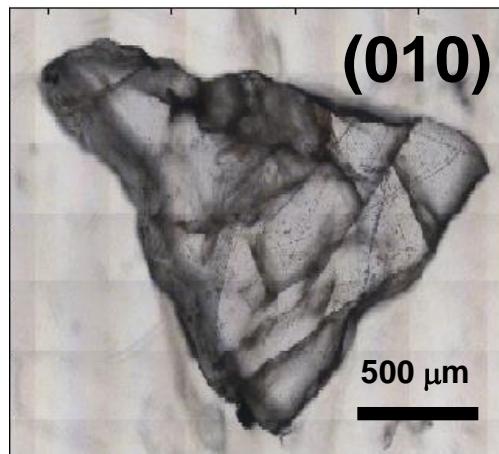
## $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4 \bullet 2(\text{H}_2\text{O})$



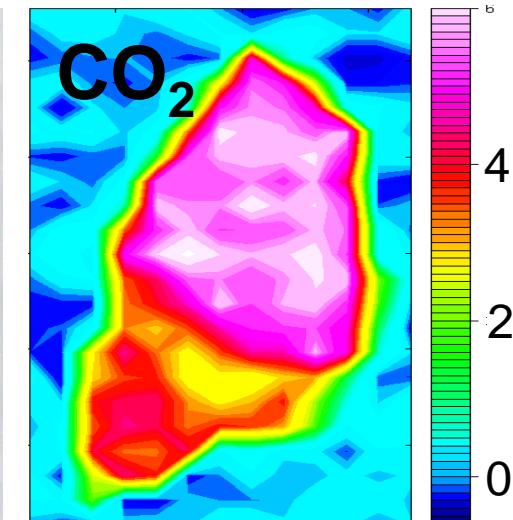
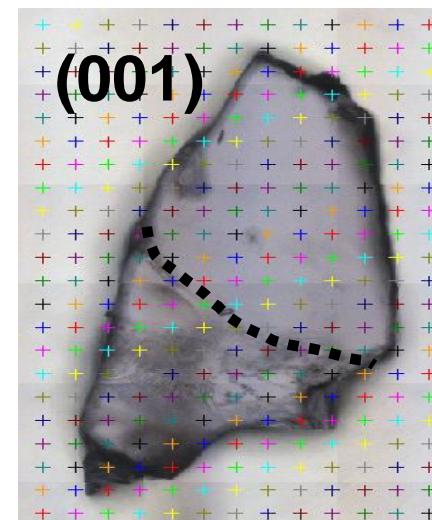
# Materia organica nelle rocce metamorfiche degli Iblei (Sicilia)





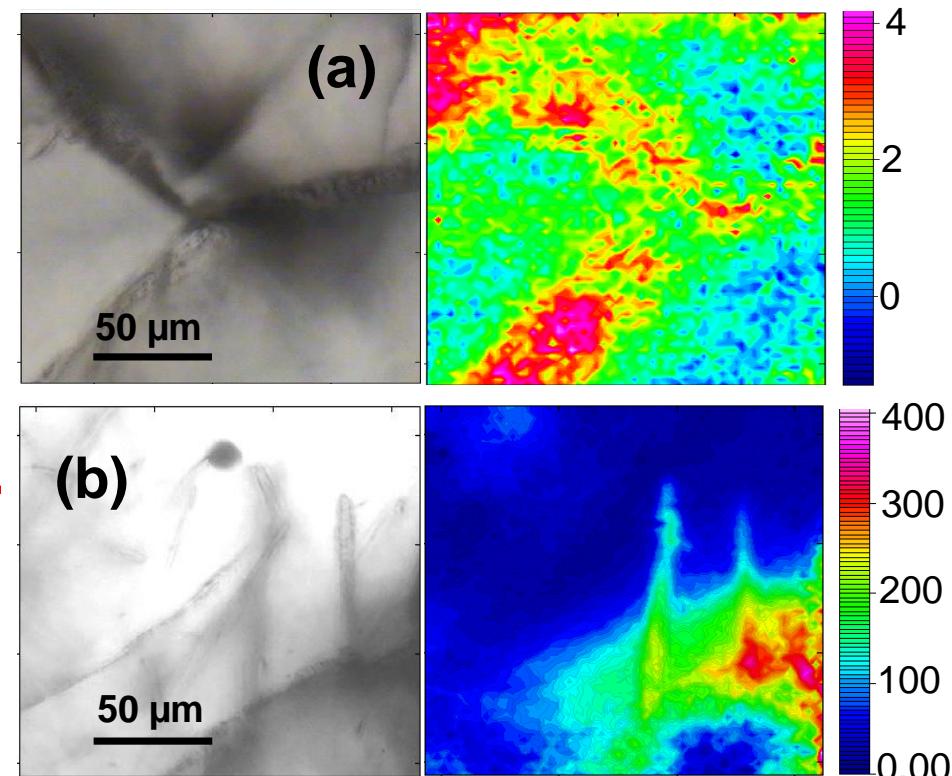
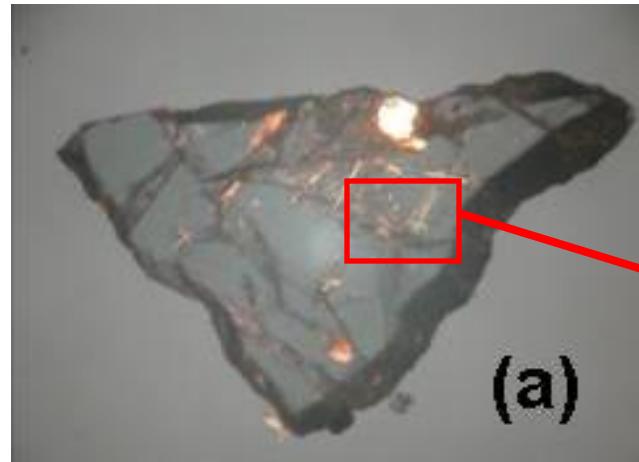


Zoning of  
 $\text{H}_2\text{O}$  and  $\text{CO}_2$   
in cordierite



# microspectrometric **imaging** of H<sub>2</sub>O in cordierite: focal plane array of detectors (FPA)

**Resolution**  
 $\sim 5 \mu\text{m}$ !



## $\text{H}_2\text{O}$ il leucite from the final explosive level of the Alban Hills: hydration < 625° C

