Analysis of aqueous fluids by Raman spectroscopy

Marie-Camille CAUMON

geoRessources

Outline

1. Geological fluids
2. Differential Raman scattering cross sections
3. CO_2 & H_2O
4. Experimental HP-HT devices
5. Some examples

What are geological fluids?

The chemist's fluid:

- Water-based
- Room temperature
- Eq. atmospheric gases
- Low salt concentration
- Easy to sample

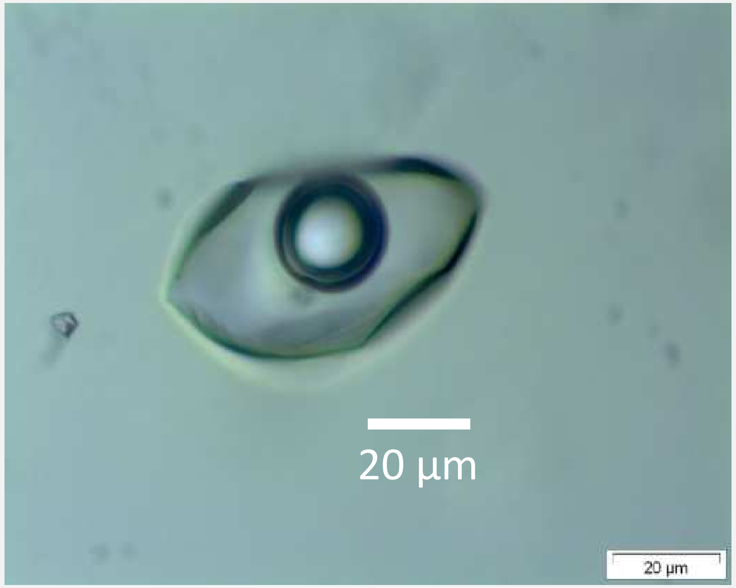
- Chemistry of diluted media
- Classical analytical techniques

What are geological fluids?

The geologist's fluid :

– Large temperature range (< 0°C → > 1000 °C)
– High pressure (atm. P → > 2 GPa)
– Complex chemical systems (large salt concentration, organic species, dissolved gases…)
– Low water content (silicate fluids)
– Samples?

- Specific chemistry (Pitzer, etc.)
- Specific analytical tools



Entrapped in fluid inclusions = µvolumes

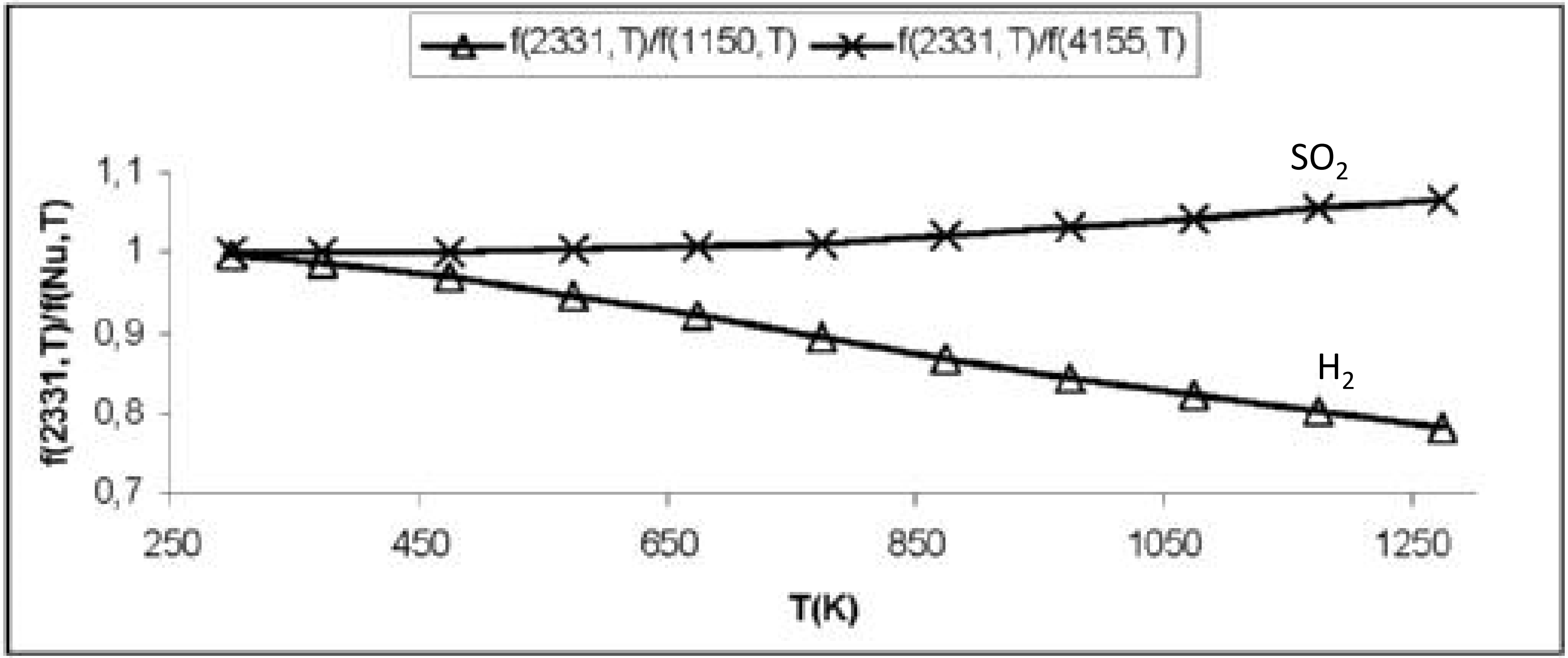
- Raman spectroscopy of geological fluids:
  - Molecular composition = f(P,T,V)
  - Water structure
  - Localized: µvolumes
  - Non-destructive
  - ~ Quantitative

Relative differential Raman scattering cross sections

Relative differential Raman scattering cross sections

Gas:

$$\frac{\partial\sigma}{\partial\Omega} = \frac{(2\pi)^4 b_j^2 g_j\left(45\alpha_j^2 + 7\gamma_j^2\right)\left(\nu_0 - \nu_j\right)^4}{45\left[1 - \exp(-\frac{hc\nu_j}{kT})\right]}$$



Variation of RDRSCS with T

Garci Baonza *et al.*, *EMU Notes vol.12,* 2012

Differential Raman scattering cross sections

Gas:

$$\frac{\partial\sigma}{\partial\Omega} = \frac{(2\pi)^4 b_j^2 g_j \left(45\alpha_j^2 + 7\gamma_j^2\right)\left(\nu_0 - \nu_j\right)^4}{45\left[1 - \exp\left(-\frac{hc\nu_j}{kT}\right)\right]}$$

Schrötter & Klöckner 1979

- For one gas: $A_i = I_0 \times C_i \times \frac{\partial\sigma_i}{\partial\Omega} \times t \times \xi_i$

- For a gas mixture: $\frac{C_i}{\sum C_i} = \frac{A_i/\left(\frac{\partial\sigma_i}{\partial\Omega}\times\xi_i\right)}{\sum A_i/\left(\frac{\partial\sigma_i}{\partial\Omega}\times\xi_i\right)} = \frac{A_i/\sigma_i^*}{\sum A_i/\sigma_i^*}$

Wopenka & Pasteris, Appl. Spectr. 1986

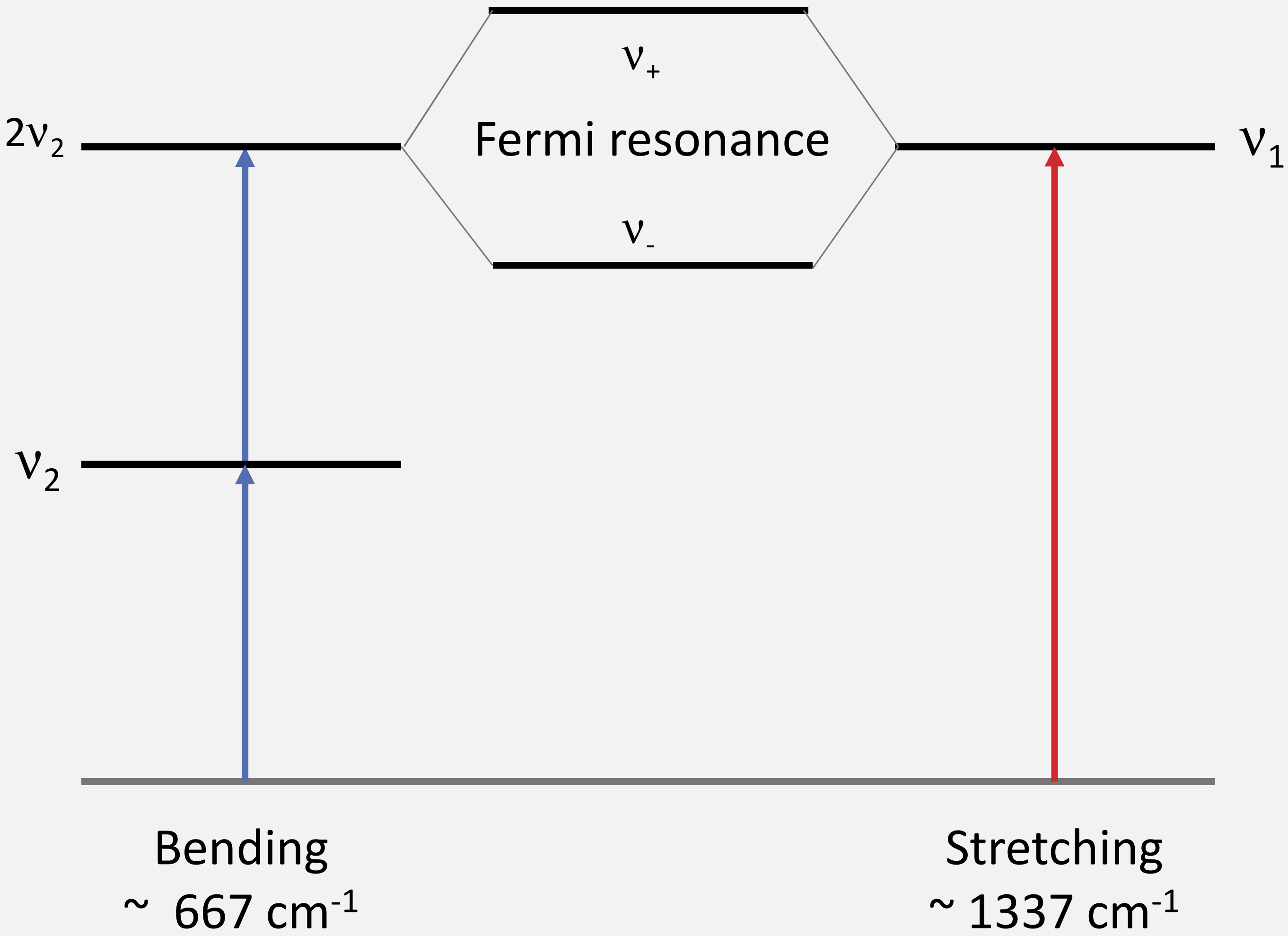
- In liquid: $\frac{\partial\sigma}{\partial\Omega}(liquid) = \frac{\partial\sigma}{\partial\Omega}(gas) \times L$ $\quad L = \frac{n_j(n_j+2)^2(n_0+2)^2}{81n_0} \approx \frac{(n_0+2)^4}{81}$

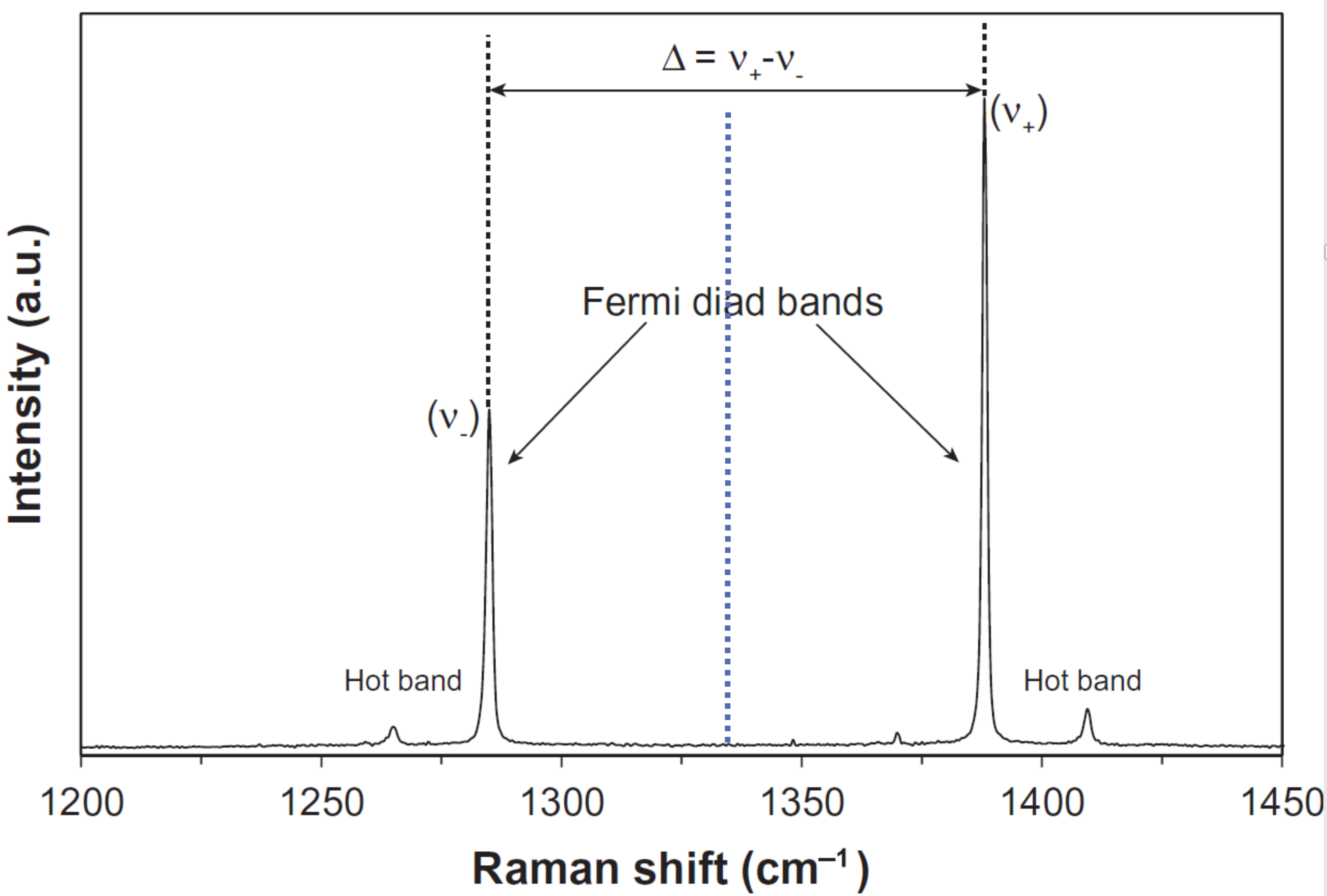
L: internal field effect factor

Eckhardt & Wagner, J Mol Spectr 1966

CO_2 and water

The Raman spectrum of CO_2





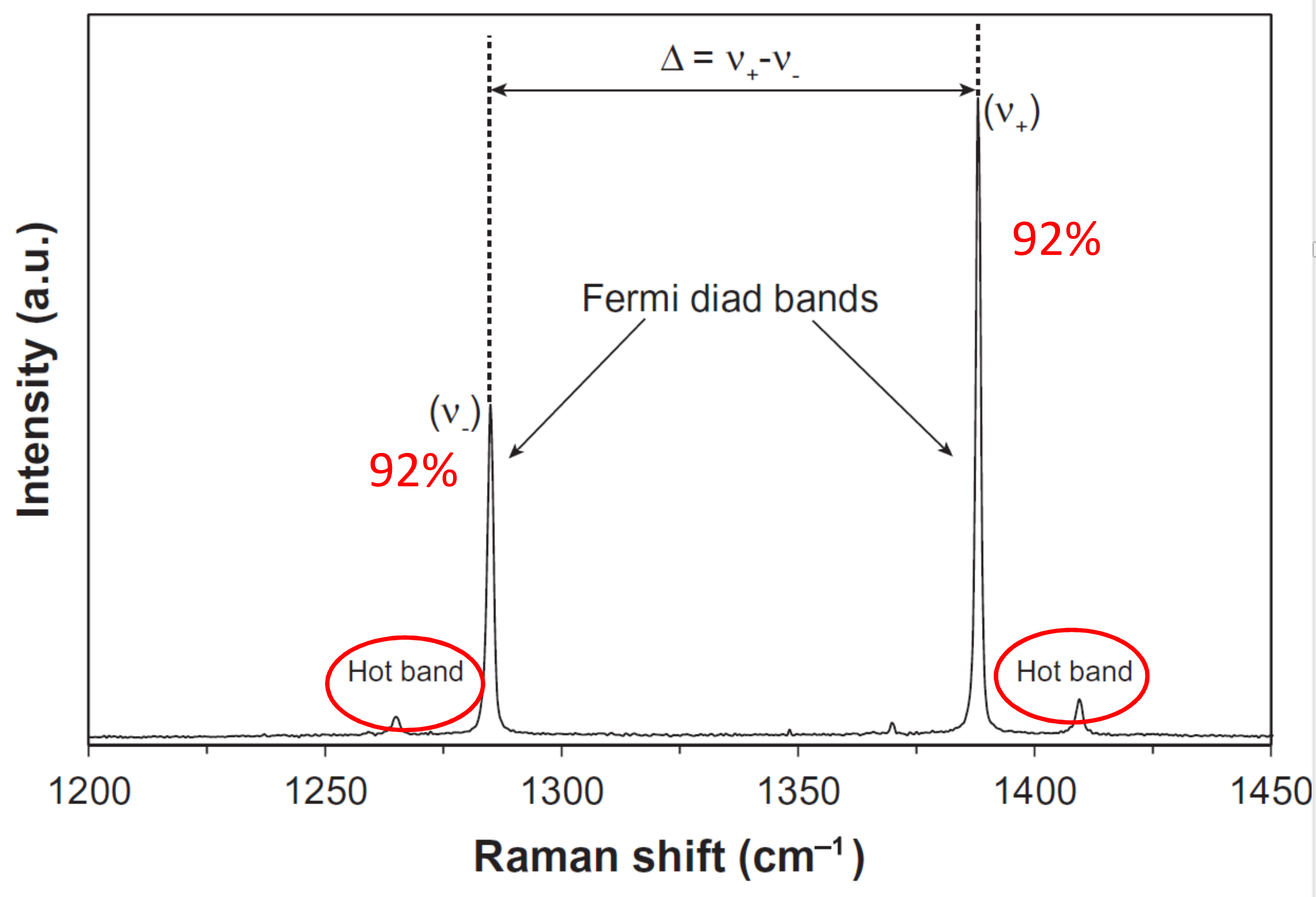
Fall *et al.* GCA 2011

TABLE II. Some CO_2 transitions giving bands in the 4.3-μ region.

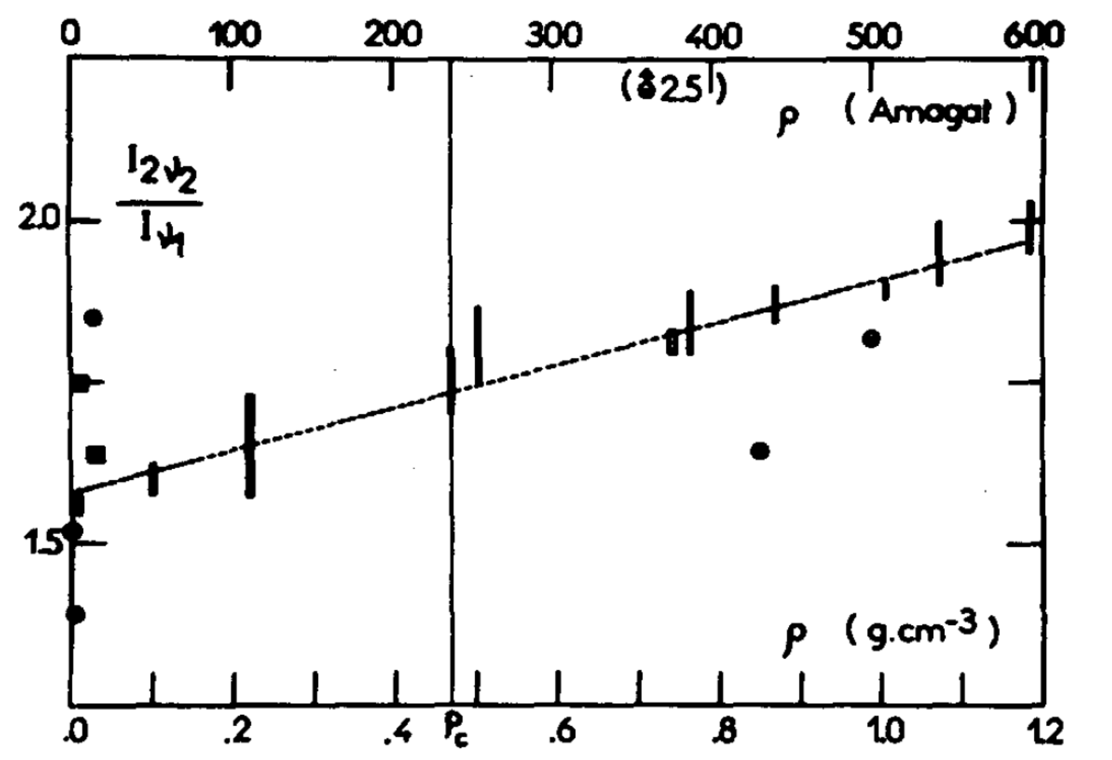
Lower state	Upper state	Lower-state po	
$v_1v_2{}^lv_3$	$v_1v_2{}^lv_3$	300°K	1273°K
00^00	00^01	0.920	0.211
01^10	01^11	0.074	0.199
02^20	02^21	0.003	0.094
03^30	03^31	<0.001	0.044
04^40	04^41	<0.001	0.021
00^01	00^02	≪0.001	0.015
00^02	00^03	≪0.001	0.001

Tourin, JOSA 1961

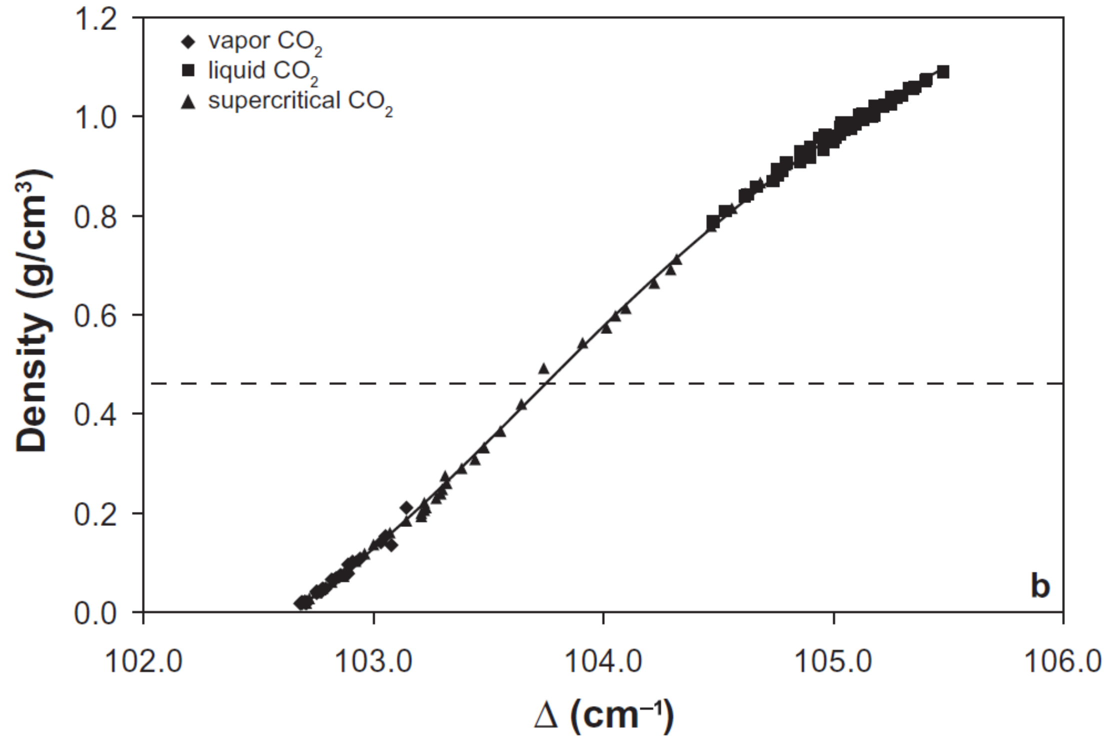
At room temperature, 92% of CO_2 molecules are in the ground vibrational state.



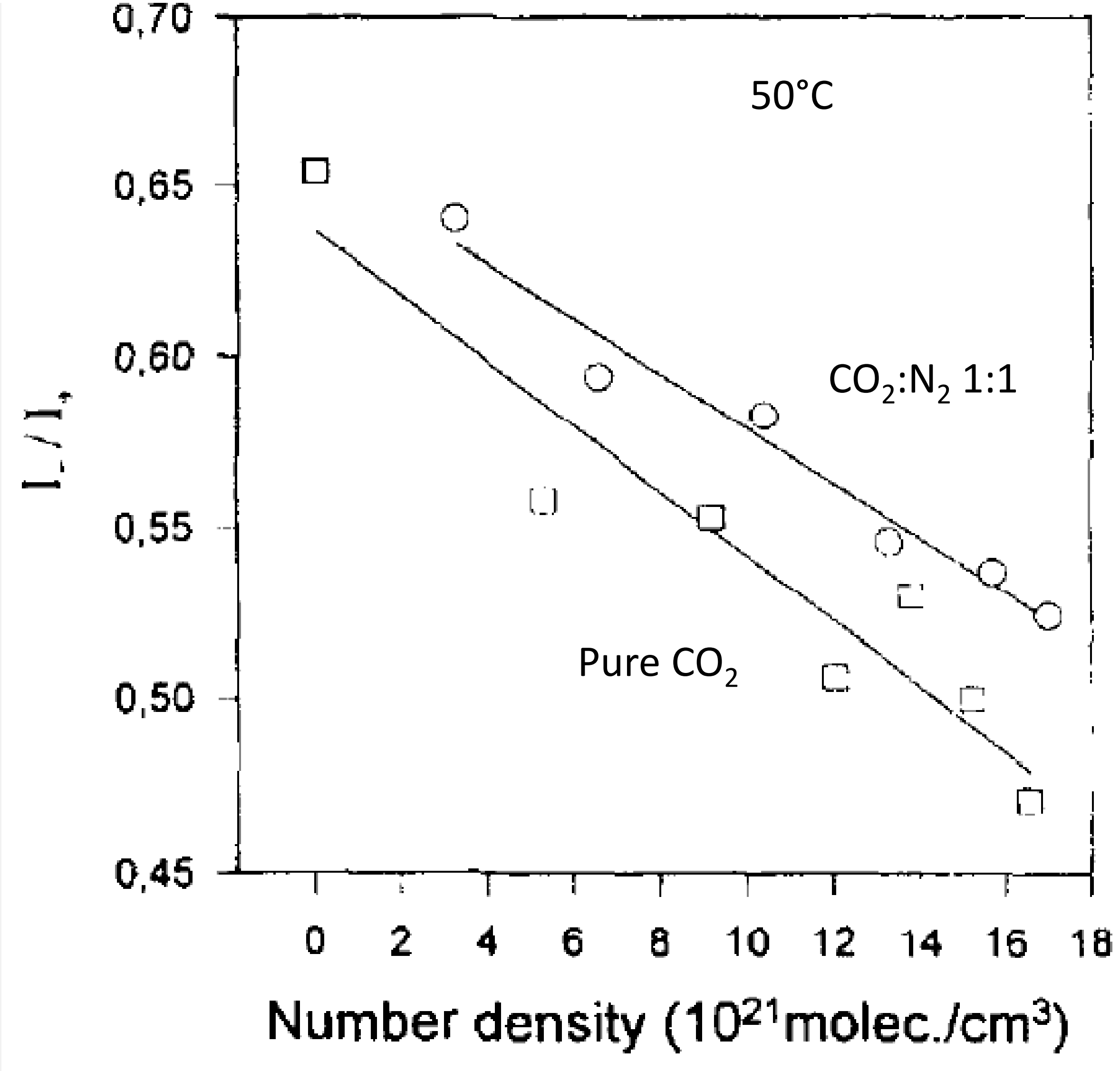
Density effects on Fermi diad splitting and intensity



Garrabos *et al.* J Chem Phys, 1980



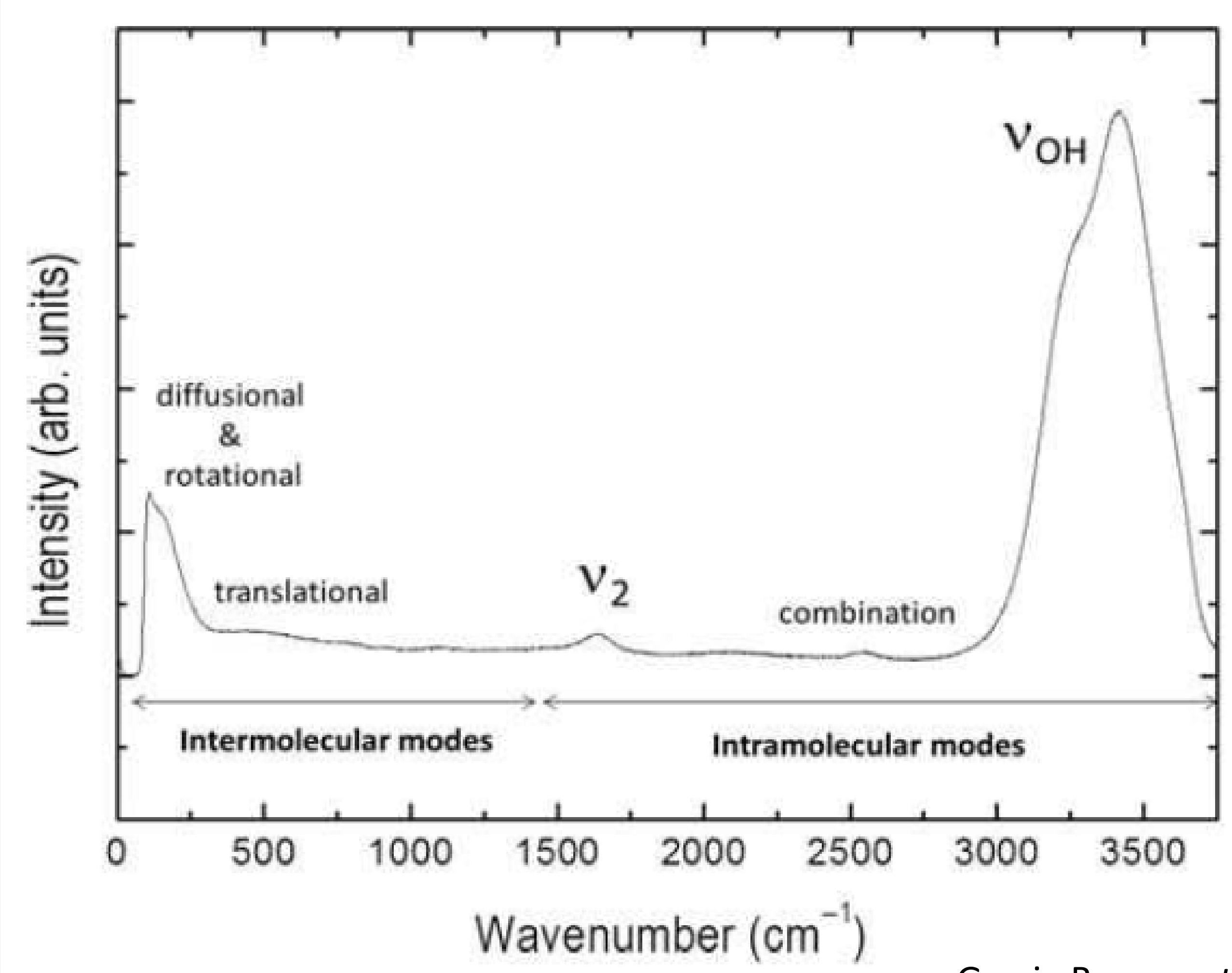
Fall *et al.* GCA 2011



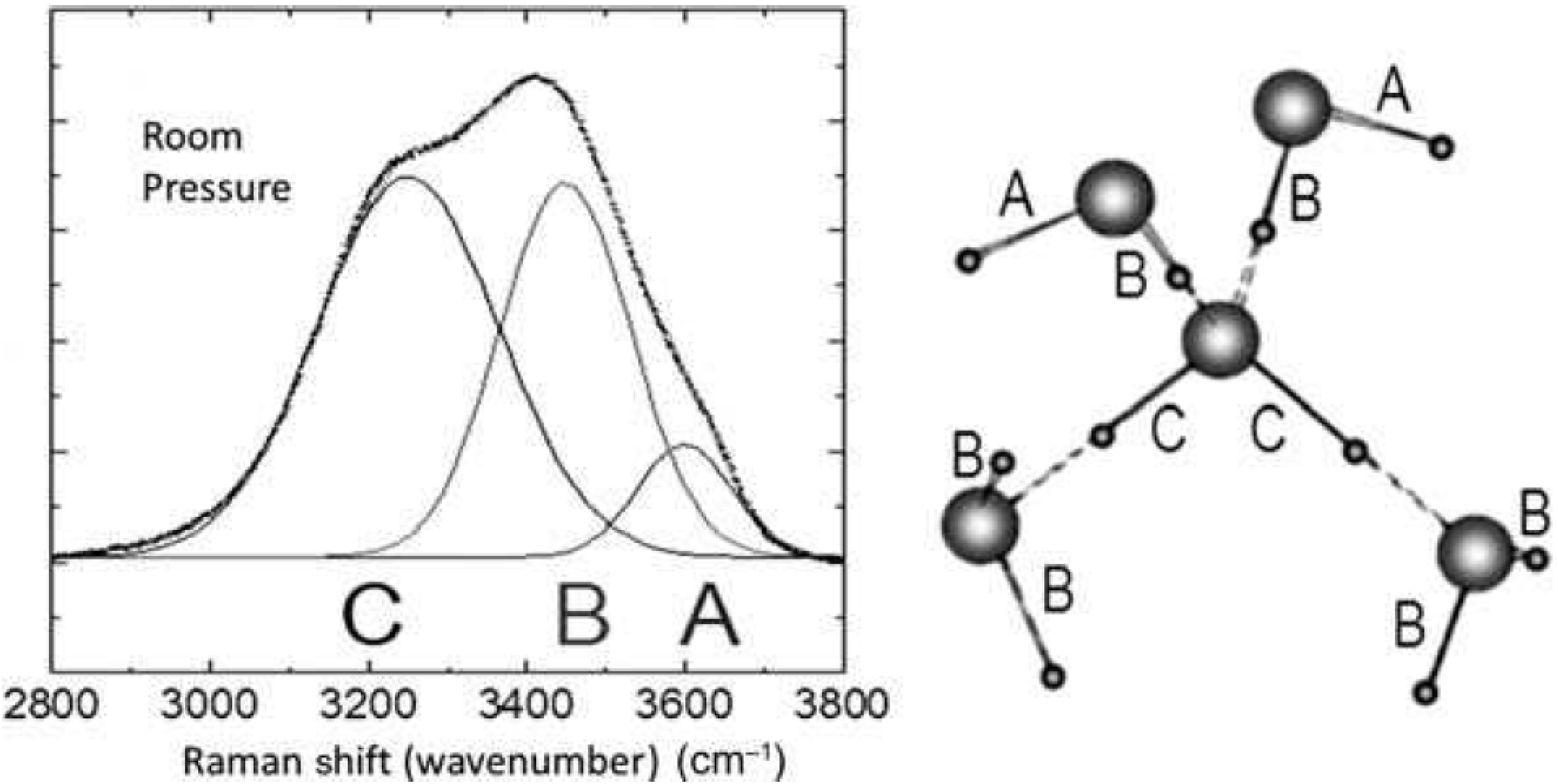
Effect of gas mixture composition

Hacura, Phys Lett A 1997

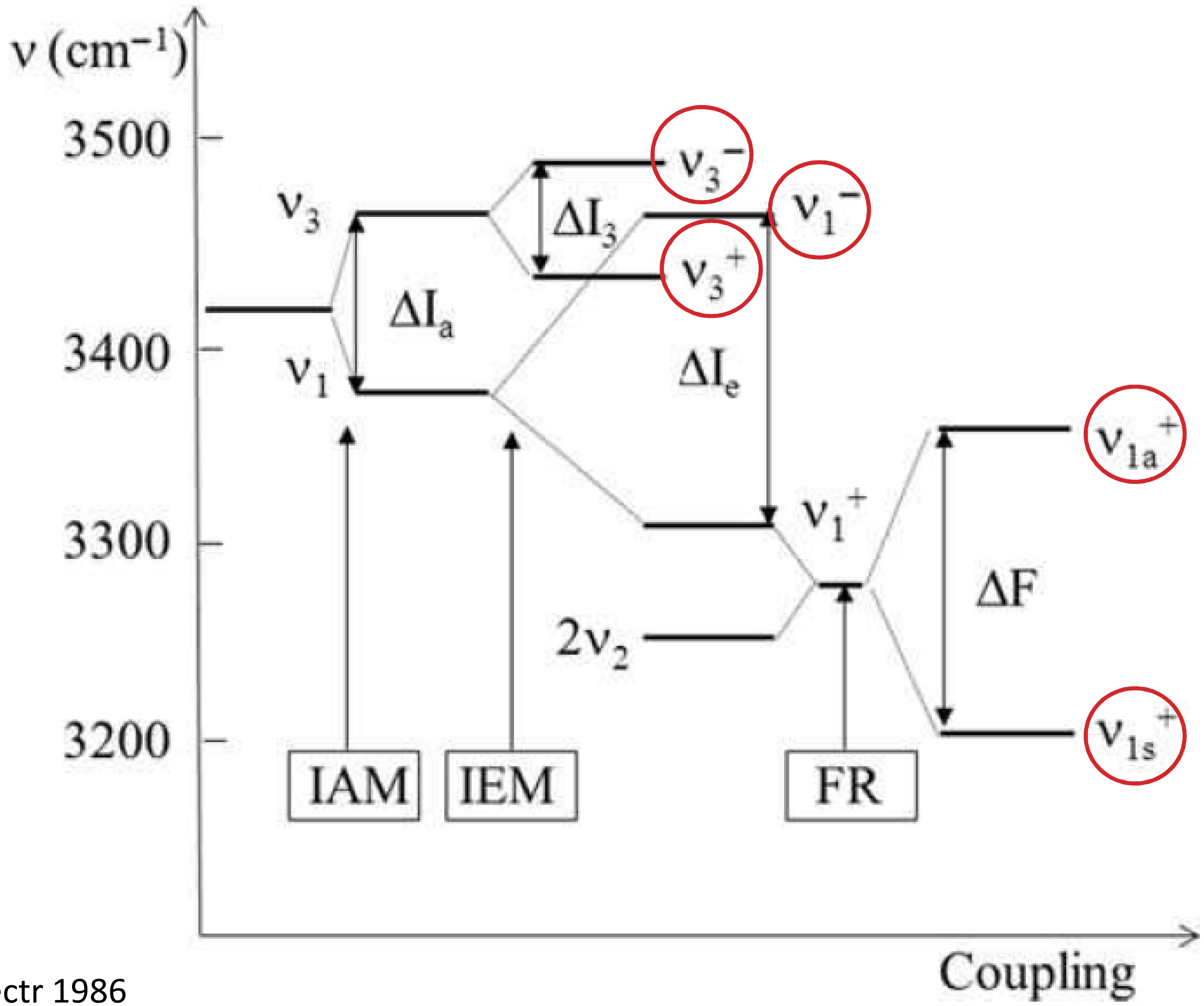
Raman spectroscopy of liquid water and aqueous solutions



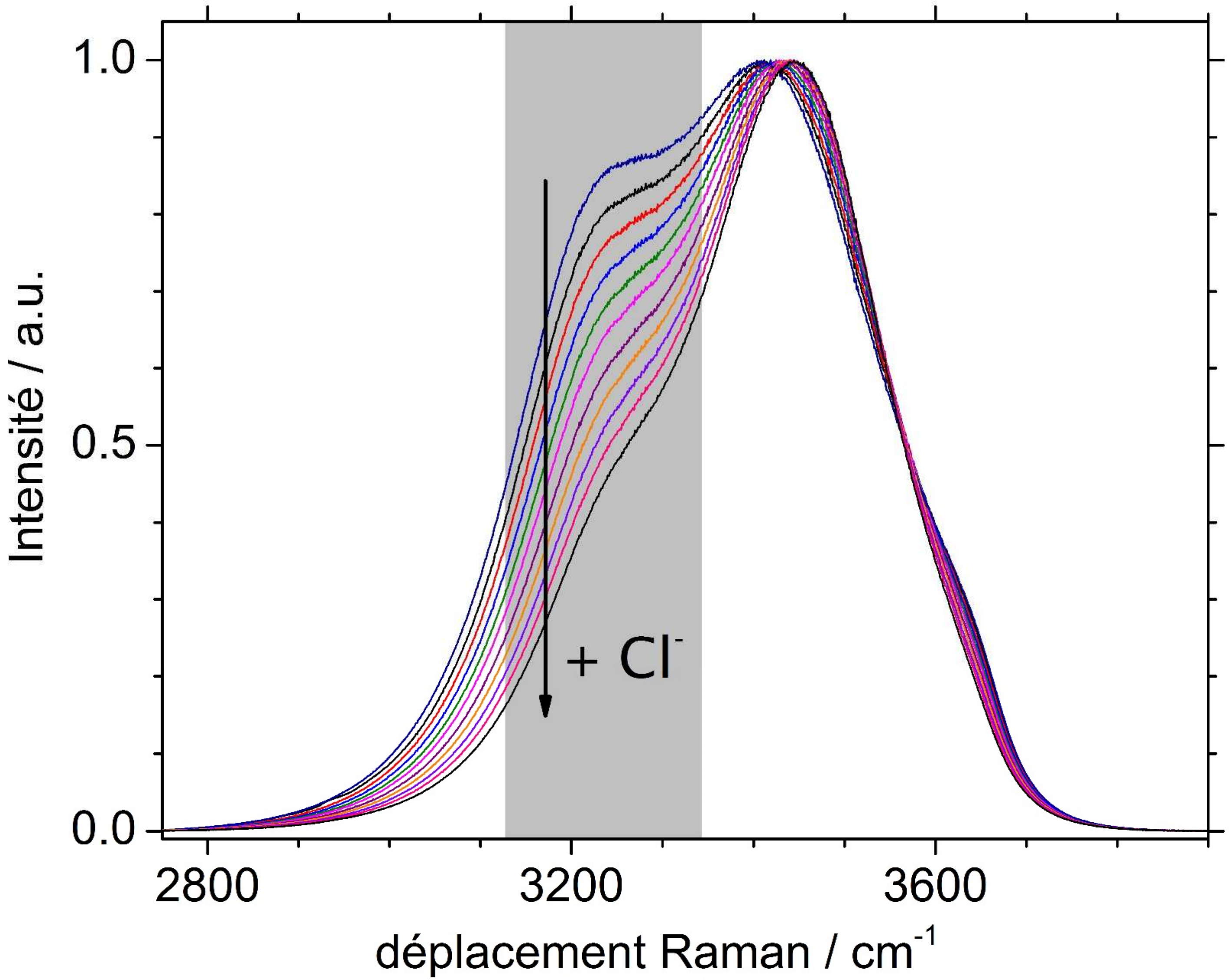
Garcia Baonza *et al., EMU Notes vol.12,* 2012



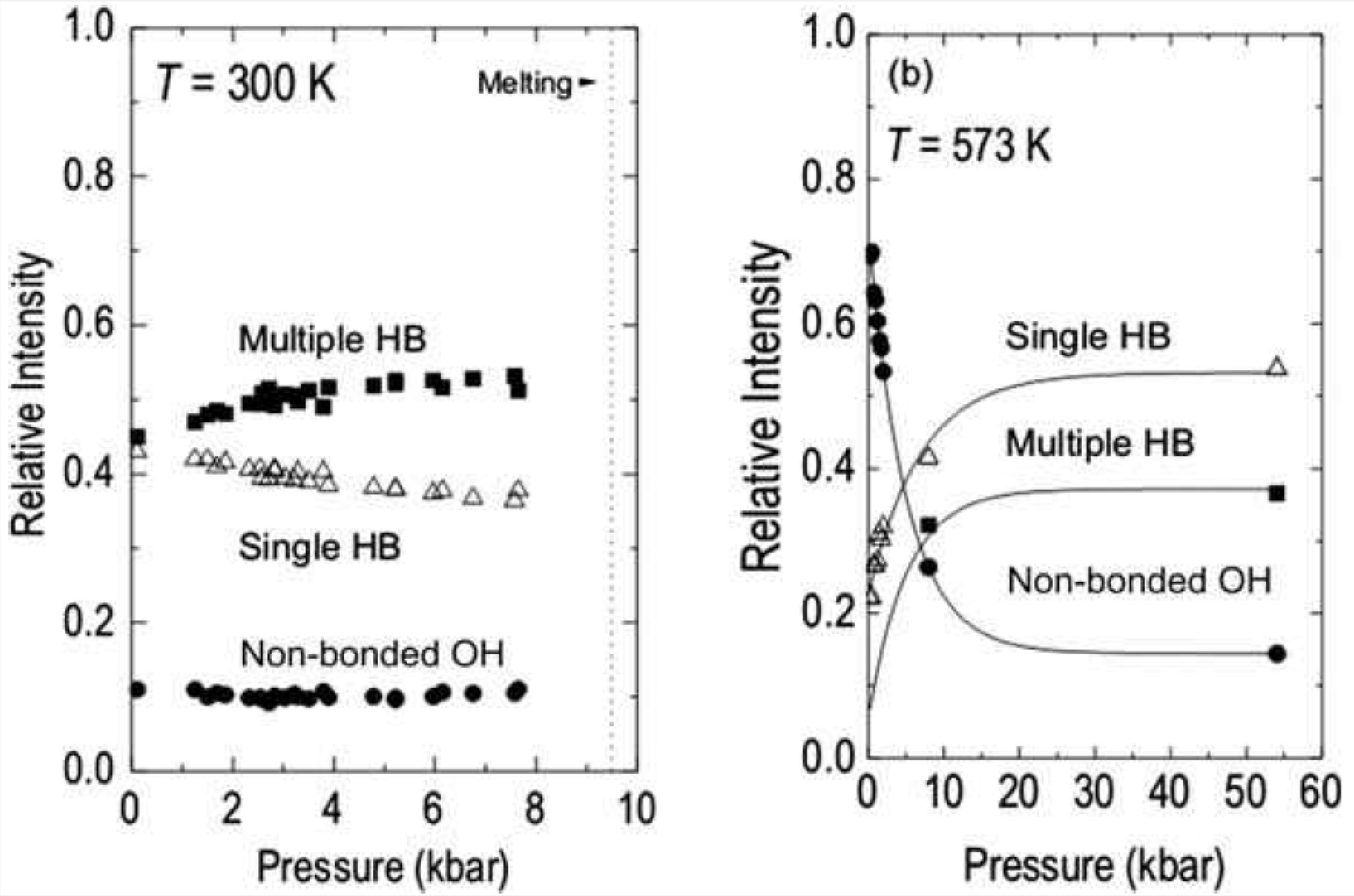
Garcia Baonza *et al.*, *EMU Notes vol.12*, 2012



Rull & Saja J Raman Spectr 1986



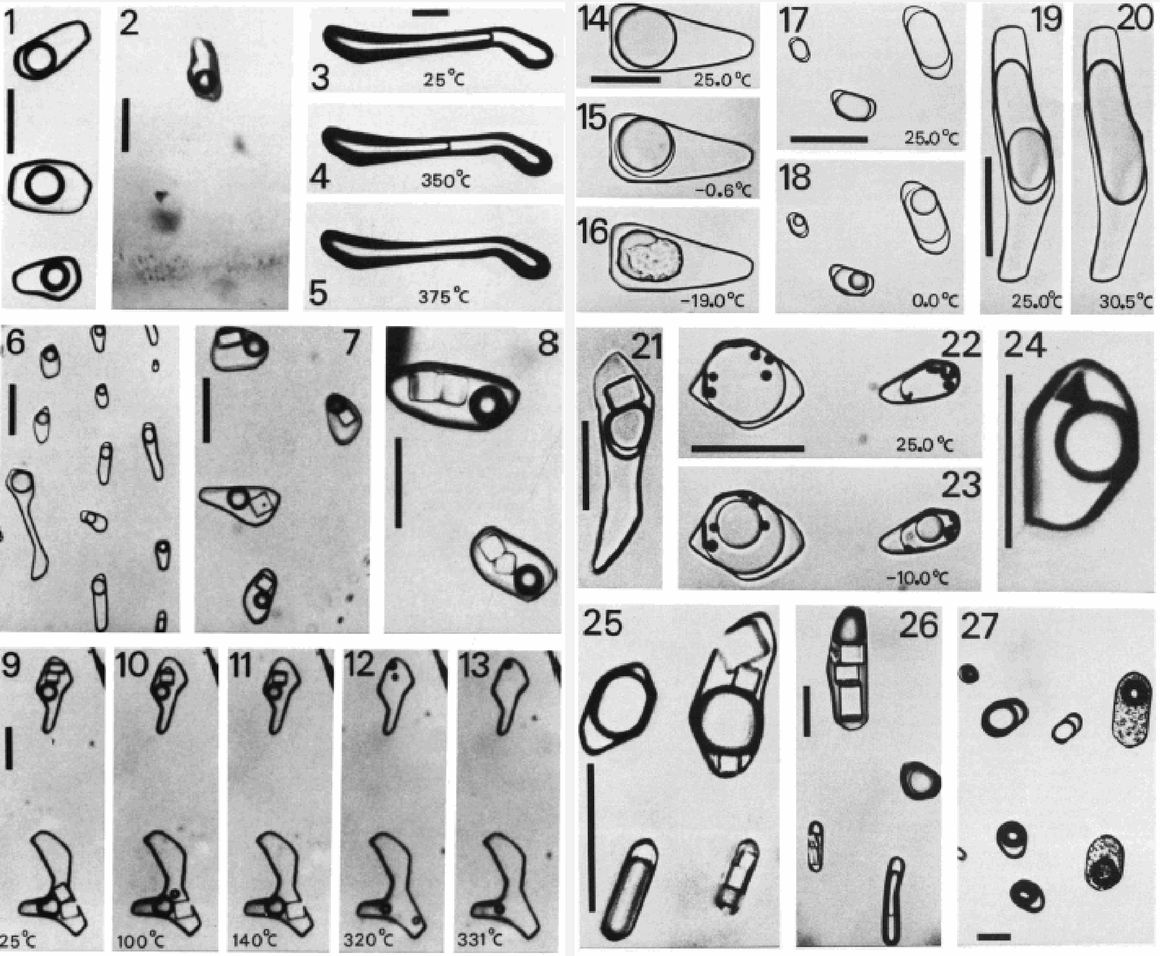
Chlorinity effect on H-bonds.



Garcia Baonza *et al., EMU Notes vol.12,* 2012

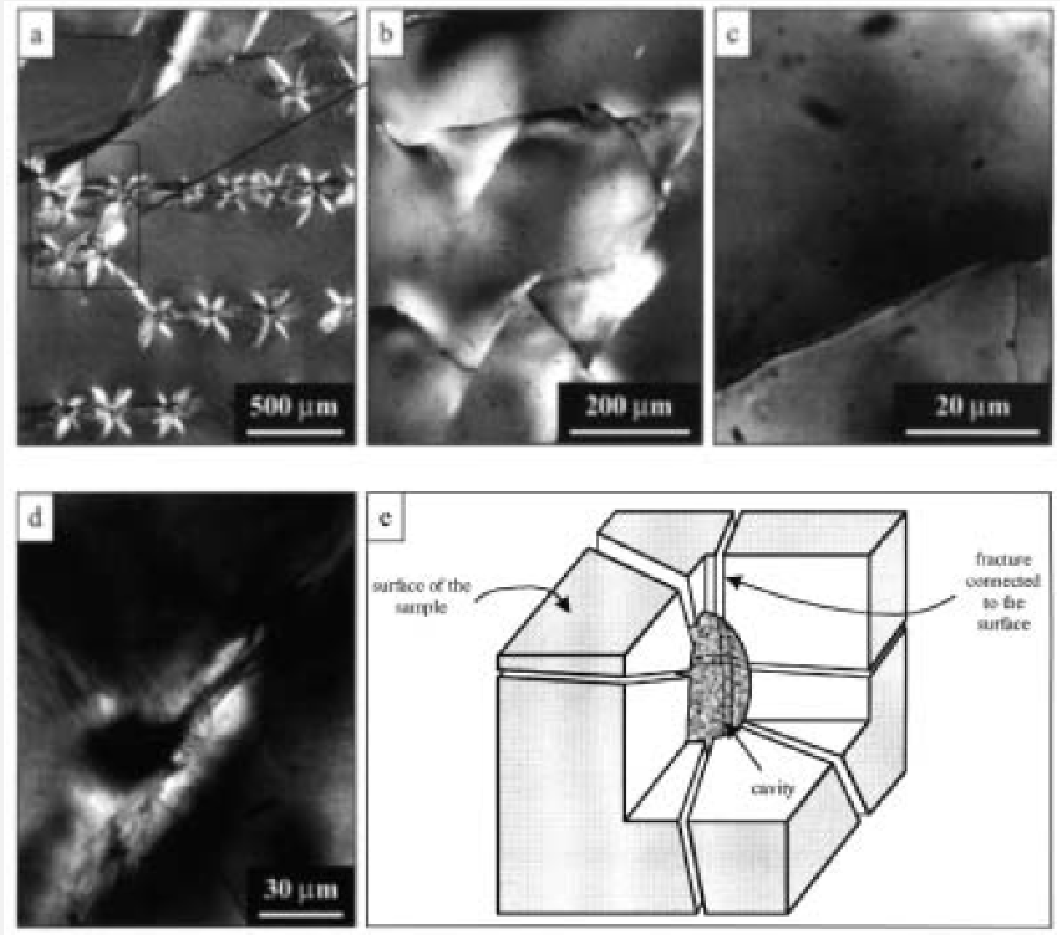
Experimental devices for the study of geological fluids by Raman spectroscopy

1. Synthetic fluid inclusions



From natural or lab-growth crystal (crack & heal)

Sterner & Bodnar, GCA 1984



Creation of microcavities by laser ablation

Dubessy *et al.*, EJM 2000

2. autoclaves

With sapphire windows

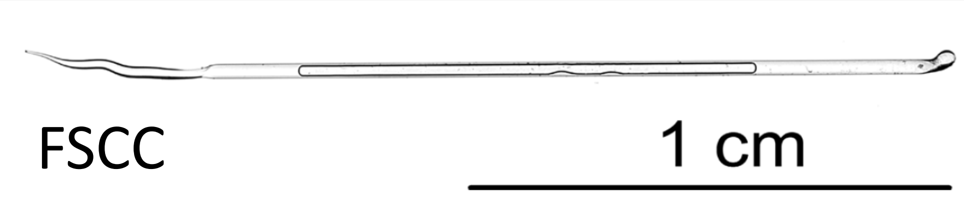
With immersion probes

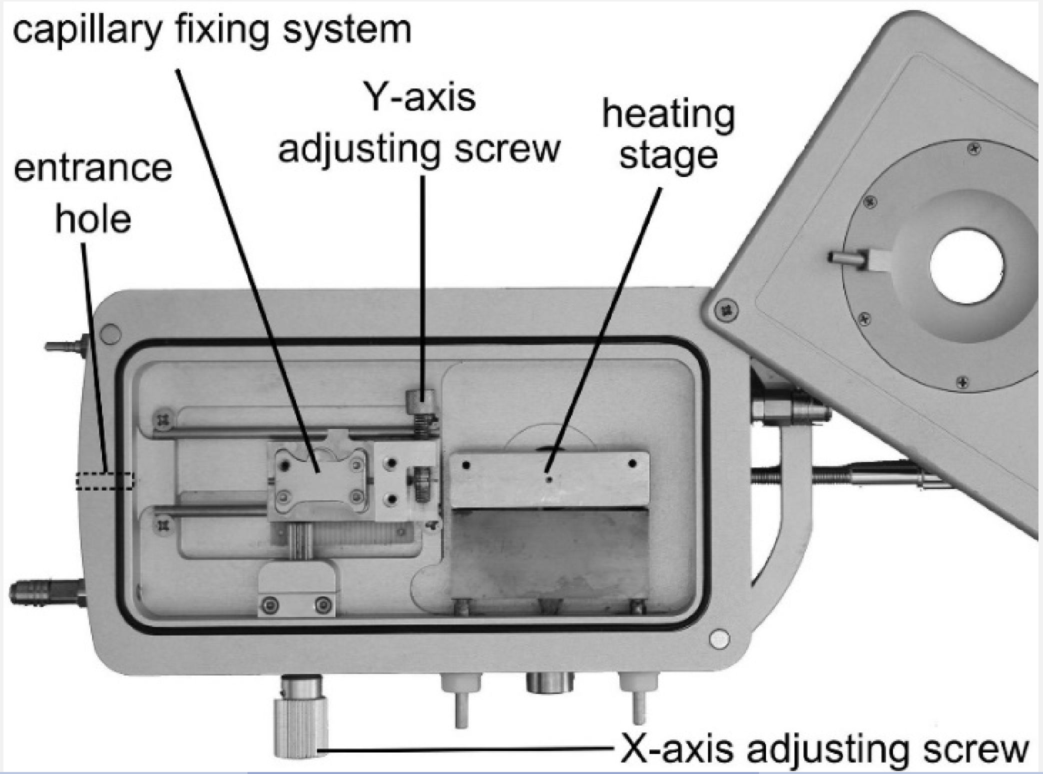
5-200 bar
25-300 °C

Chou *et al.*, GCA 2008

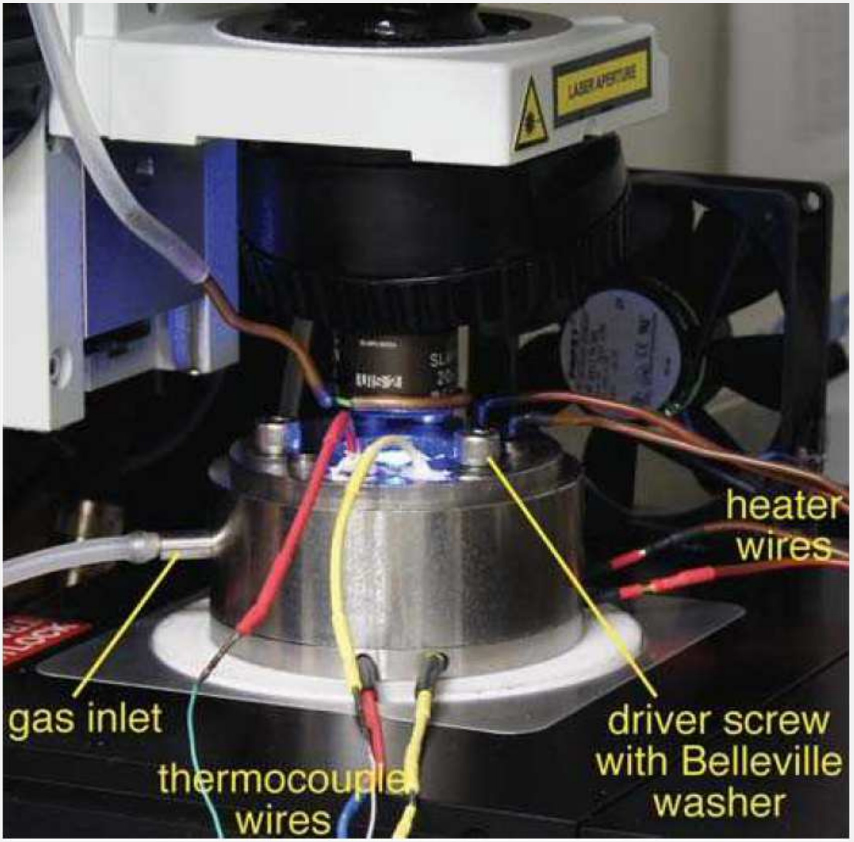
3. Silica capillary cells

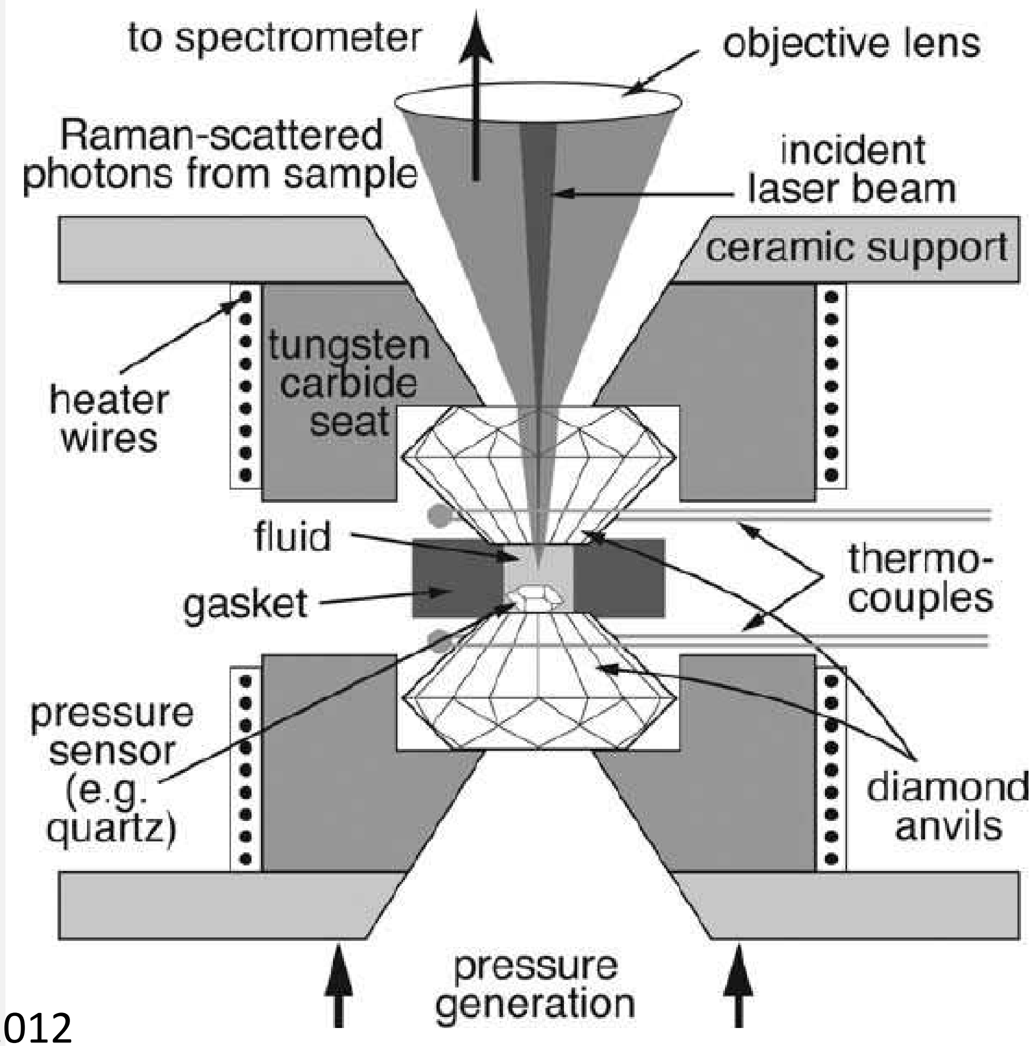
1-2000 bar
-196 – 400 °C





4. HDAC



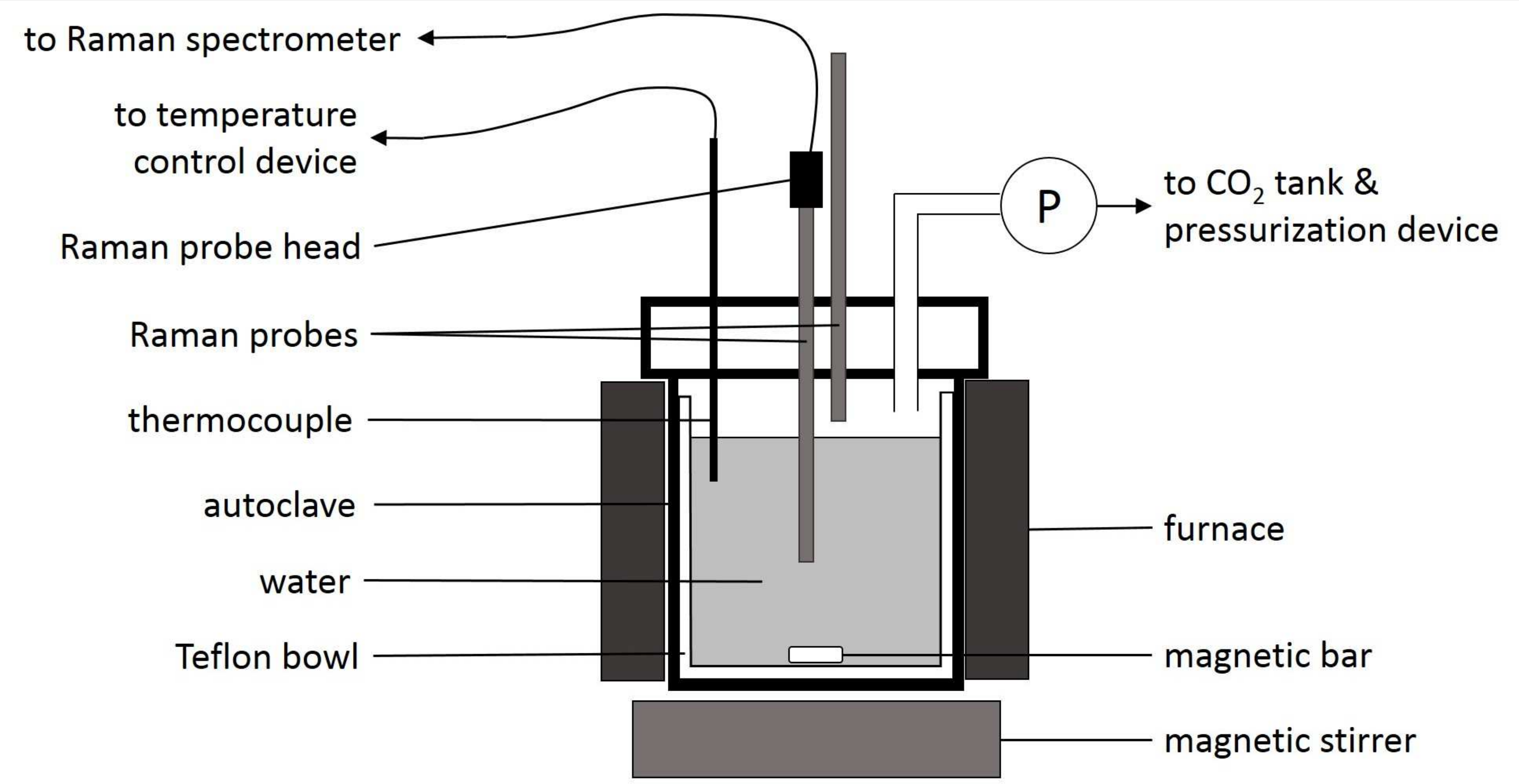


Up to ~1000 °C
1-20 GPa

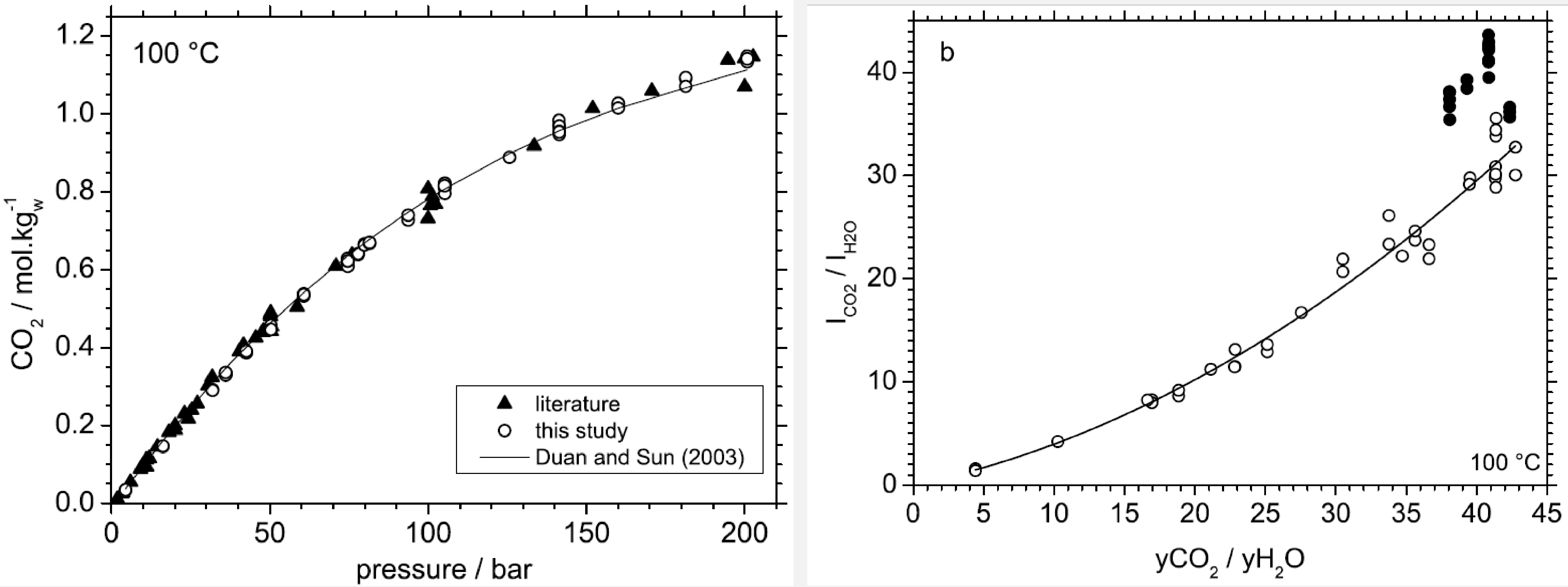
Schmidt & Chou, EMU Notes 12, 2012

Some examples of geofluid studies by Raman spectroscopy

Gas solubility: CO_2

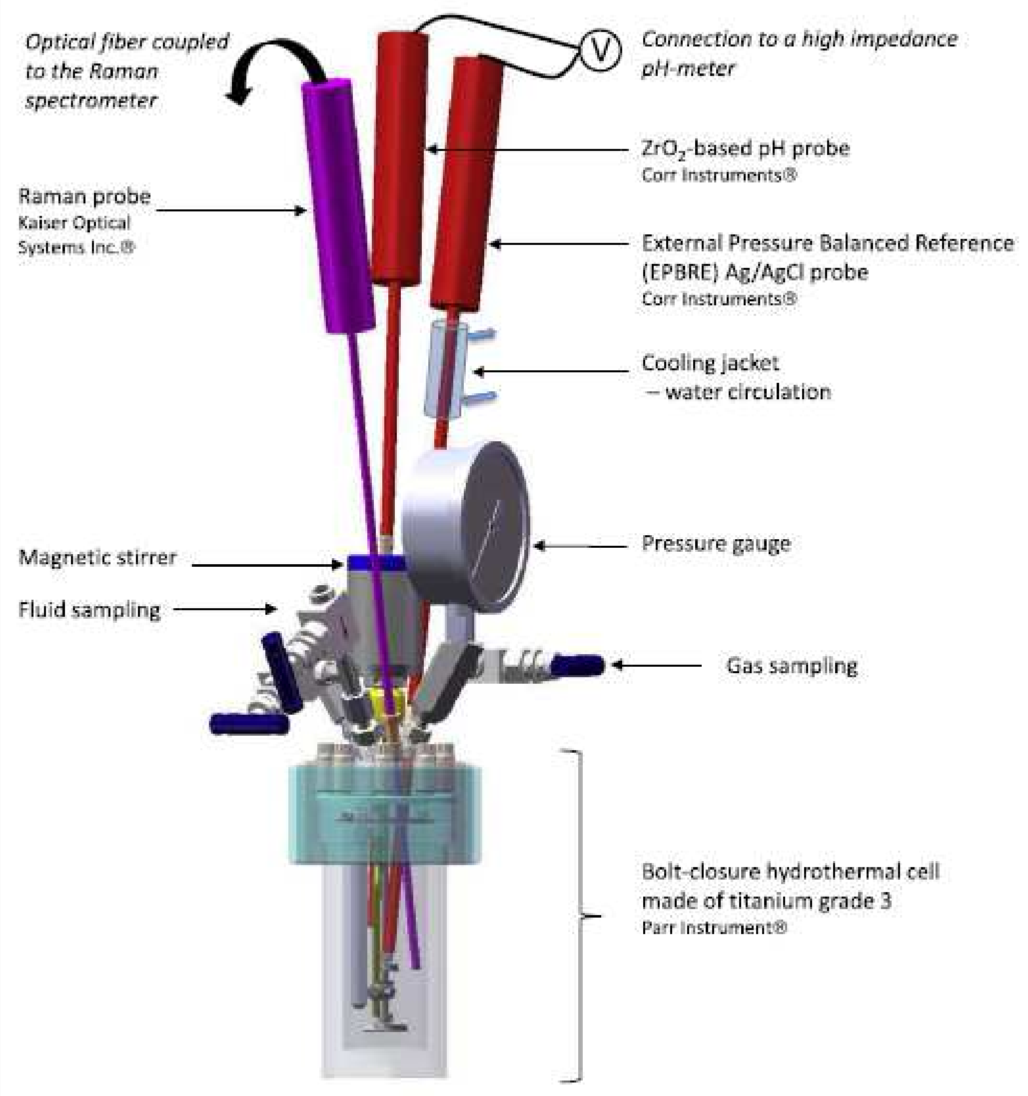


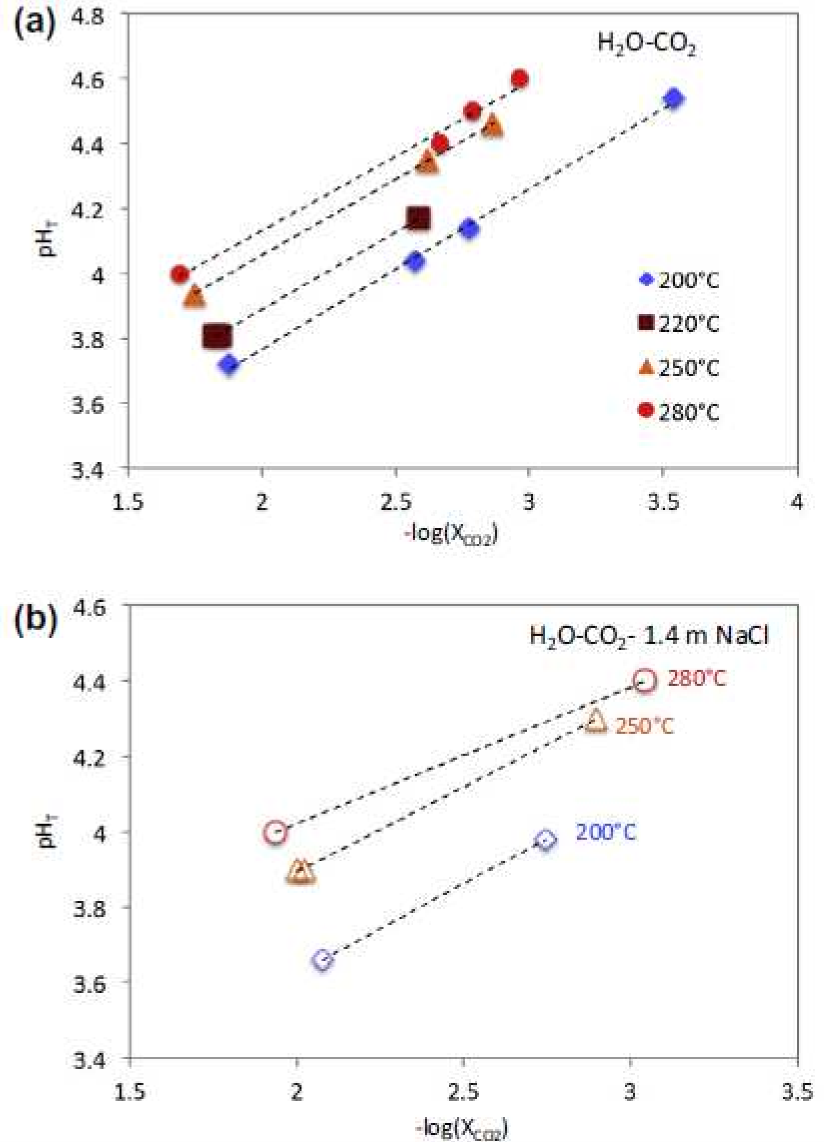
Caumon *et al., IJGGC 2016*



Caumon *et al., IJGGC 2016*

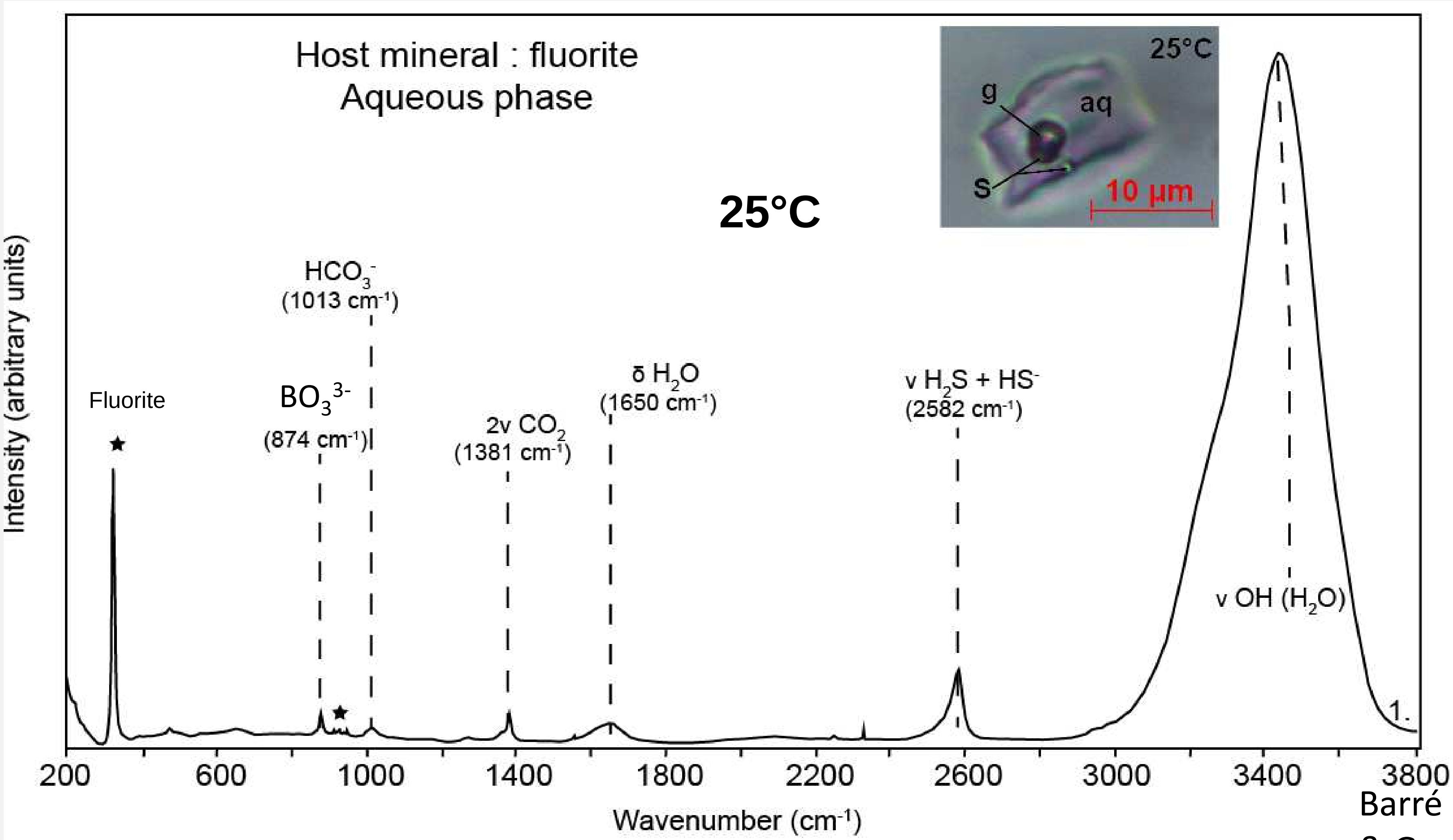
CO_2 solubility & pH *vs.* temperature and salinity



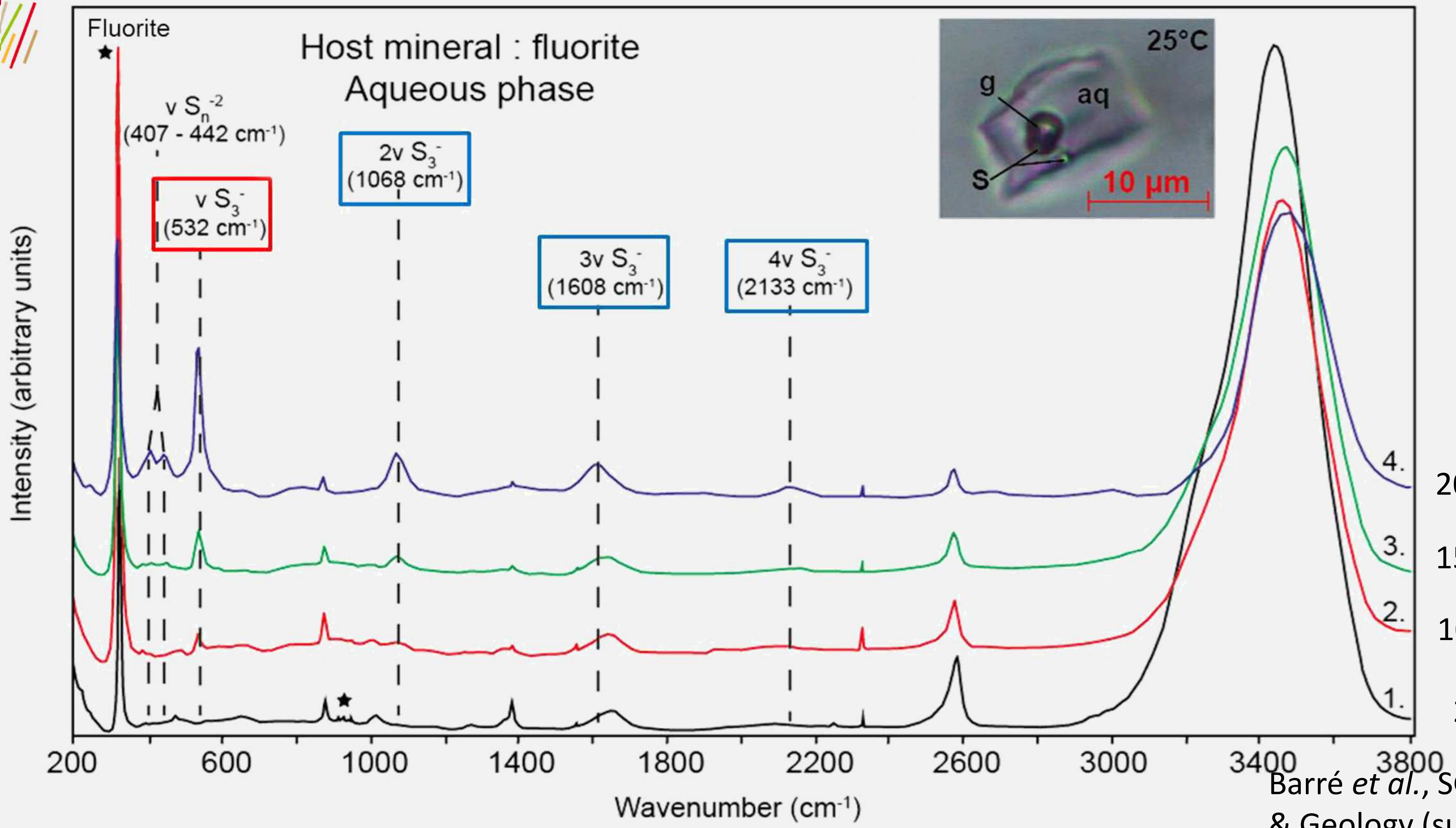


Truche *et al.*, GCA 2016

Sulfur speciation *vs.* temperature



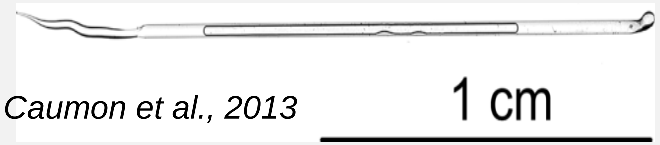
Barré *et al.*, SGA 2015
& Geology (submitted)



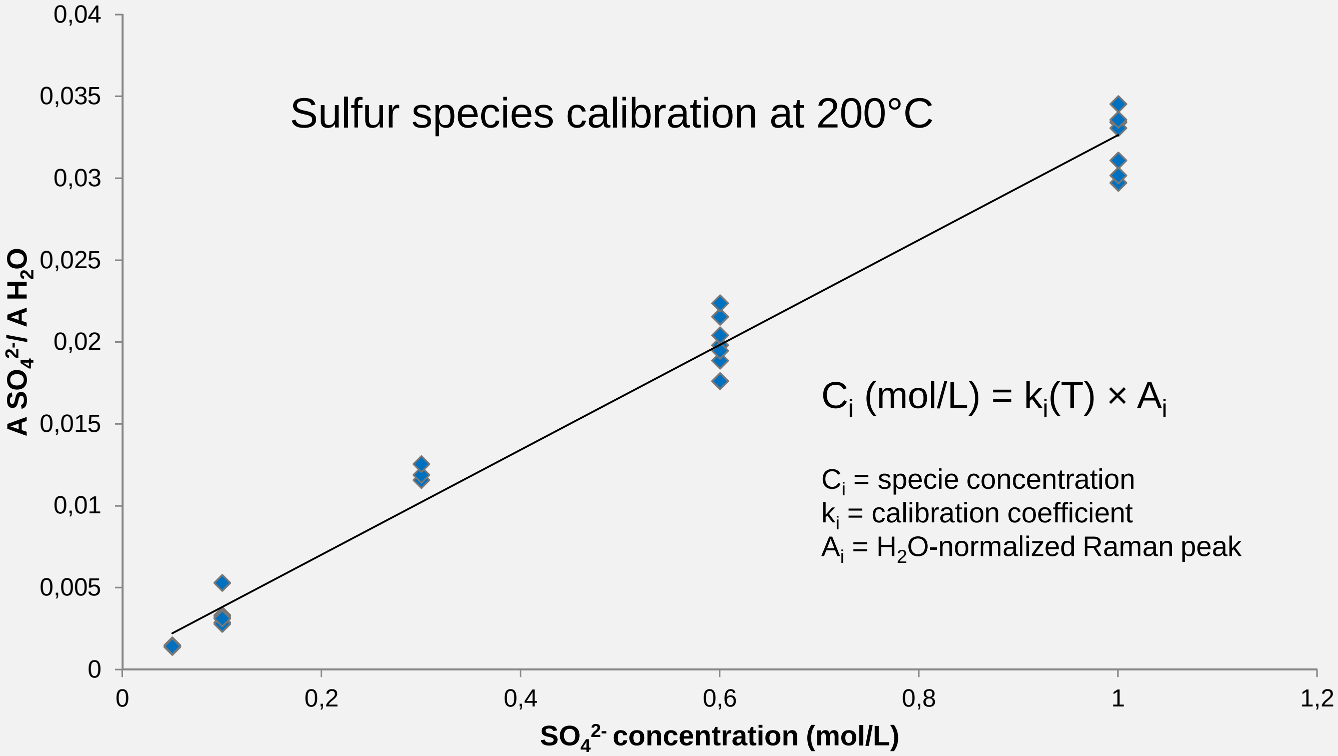
Barré *et al.*, SGA 2015
& Geology (submitted)

Standard solutions :

SO_4^{2-} → Na_2SO_4
HSO_4^- → H_2SO_4
H_2S → Thioacetamid (C_2H_5NS)
S_3^- → given by *Pokrovski and Dubessy (2015)*



Caumon et al., 2013



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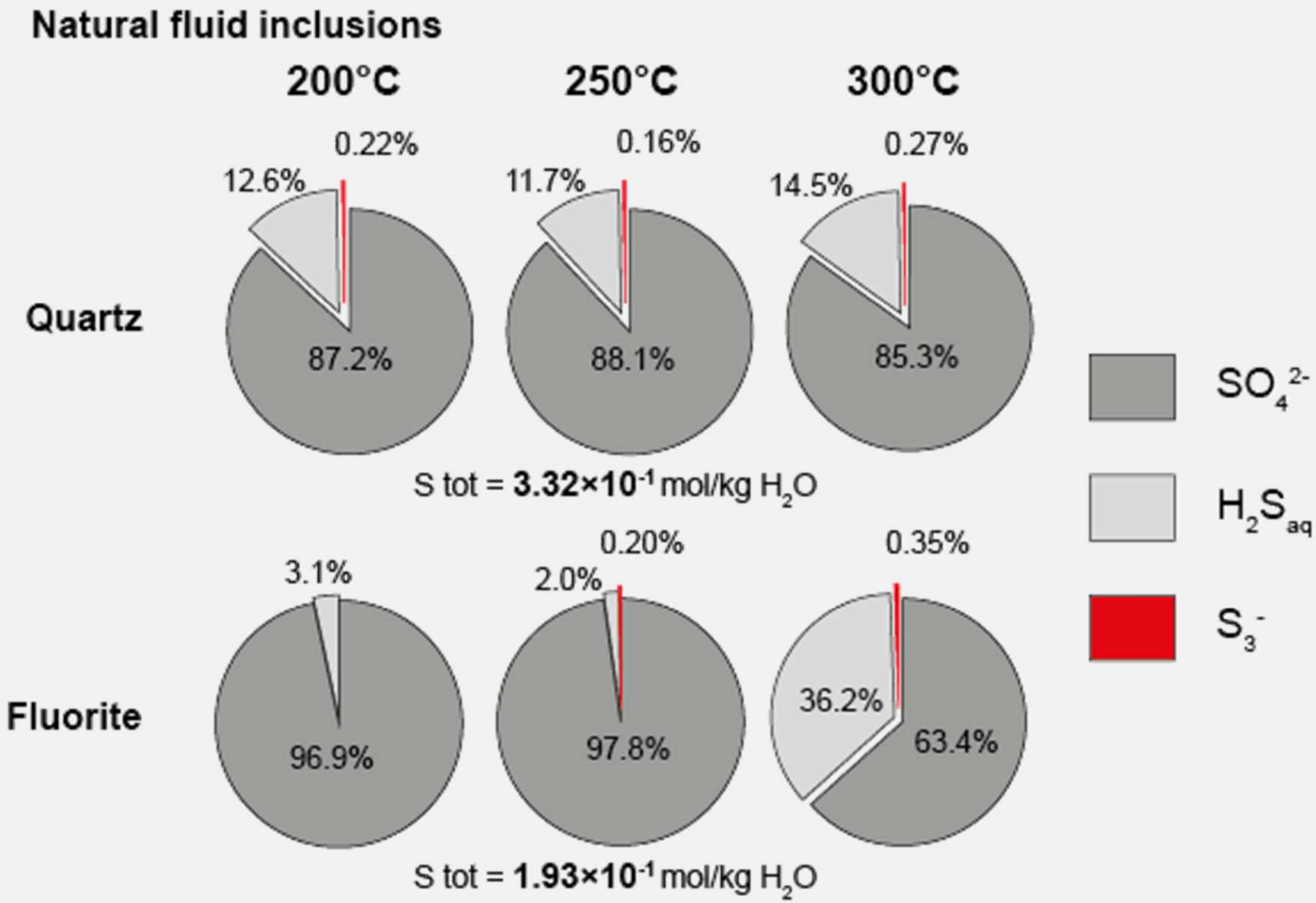
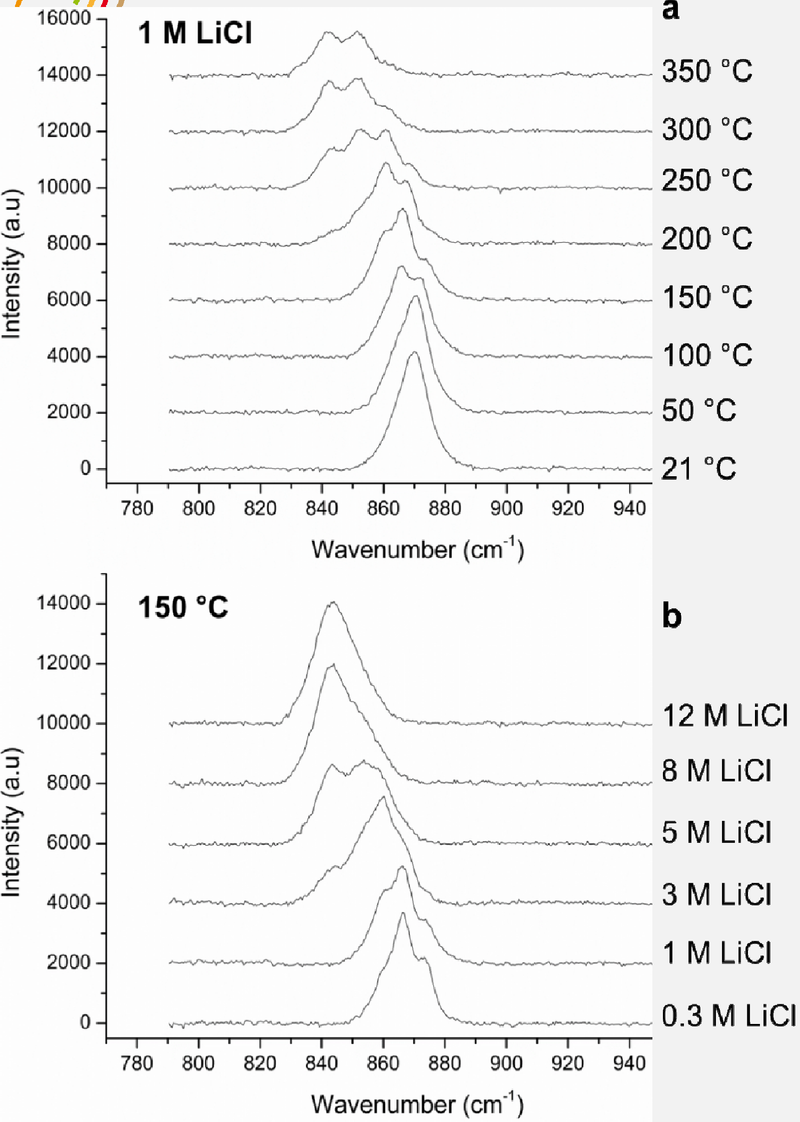
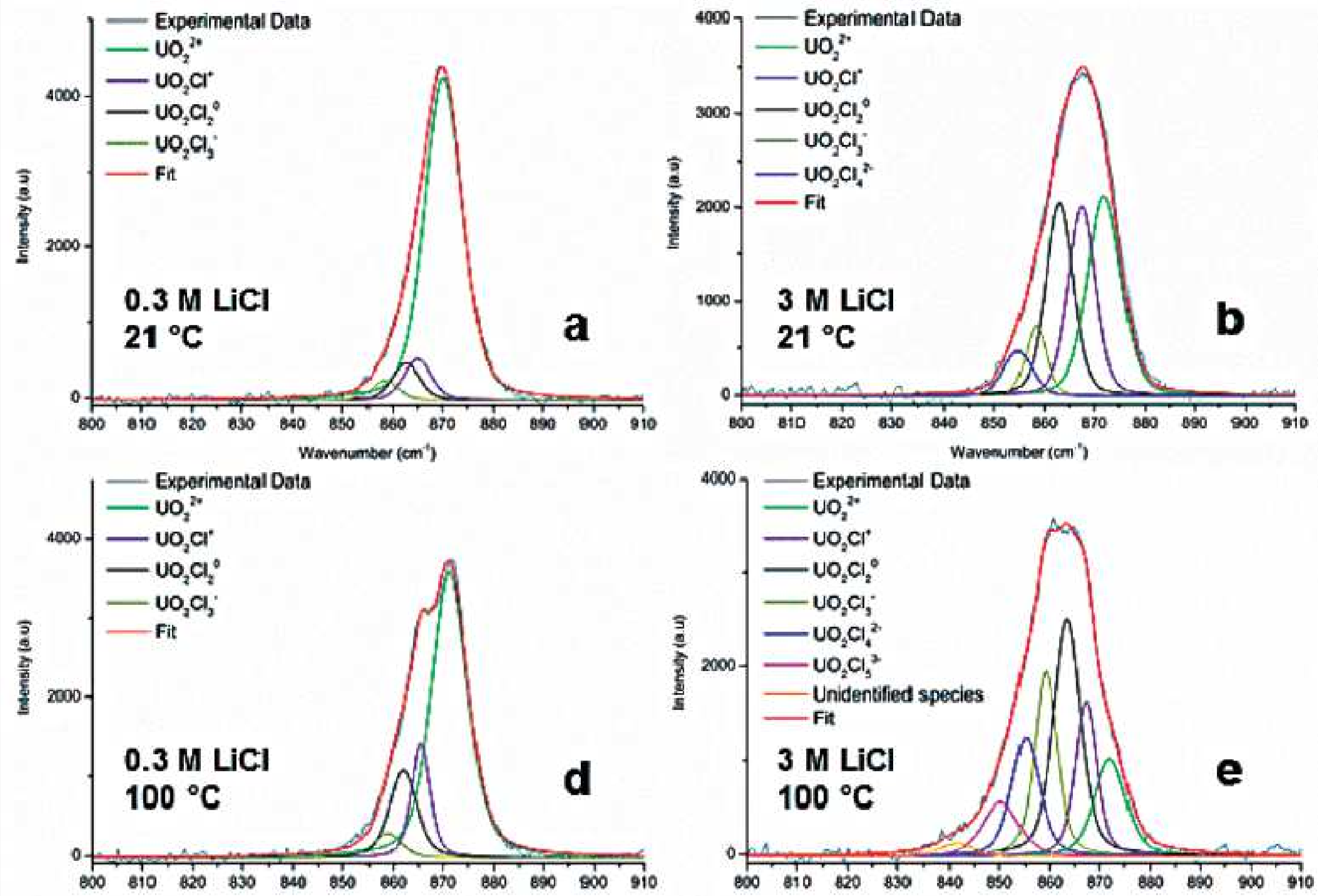


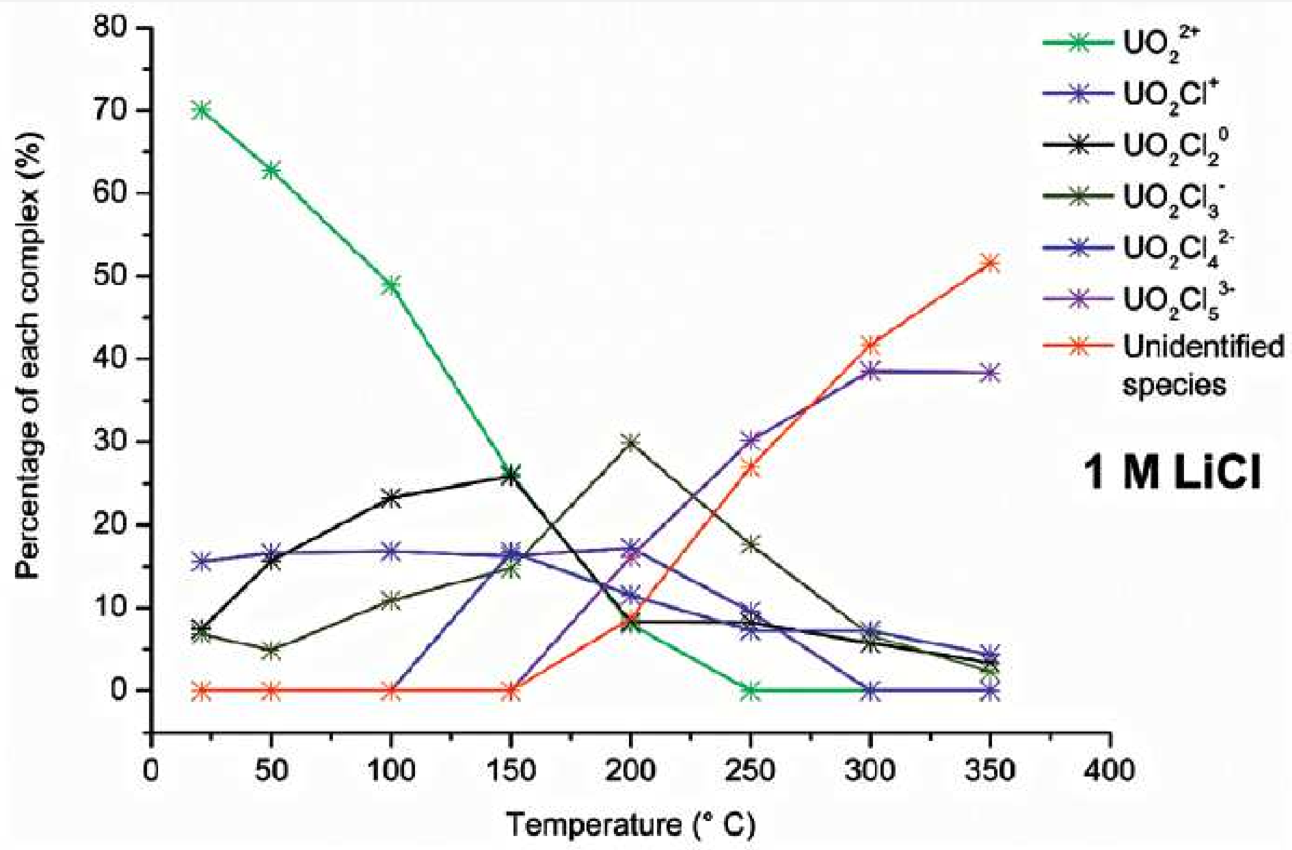
Barré *et al.*, SGA 2015
& Geology (submitted)

Uranyl speciation in LiCl solutions





Dargent *et al.*, EJM 2013



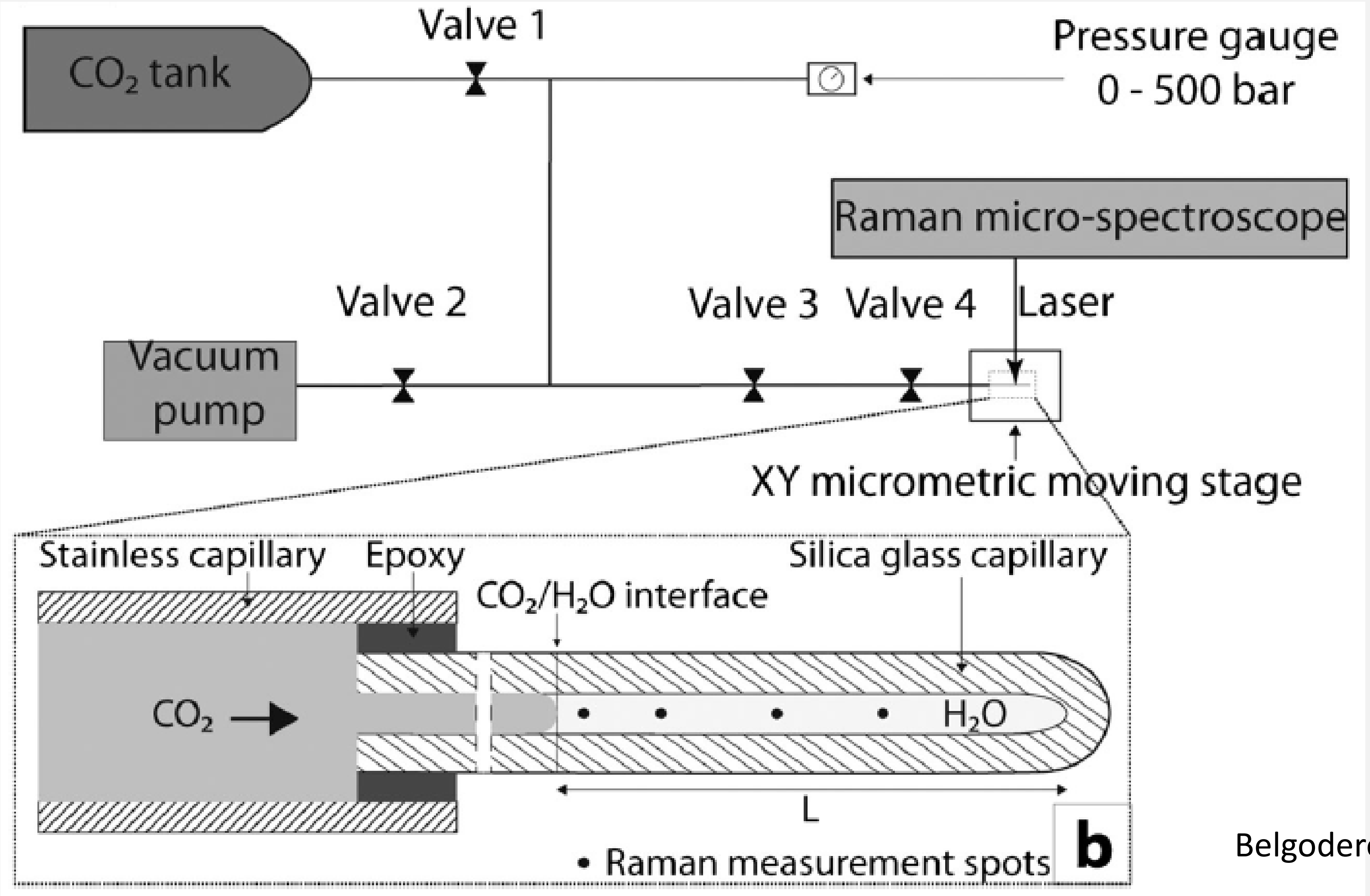
Speciation diagram vs. temperature and LiCl concentration

Calculation of equilibrium constants K_{n+1}

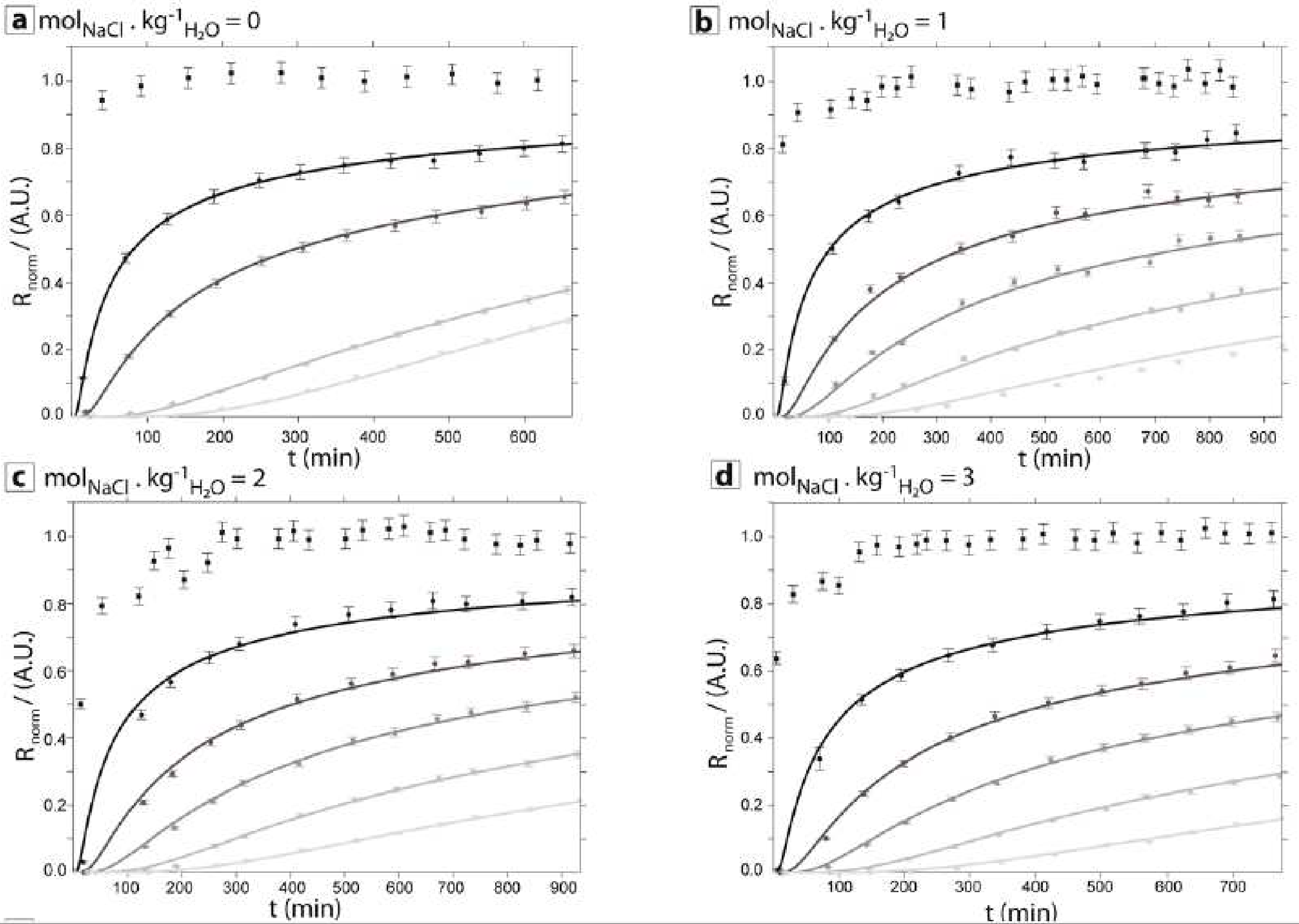
$UO_2Cl_n^{2n}{}_{(aq)} + Cl^-_{(aq)} = UO_2Cl_{n+1}^{1n}{}_{(aq)}$

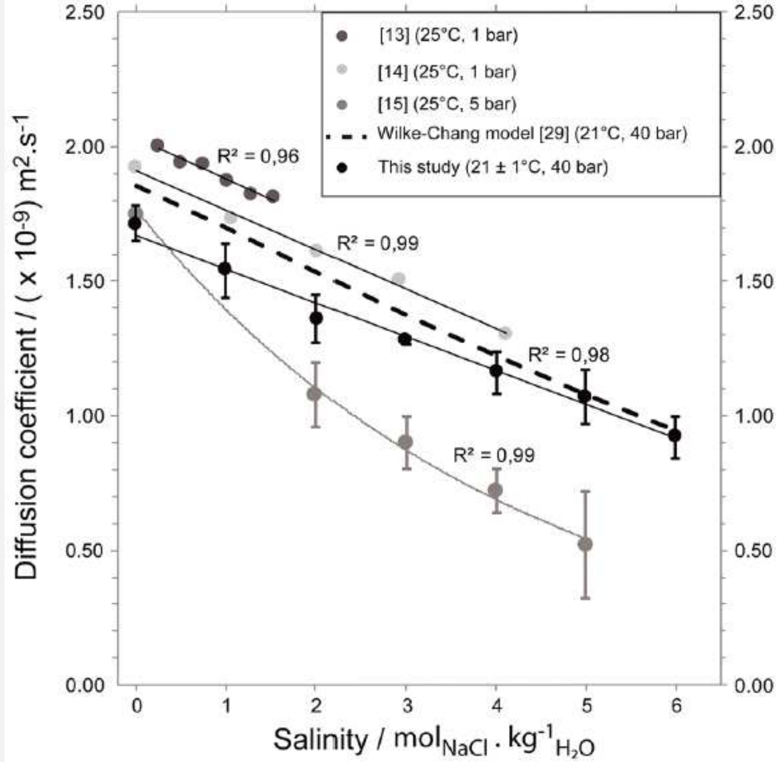
Dargent *et al.*, EJM 2013

Diffusion of CO_2 in water



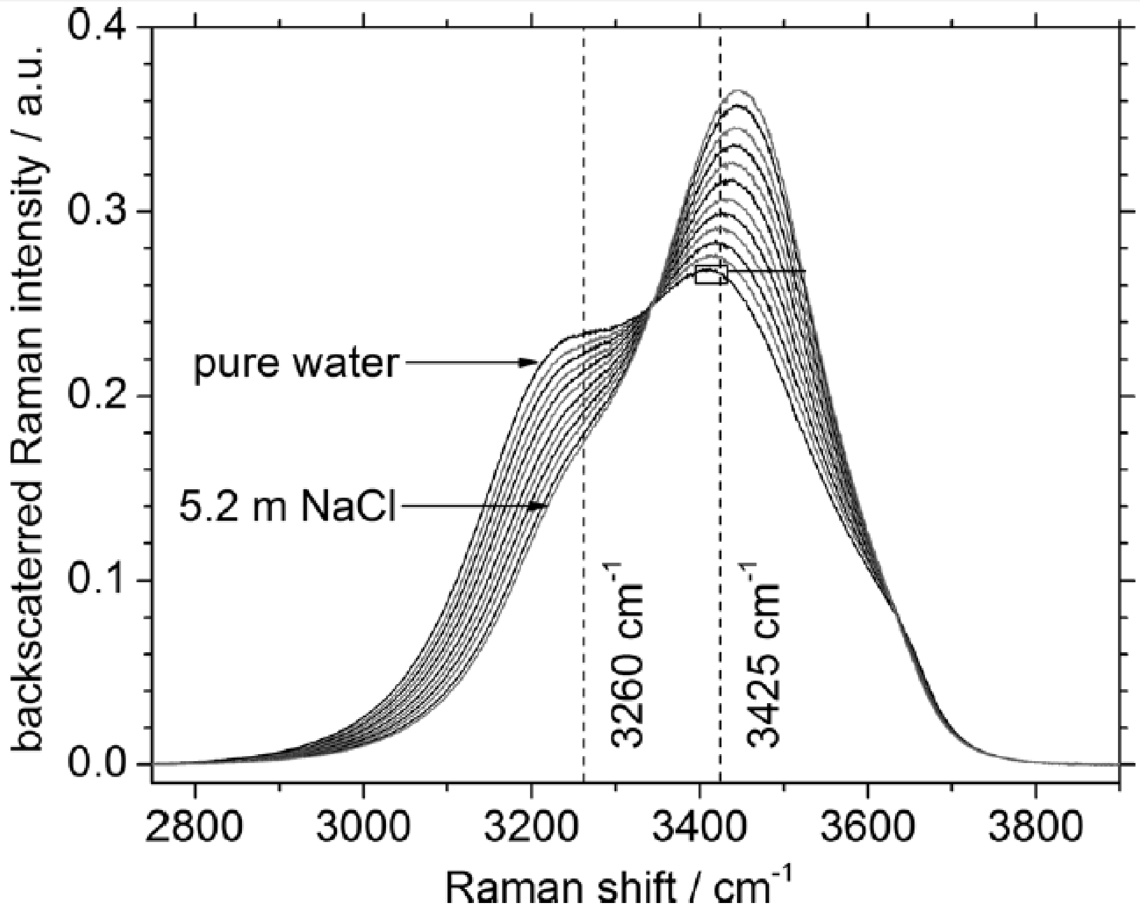
Belgodere *et al.*, J Raman Spectr 2015

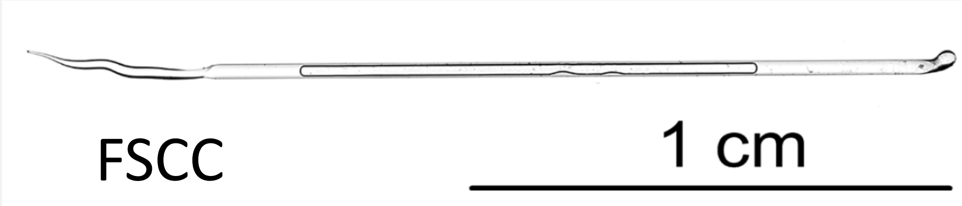




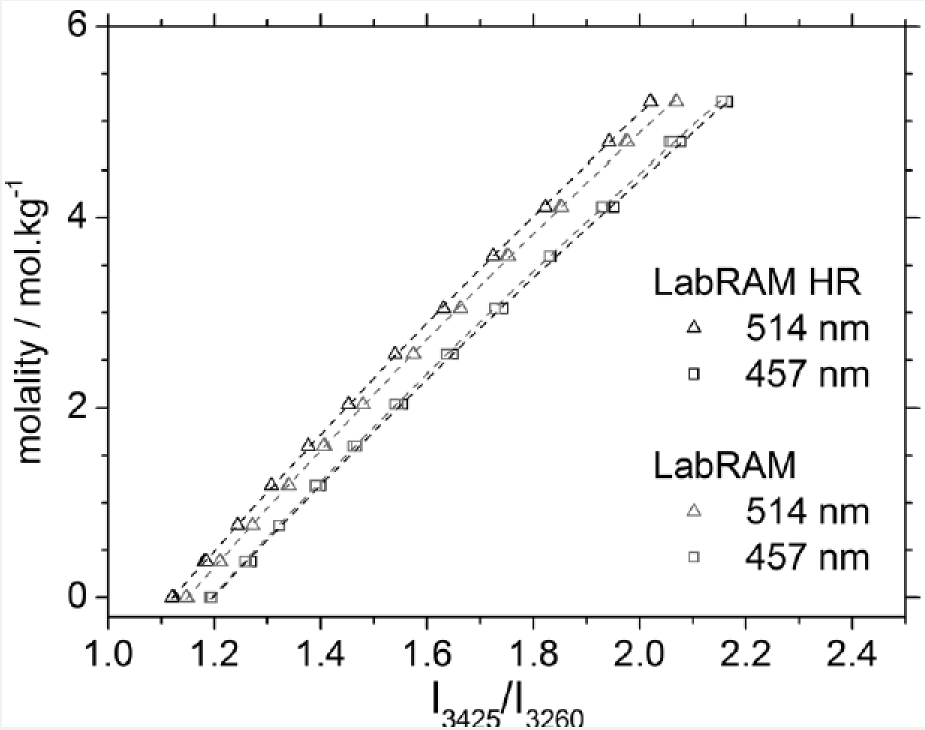
Belgodere *et al.*, J Raman Spectr 2015

Salinity of fluid inclusions

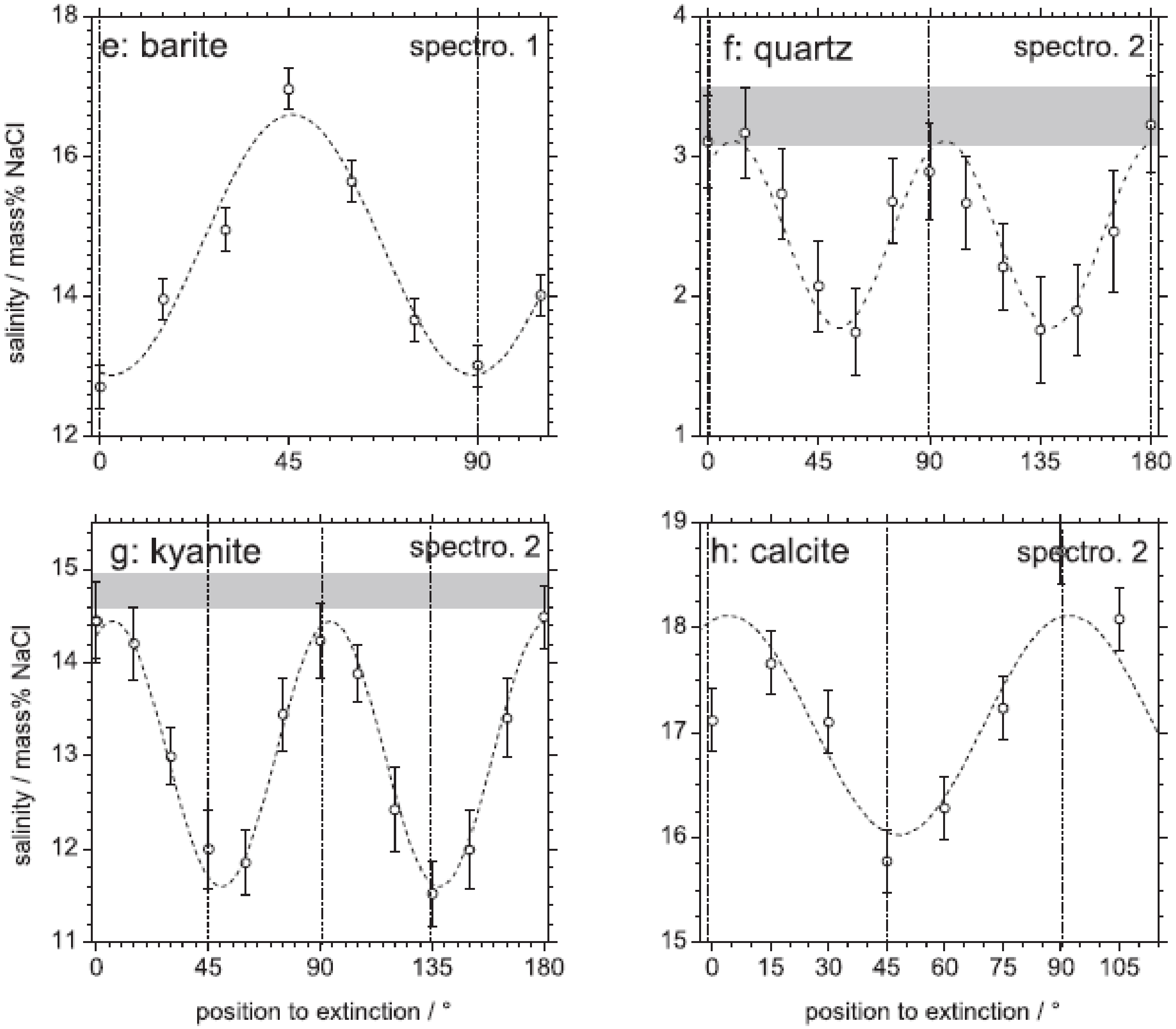




Fused Silica Capillary Capsules



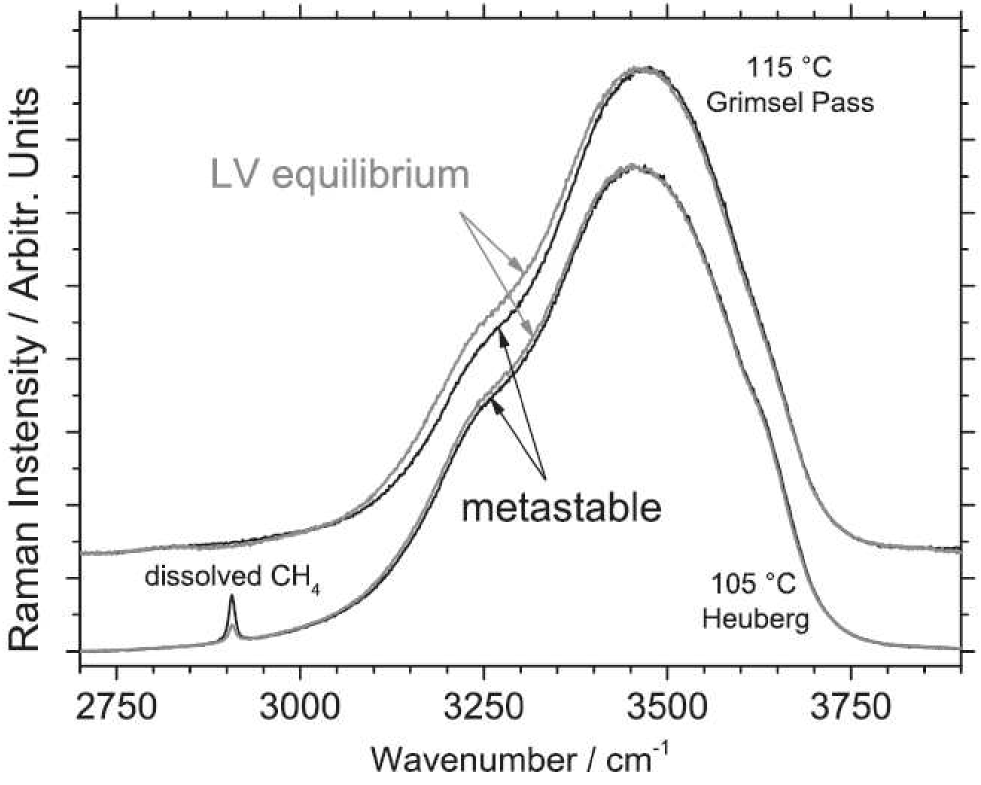
Caumon *et al.*, EJM 2013

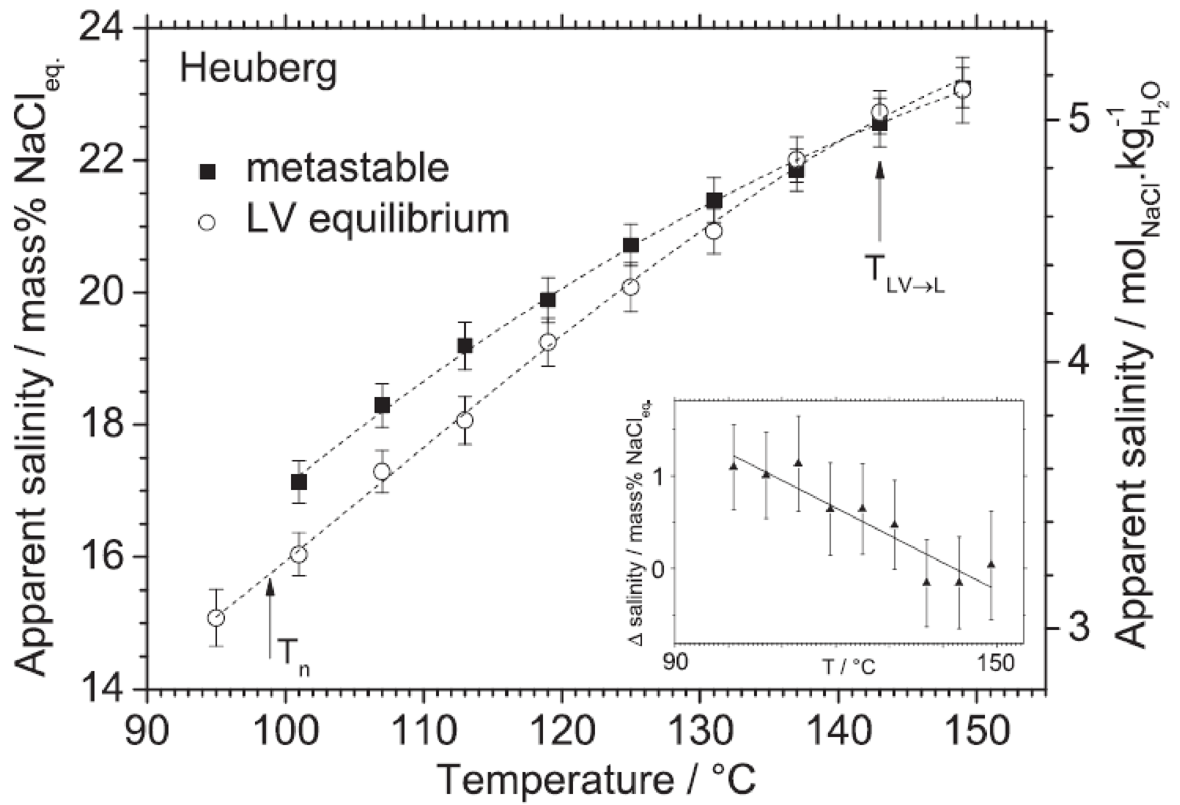


Salinity of fluid inclusions must be measured putting the host crystal at its extinction position.

Salinity meas. in birefringent minerals

Caumon *et al.*, J Raman Spectr 2015





Salinity of metastable inclusions

Distorsion of H-bonds in the metastable state.

Tarantola & Caumon, J Raman Spectr 2015

References

EMU Notes in Mineralogy, Vol. 12 (2012), Chapter 8, 279–320

Raman Spectroscopy of Gases, Water and other Geological Fluids

VALENTIN GARCIA-BAONZA[1], FERNANDO RULL[2] and JEAN DUBESSY[3]

4. Raman Scattering Cross Sections in Gases and Liquids

H. W. Schrötter and H. W. Klöckner

With 14 Figures

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Raman microspectrometry of fluid inclusions

Ernst A.J. Burke*

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Raman spectroscopy for fluid inclusion analysis

Maria Luce Frezzotti [a,b,*], Francesca Tecce [b], Alessio Casagli [a]

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