

ACROFI 2008
12 - 14th November
Kharagpur / India

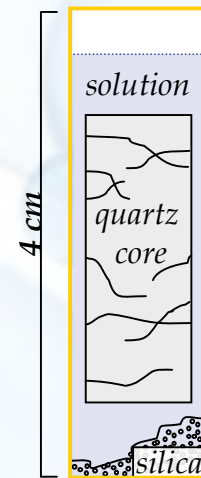
*Stable and metastable hydrate nucleation
in synthetic fluid inclusions
in the $\text{CaCl}_2\text{-H}_2\text{O}$ system*

Synthesis of fluid inclusions

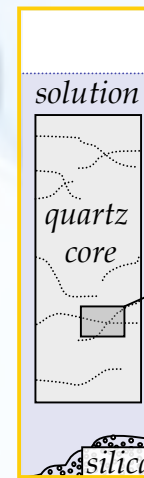
Synthesis in cold seal pressure vessels:



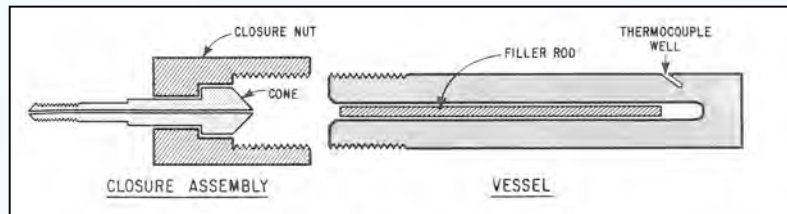
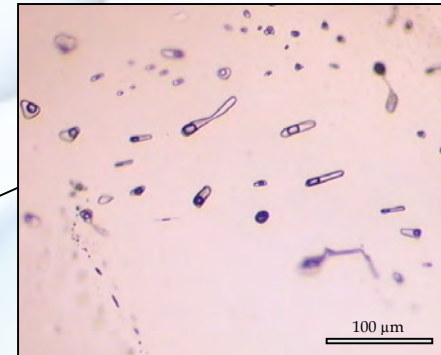
*Hydrothermal laboratory:
max. 10 kbar/800°C*



Welded gold capsule



Gold capsule after the synthesis



Two weeks of synthesis in cold seal pressure vessels in the hydrothermal laboratory



Double polished quartz discs with fluid inclusions



CaCl₂-H₂O System

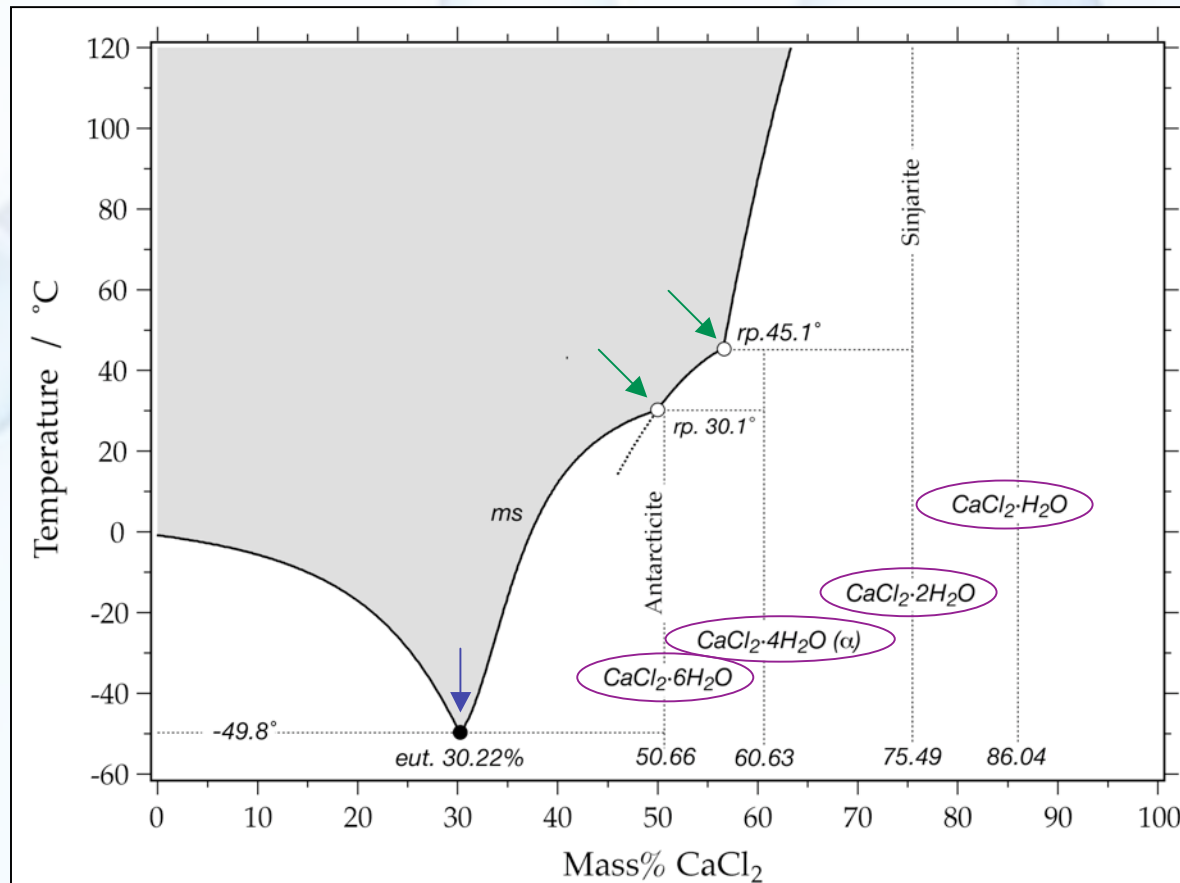
Four hydrates:

* CaCl₂·6H₂O (antarcticite)

* CaCl₂·2H₂O (sinjarite)

* CaCl₂·4H₂O (α-, β-, γ-modification)

* CaCl₂·H₂O



Eutecticum:

$T_E = -49.8\text{ °C}$
30.22 mass% CaCl₂

Peritecticum:

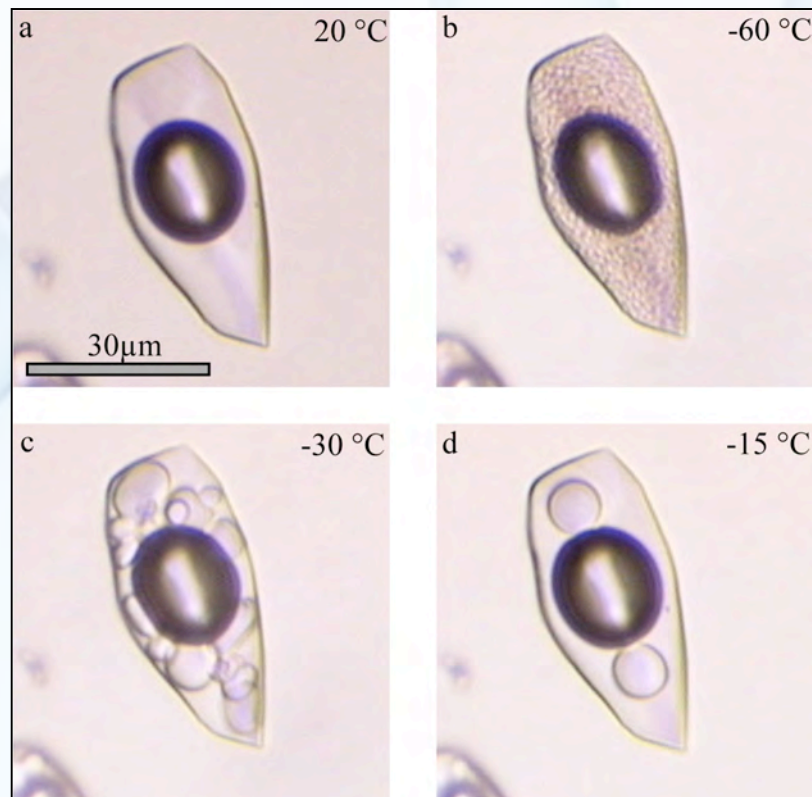
$T_{P1} = +30.1\text{ °C}$
50.66 mass% CaCl₂

$T_{P2} = +45.1\text{ °C}$
60.63 mass% CaCl₂

Freezing behaviour in the $\text{CaCl}_2\text{-H}_2\text{O}$ System

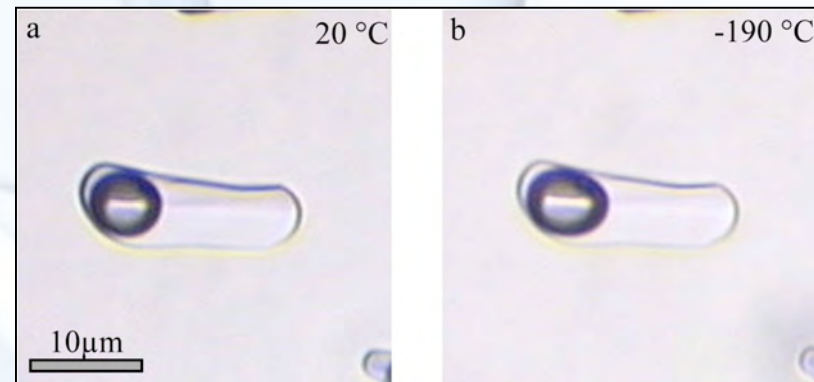
Different freezing behaviours:

- *Inclusions < eutectic composition*
 - nucleation of ice



15 mass% $\text{CaCl}_2\text{-H}_2\text{O}$

- *Inclusions with eutectic composition*
 - liquid down to -190 °C

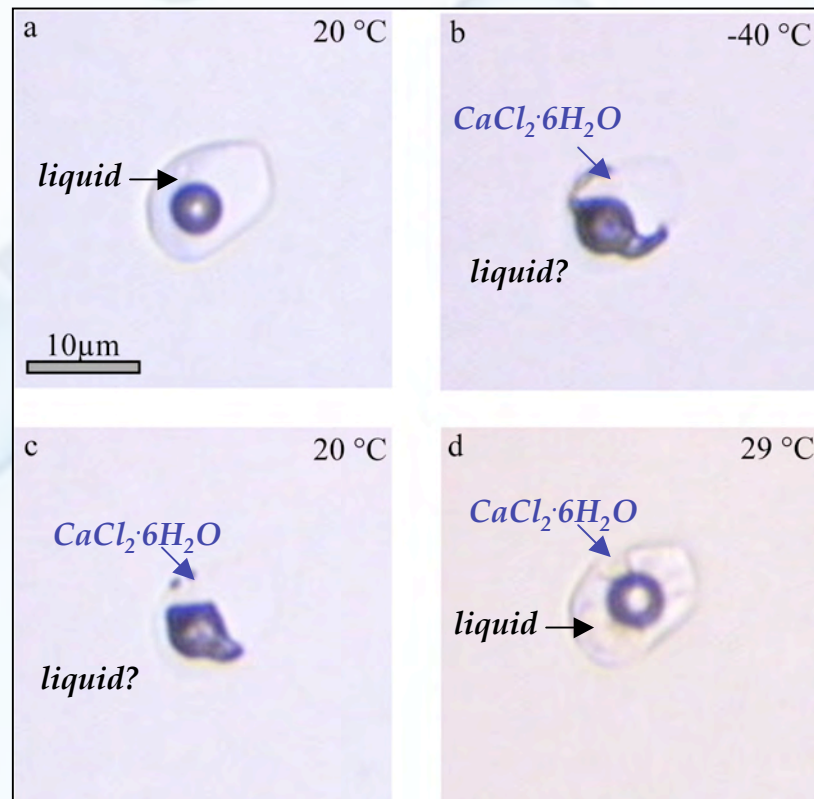


30 mass% $\text{CaCl}_2\text{-H}_2\text{O}$

- *Inclusions > eutectic composition*
 - 4 Types of $\text{CaCl}_2\text{-HYDRATE}$ nucleation

$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (antarcticite)

Type 1: Nucleation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

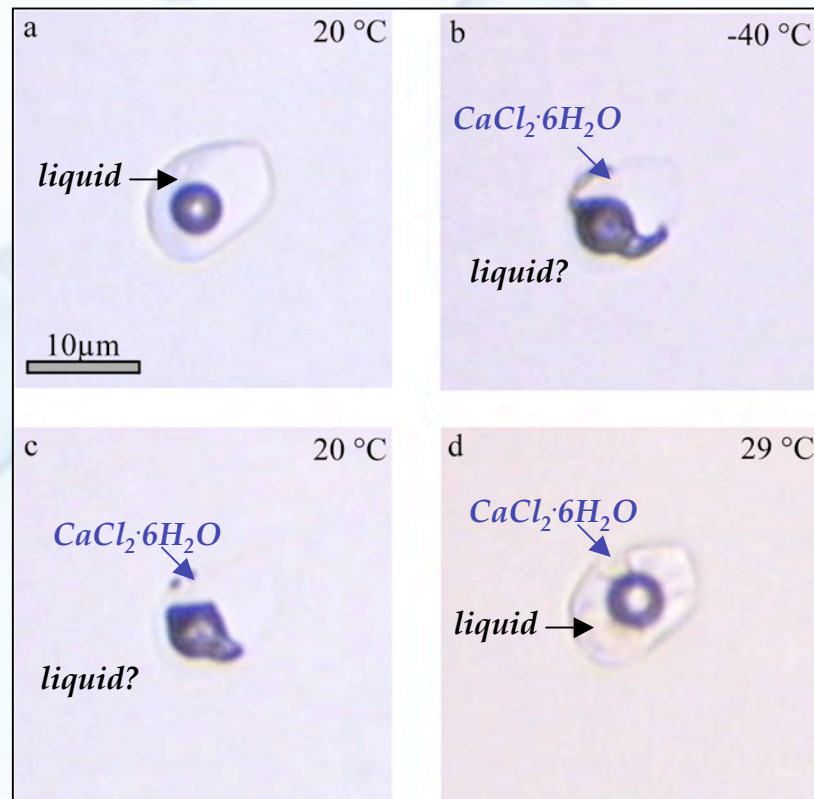


50 (±1) mass% CaCl_2 - H_2O

- a) *Liquid CaCl_2 -brine at room temperature*
 - b) *Nucleation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$*
 - c) *Re-crystallisation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$*
 - d) *Melting of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$*
- + vapour phase; stable at all temperatures

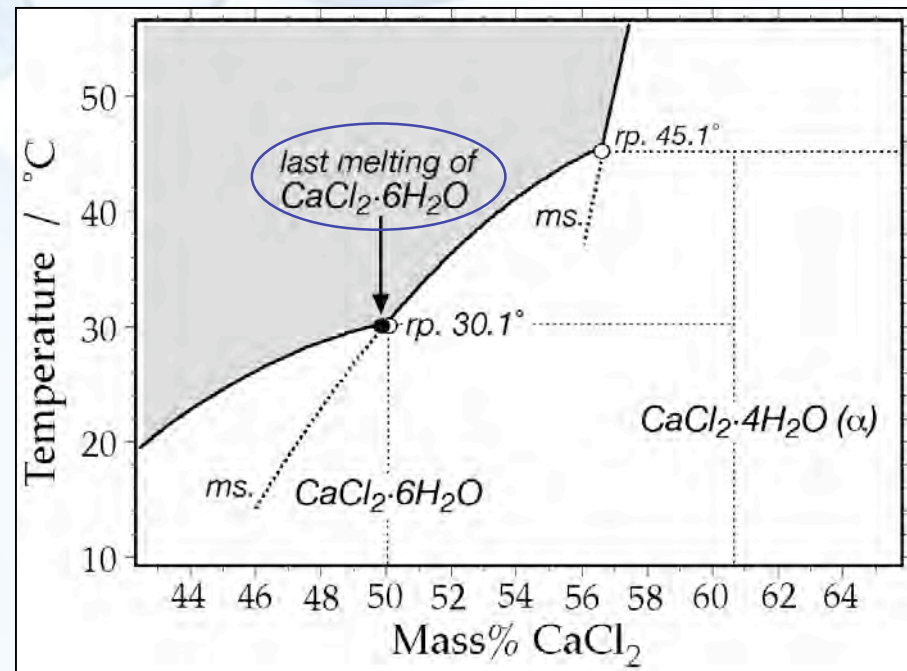
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (antarcticite)

Type 1: Nucleation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

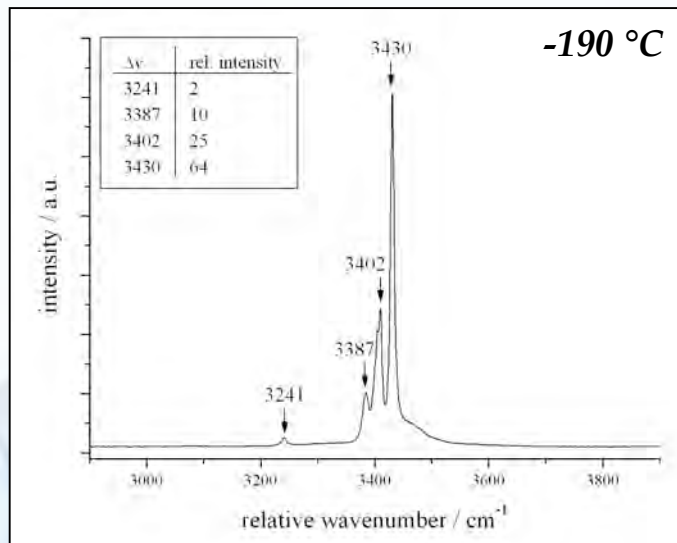


50 (±1) mass% $\text{CaCl}_2\text{-H}_2\text{O}$

- ✓ peritectic point: +30.1 °C (50.66 mass% CaCl_2)
- ✓ crystallisation temperature of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ between -40 to -65 °C
- ✓ melting of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$: +29.8 (±0.8)



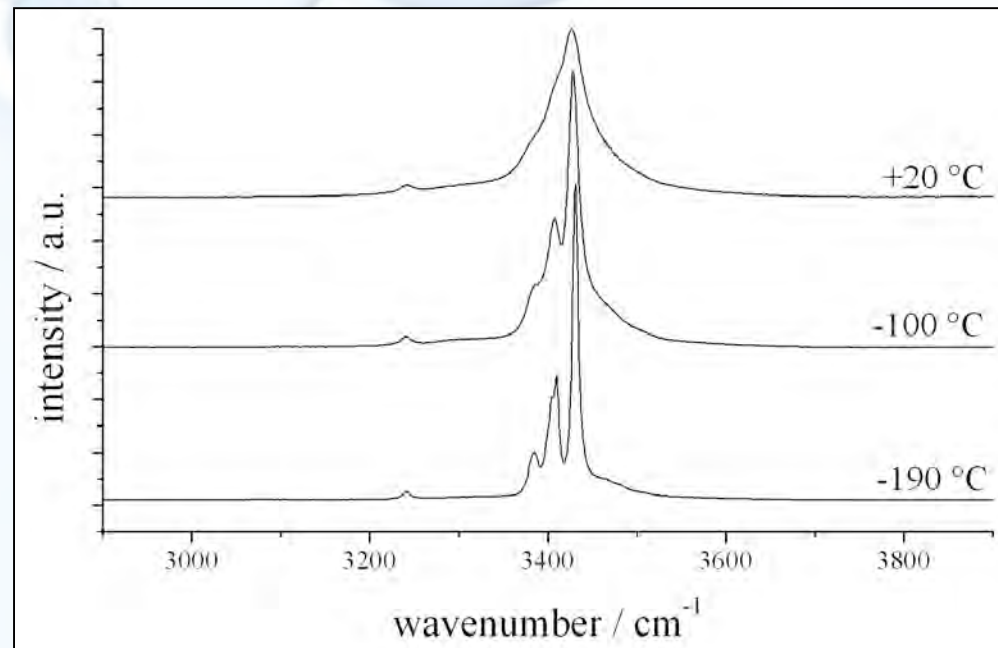
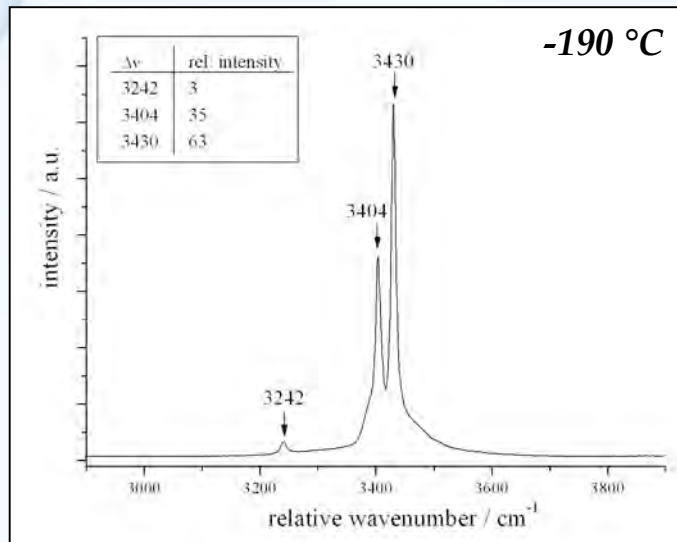
Raman spectra of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (antarcticite)



Raman spectra of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ at -190 °C

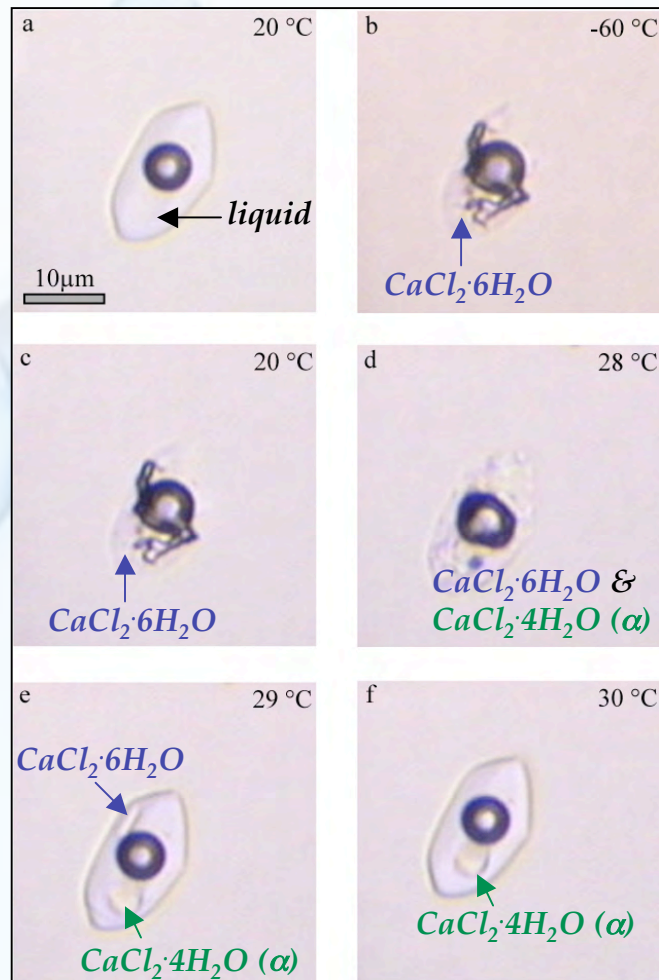
Relative intensities and occurrence of peaks are depend on the crystallographic orientation of the hydrate crystal!

Raman spectra of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ at different temperatures!



$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (α)

Type 2: Nucleation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ & $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (α)



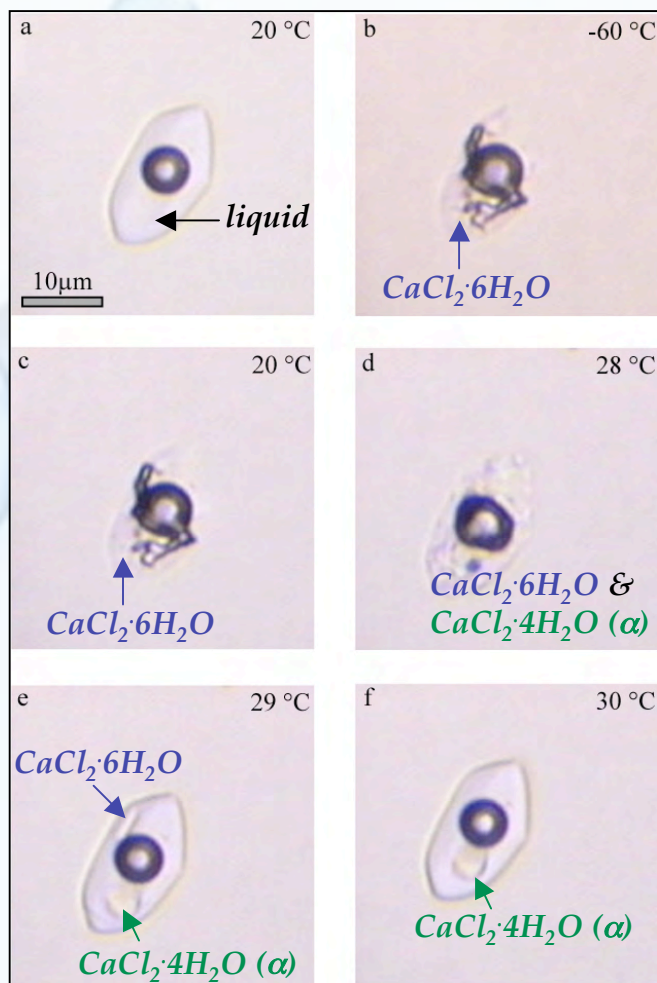
50 (±1) mass% $\text{CaCl}_2\text{-H}_2\text{O}$

- a) Liquid CaCl_2 -brine at room temperature
- b) Nucleation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
- c) Re-crystallisation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
- d) Peritectic reaction: $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \text{L} \Rightarrow \text{CaCl}_2 \cdot 4\text{H}_2\text{O} (\alpha) + \text{L}$
- e) $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \text{CaCl}_2 \cdot 4\text{H}_2\text{O} (\alpha) + \text{L}$
- f) Melting of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O} (\alpha)$

+ vapour phase; stable at all temperatures

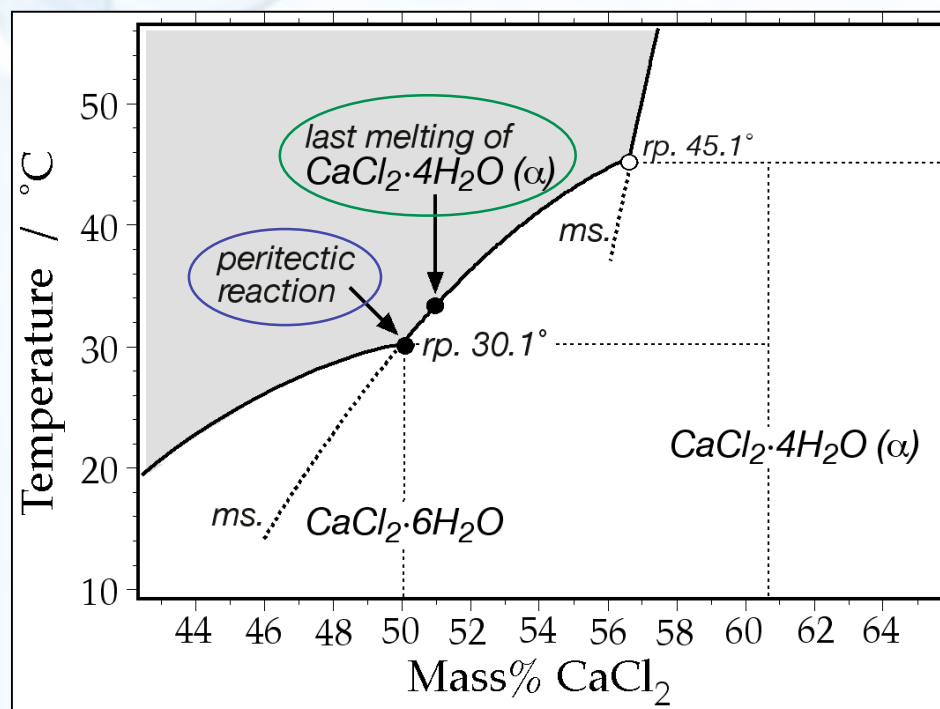
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (α)

Type 2: Nucleation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ & $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (α)

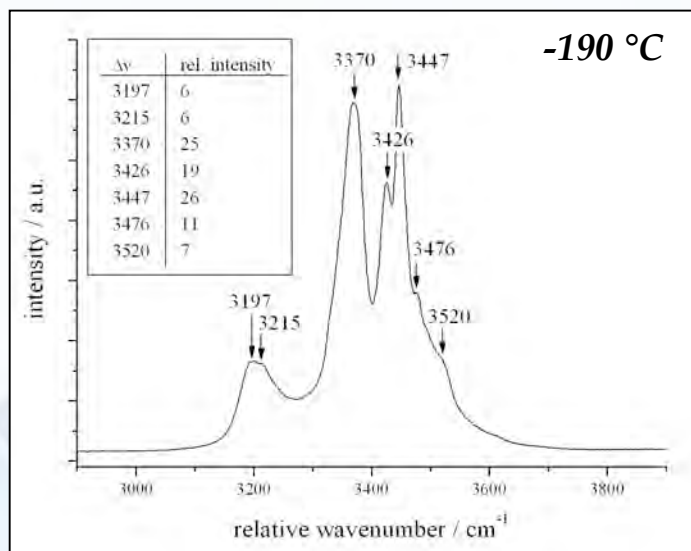


50 (±1) mass% CaCl_2 - H_2O

- ✓ crystallisation temperature of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ between -40 to -65 °C
- ✓ peritectic reaction at ~ +29 °C
 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ + liqu. to $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (α) + liqu.
- ✓ melting of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (α) at +32.5 (±0.3) °C



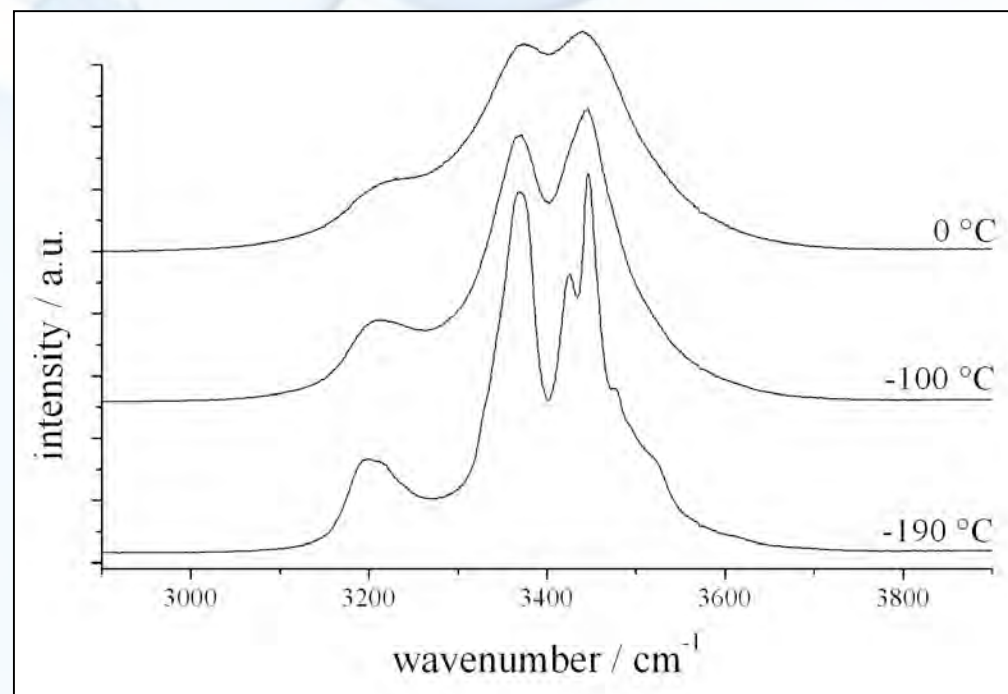
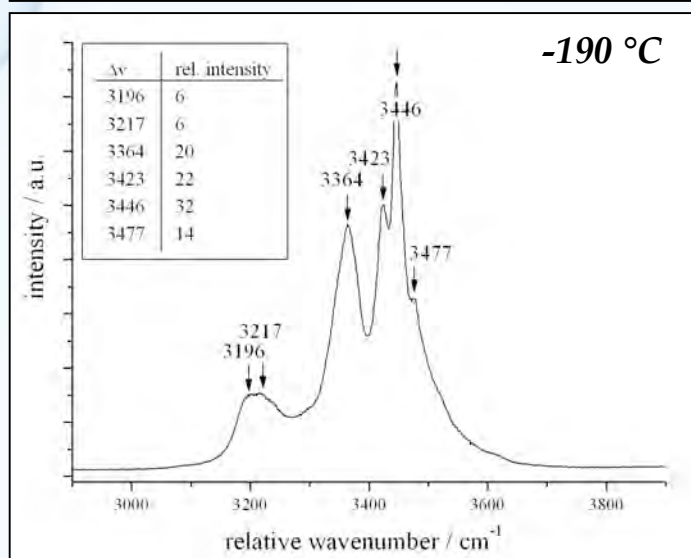
Raman spectra of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (α)



Raman spectra of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (α) at -190 °C

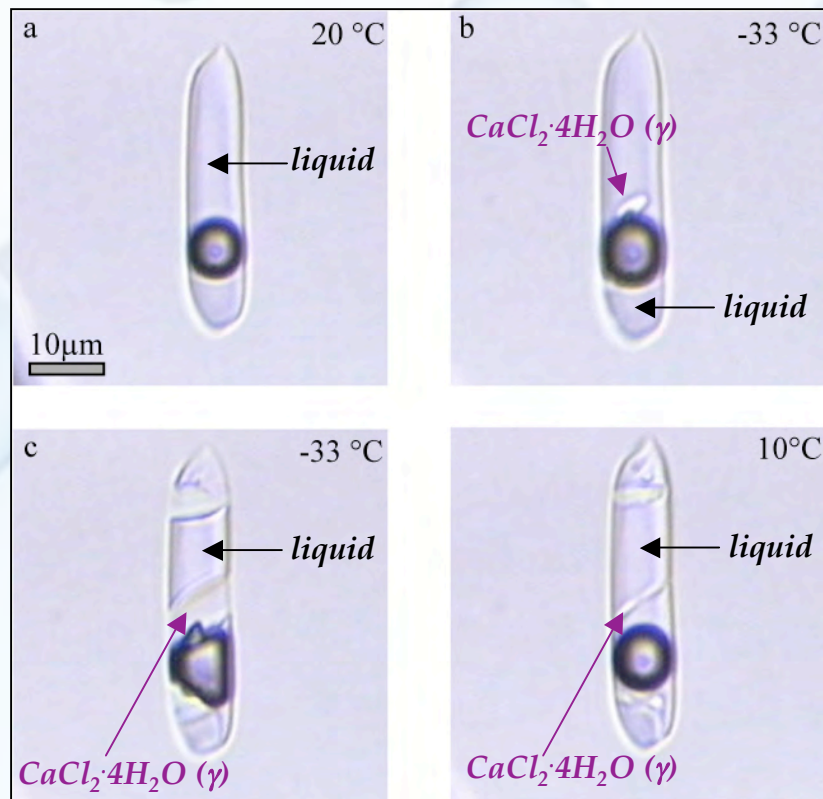
Relative intensities and occurrence of peaks depend on the crystallographic orientation of the hydrate crystal!

Raman spectra of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (α) at different temperatures!



$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ)

Type 3: Nucleation of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ)



50 (± 1) mass% $\text{CaCl}_2\text{-H}_2\text{O}$

a) Liquid CaCl_2 -brine at room temperature

b) Nucleation of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ)

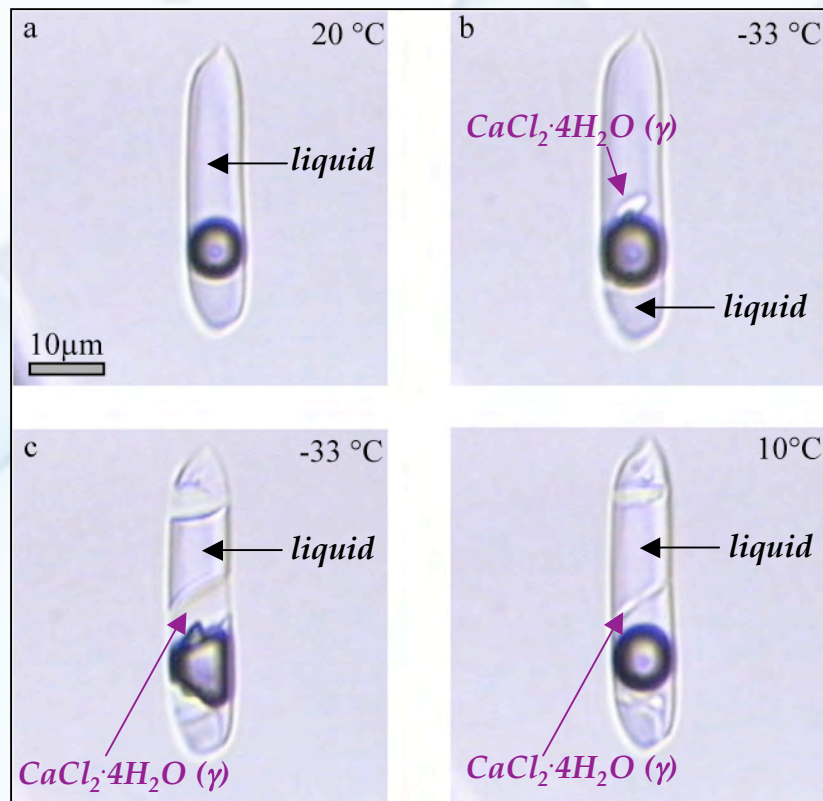
c) Growing of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ)

d) Melting of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ)

+ vapour phase; stable at all temperatures

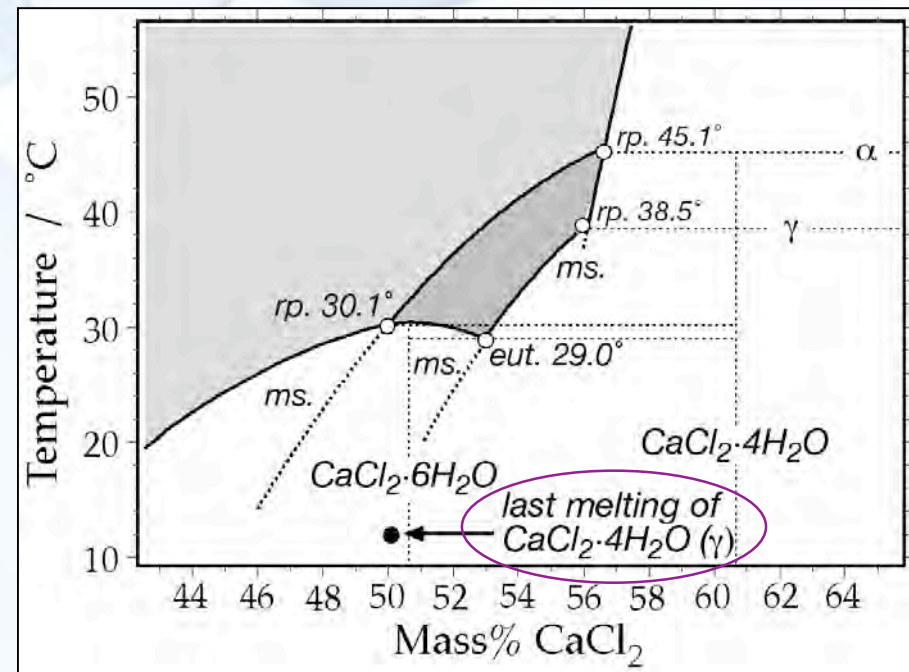
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ)

Type 3: Nucleation of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ)

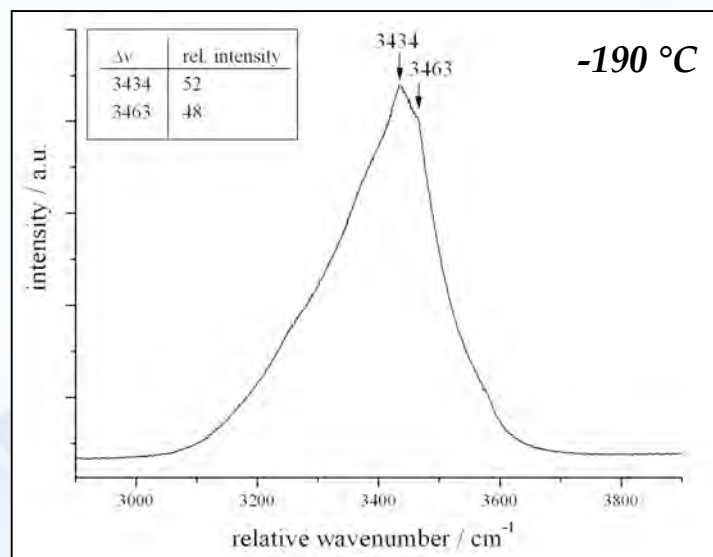


50 (±1) mass% $\text{CaCl}_2\text{-H}_2\text{O}$

- ✓ crystallisation temperature of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ) at about -30 to °C
- ✓ melting of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ) at +11.5 (±0.3) °C



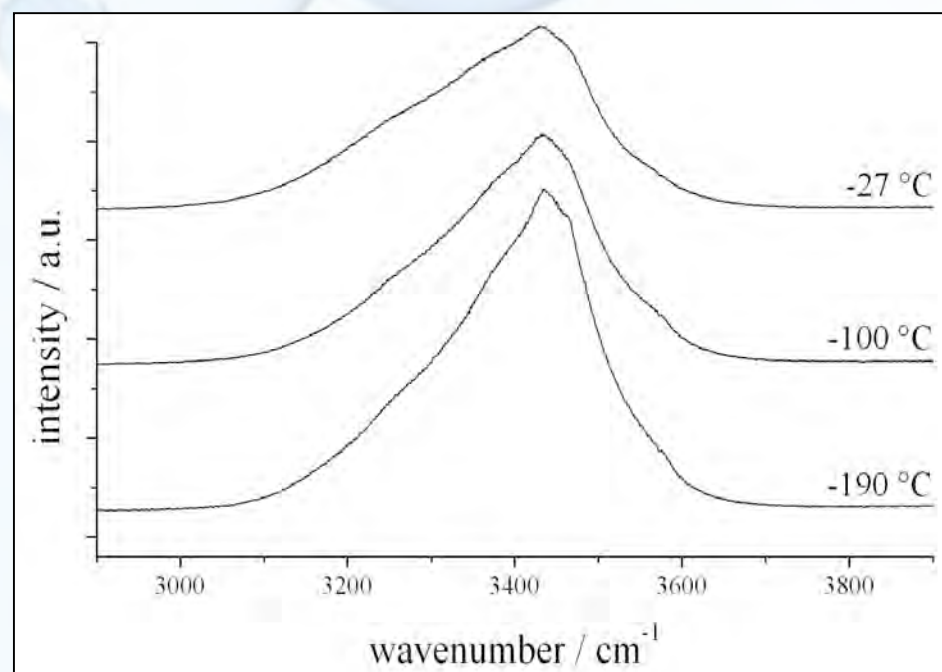
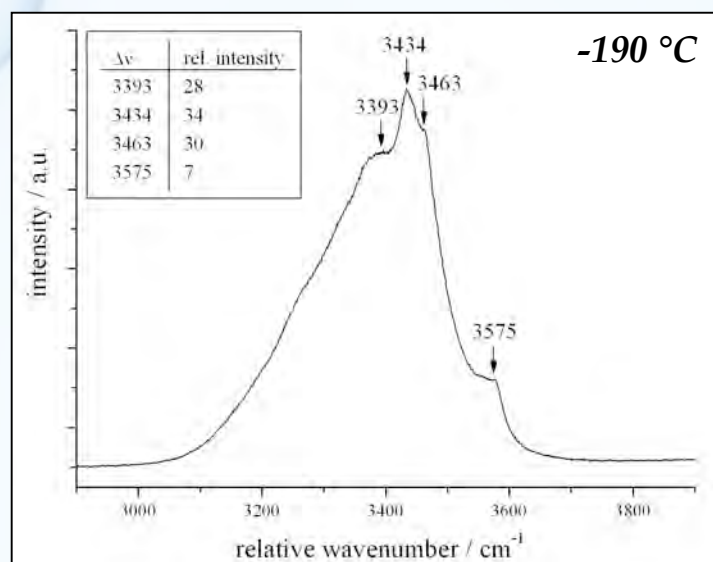
Raman spectra of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ)



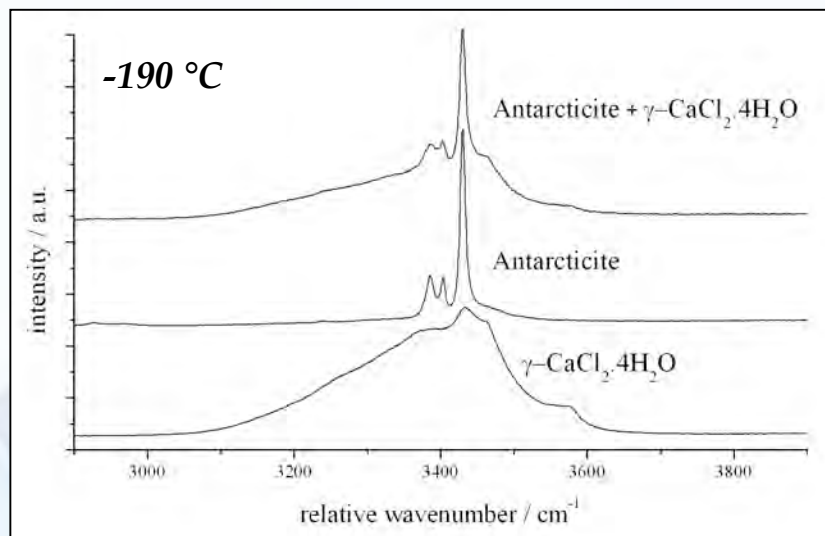
Raman spectra of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ) at -190 °C

Relative intensities and occurrence of peaks depend on the crystallographic orientation of the hydrate crystal!

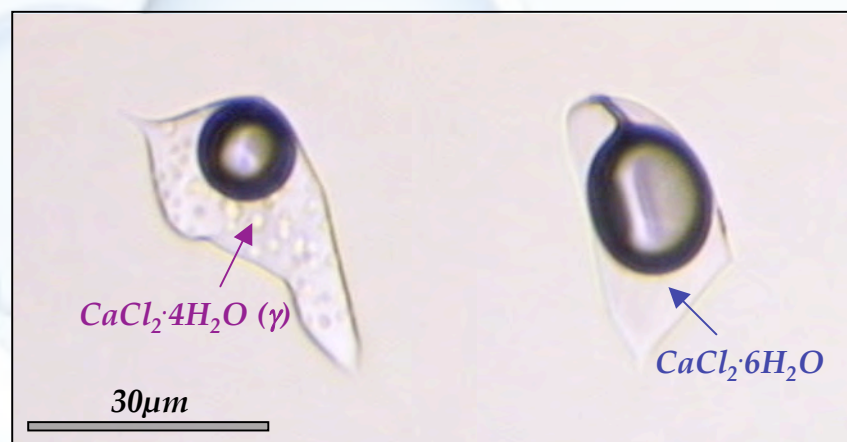
Raman spectra of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ) at different temperatures!



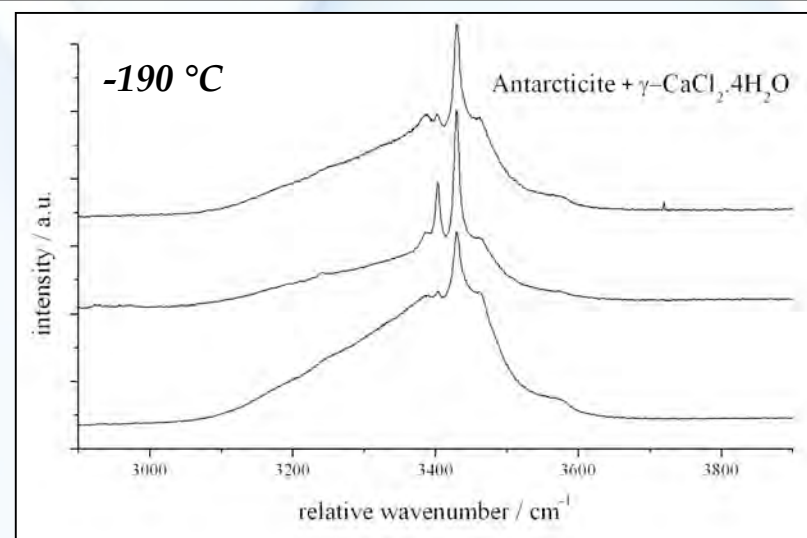
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ & $\text{CaCl}_2 \cdot 4\text{H}_2\text{O} (\gamma)$



Raman spectra of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 4\text{H}_2\text{O} (\gamma)$

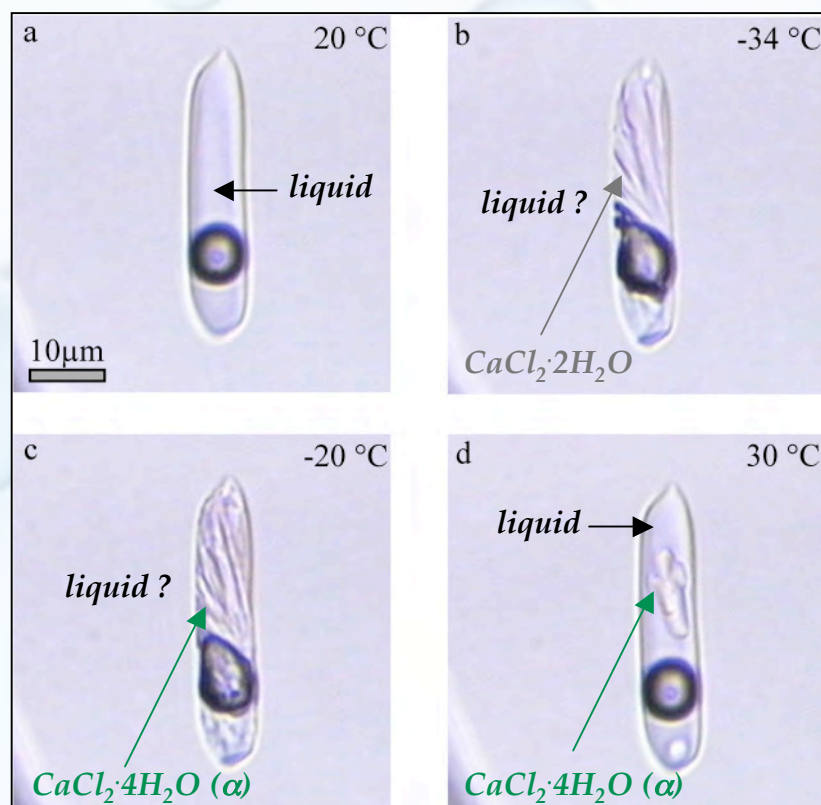


Combined Raman spectra of
 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ &
 $\text{CaCl}_2 \cdot 4\text{H}_2\text{O} (\gamma)$



$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (sinjarite)

Type 4: Nucleation of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

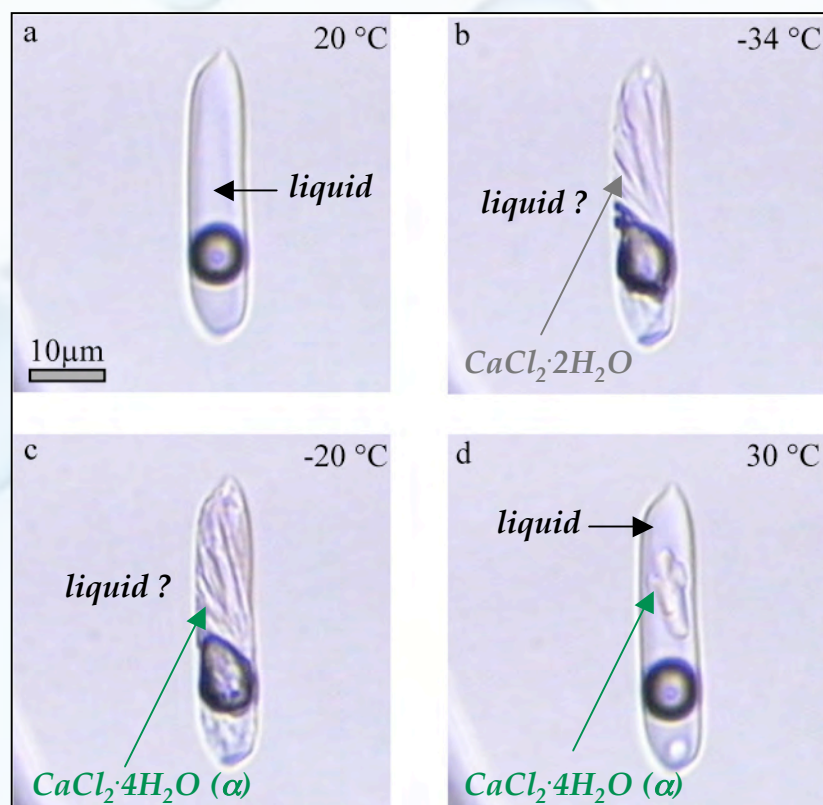


50 (±1) mass% $\text{CaCl}_2\text{-H}_2\text{O}$

- a) *Liquid CaCl_2 -brine at room temperature*
 - b) *Nucleation of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$*
 - c) *Phase transition of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to $\text{CaCl}_2 \cdot 4\text{H}_2\text{O} (\alpha)$*
 - d) *Melting of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O} (\alpha)$*
- + vapour phase; stable at all temperatures

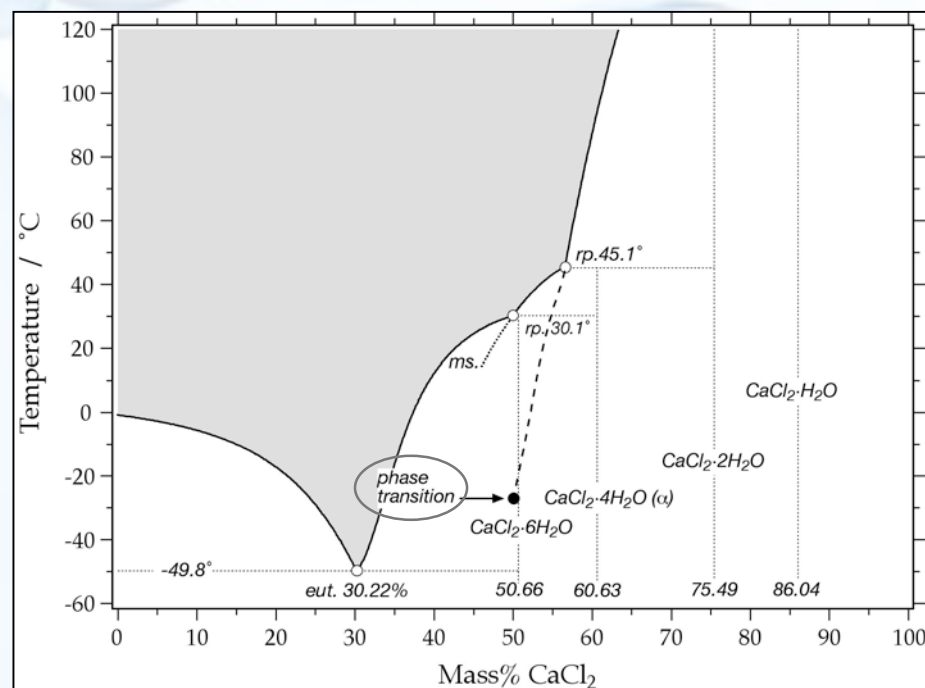
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (sinjarite)

Type 4: Nucleation of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$



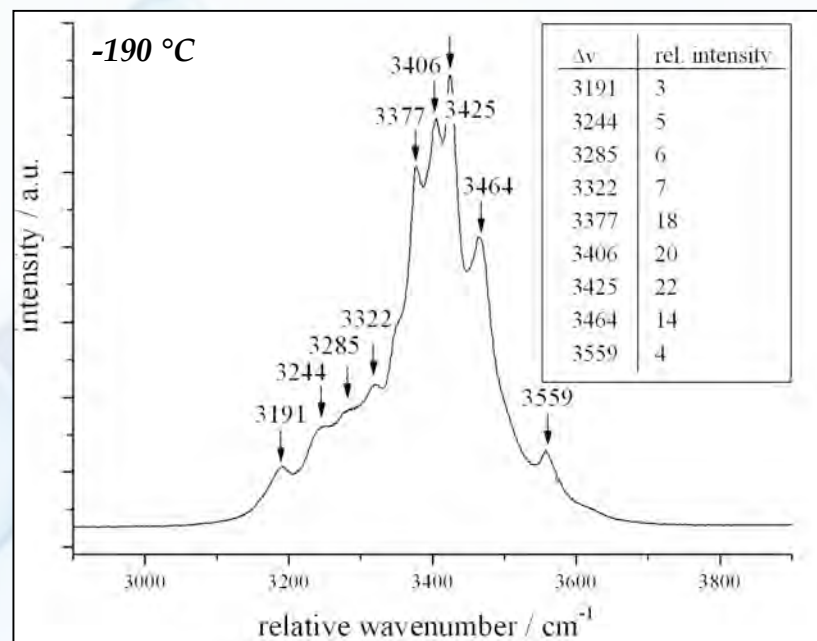
50 (±1) mass% $\text{CaCl}_2\text{-H}_2\text{O}$

- ✓ crystallisation temperature of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ at about -35 to °C
- ✓ phase transition from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to $\alpha\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$ (around -28 °C)
- ✓ melting of $\alpha\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$ at +32.5 (±0.3) °C



Raman spectra of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (sinjarite)

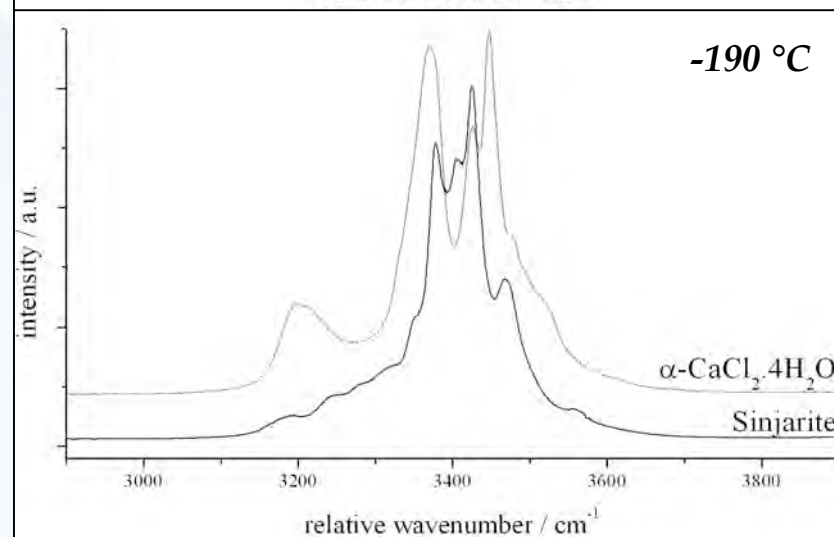
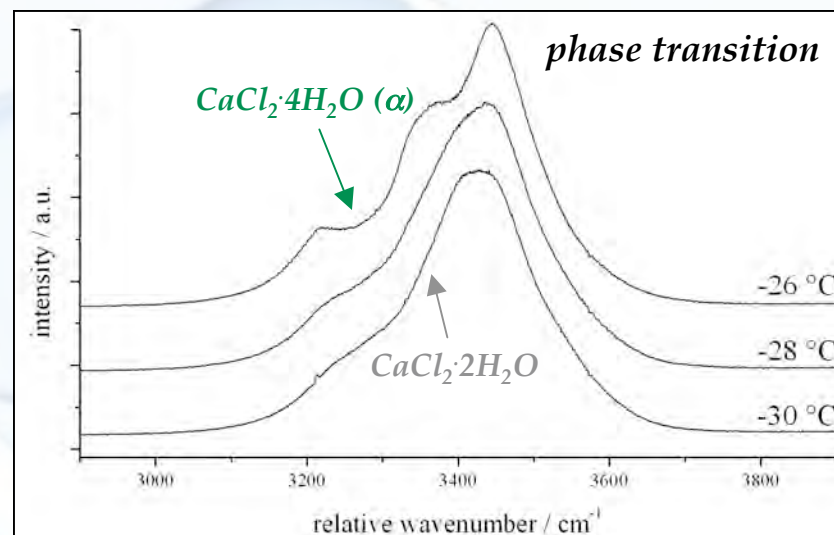
Raman spectrum of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ at -190°C



Comparison of Raman spectra of the same inclusion:

- Cooling to -190°C \Rightarrow $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
- Heating to -26°C \Rightarrow Phase transition
- Cooling to -190°C \Rightarrow $\text{CaCl}_2 \cdot 4\text{H}_2\text{O} (\alpha)$

Measurements taken on the same relative position in the inclusion!



Summary

- ✓ *Inclusions < eutectic composition: ice nucleation*
- ✓ *Inclusions with eutectic composition: metastable liquid*
- ✓ *Inclusions > eutectic composition: 4 Types of CaCl_2 -hydrate nucleation*
 - $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
 - $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (α)
 - $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (γ)
 - $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

The different freezing and melting behaviours may be obtained in the same inclusion during various microthermetrical runs!

No trend between the cooling rates and the freezing behaviour has been found yet!

thank you for your attention!

References:

Bakker R. J. (2003) *FLUIDS 1: Computer programs for analysis of fluid inclusion data and for modelling bulk fluid properties*. Chem. Geol. 194. 3-23.

Bodnar R. J., **Sterner** S. M. (1987) *Synthetic fluid inclusions*. In *Hydrothermal Experimental Techniques* (eds. G.C. Ulmer, H.L. Barnes). John Wiley & sons. New York. 423-457.

Kerrick D. M. (1987) *Cold-seal systems*. In *Hydrothermal Experimental Techniques* (eds. G.C. Ulmer, H.L. Barnes). John Wiley & sons. New York. 295-319.

Linke W. F. (1958) *Solubilities: Inorganic and metal-organic compounds. Volume I*, American Chemical Society, Washington.

Linke W. F. (1965) *Solubilities: Inorganic and metal-organic compounds. Volume II*, American Chemical Society, Washington.