# Experimental Raman Spectra of Salt Hydrates in Fluid Inclusions

Ronald J. Bakker
Miriam Baumgartner
Yvan Coquinot

contact
email: ronald.bakker@mu-leoben.at

Mineralogy and Petrology, Institute of Applied Geosciences and Geophysics, University of Leoben, Austria

Fluid Inclusion Laboratory Leoben FILL

http://fluids.unileoben.ac.at

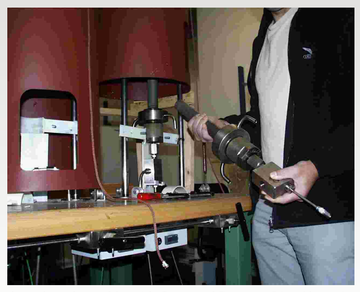
## Synthesis of Fluid Inclusions

High-Temperature-Pressure Laboratory Leoben
Limits: up to 800 ˚C and 1000 MPa

+

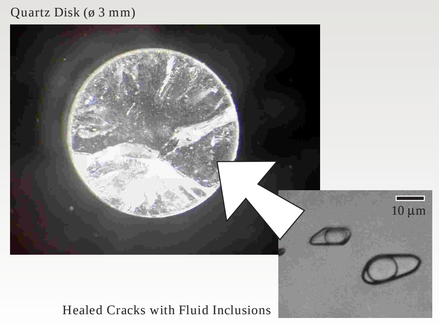
Dismantled Autoclave with Au-capsule (sample)

+



Autoclave Assembly with Oven and Pressure-Line (Argon)

+ *Time*
*Patience*
*Luck*
=



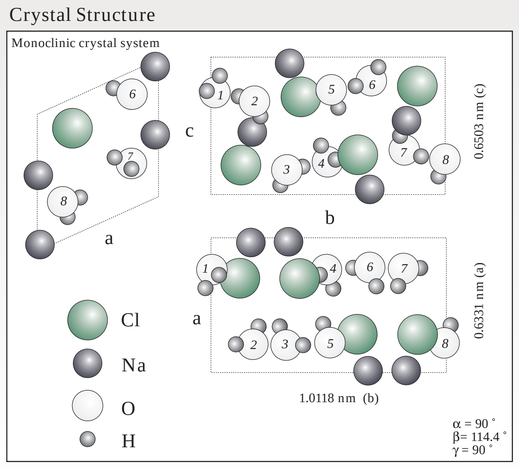

Healed Cracks with Fluid Inclusions

## Hydrohalite $NaCl{\cdot}2H_2O$

Bakker (2004) Raman Spectra of fluid and crystal mixtures in the system $H_2O$, $H_2O$-NaCl and $H_2O$-$MgCl_2$ at low temperatures: Applications to fluid-inclusion research. *The Canadian Mineralogist*, Vol. 42, pp. 1283-1314

Synthetic fluid inclusion with a 23.2 mass% NaCl solution at selected temperatures

### Crystal Structure




Fixation of $H_2O$ molecules within the crystal lattice of hydrohalite results in a limited amount of vibration possibilities, and , therefore in a limited amount of polarizability alteration. At low temperatures, the vibrations modes of $H_2O$ molecules are even more restricted, which is expressed in only a few Raman-bands with narrow widths in the range of 3000 to 3600 $cm^{-1}$. At higher temperatures, i.e. closer to the melting point of hydrohalite the vibration modes become less well defined because of an increase in resonance and hinderence as the $H_2O$ molecules get more loosly bound in the crystal lattice.

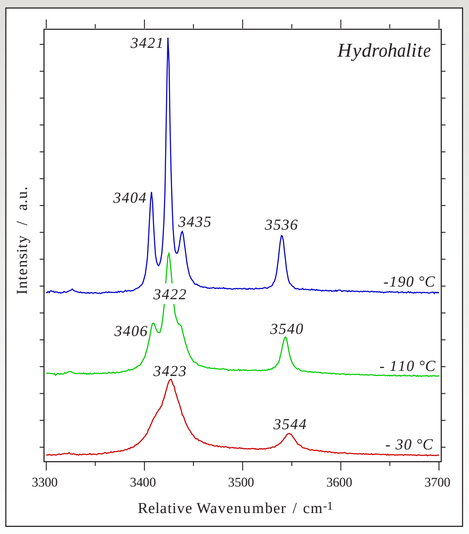
## Raman Spectroscopy

LABRAM (ISA Jobin Yvon) instrument
frequency-doubled Nd-YAG laser (100 mW source)
Wavenumber accuracy of 1.62 to 1.1 cm-1

*Combined Microthermometry*

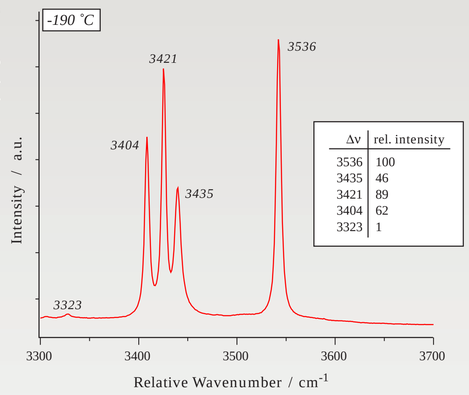
LINKAM THMSG 600 heating-freezing stage
long-working-distance objectives (Olympus 100x and 40x)

## Temperature Effect

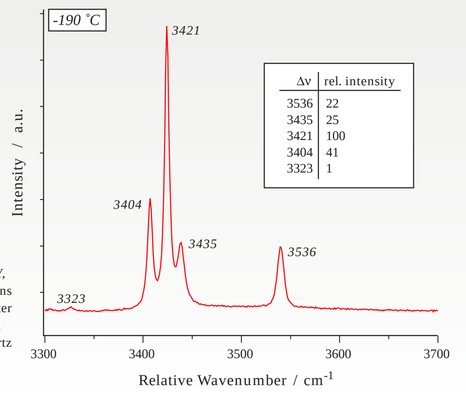



## Relative crystal orientation

The incident laser beam is polarised in one direction. Consequently, the vibrations due to the interaction with anisotropic crystals are variable intense according to the relative crystal orientation. The vibration frequencies (i.e. the relative wavenumbers) remain constant.




| Δν | rel. intensity |
|---|---|
| 3536 | 100 |
| 3435 | 46 |
| 3421 | 89 |
| 3404 | 62 |
| 3323 | 1 |



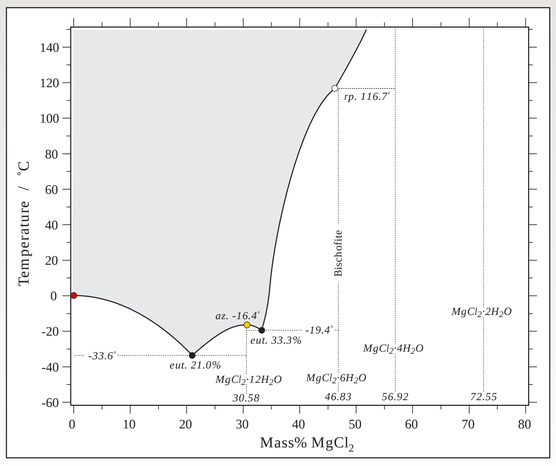

| Δν | rel. intensity |
|---|---|
| 3536 | 22 |
| 3435 | 25 |
| 3421 | 100 |
| 3404 | 41 |
| 3323 | 1 |

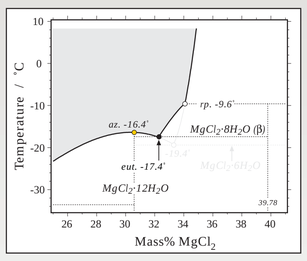
See Also:

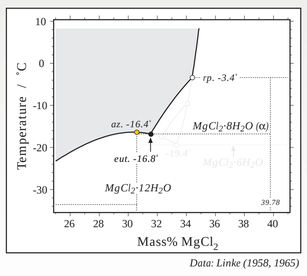
Baumgartner M, Coquinot Y, Bakker RJ (2007) Modifications of Raman spectra of pure water and brines in synthetic fluid inclusions caused by the quartz host mineral. ECROFI-XIX

## Binary $MgCl_2$ - $H_2O$ System

This fluid system consist of a variety of hydrates, eutectic points, reaction points and an azetropic point. Bischofite ($MgCl_2{\cdot}6H_2O$) is the only hydrate that is stable at room temperatures. The modifications with eight $H_2O$ molecules in the crystal lattice (α and β) may be metastably absent, especially during cooling experiments. Rapid cooling of fluid inclusions leads to the formation of metastable phase assemblages, especially in brines.

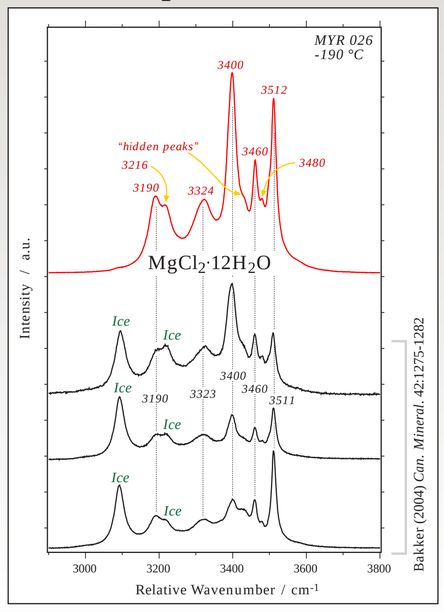


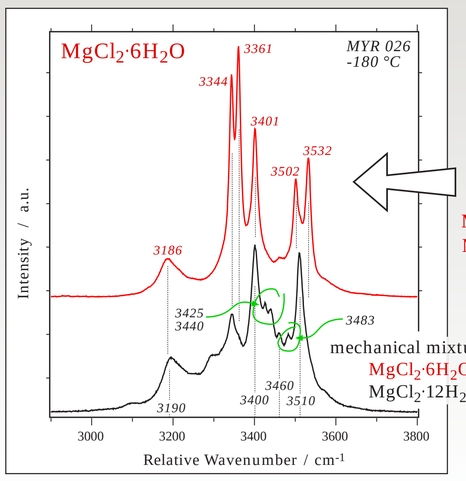




*Data: Linke (1958, 1965)*

## Raman Spectra



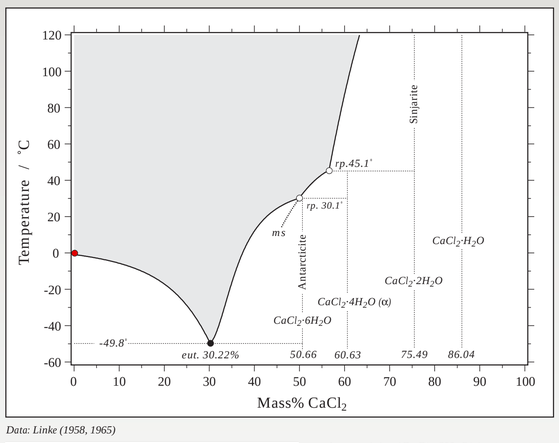

## Variety of Hydrates



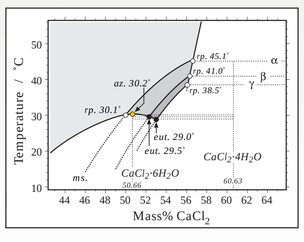

Or could it be:
$MgCl_2{\cdot}8H_2O$ (α)
$MgCl_2{\cdot}8H_2O$ (β)
?

mechanical mixture:
$MgCl_2{\cdot}6H_2O$
$MgCl_2{\cdot}12H_2O$

## Binary $CaCl_2$ - $H_2O$ System



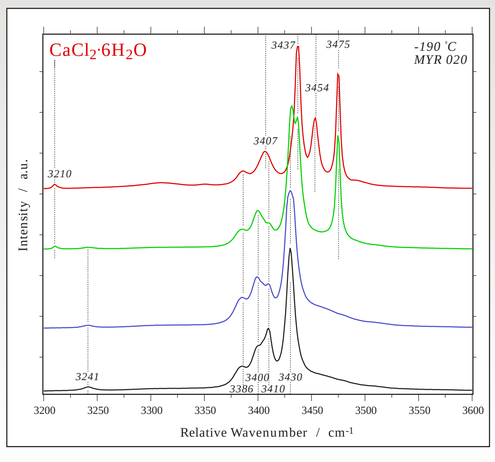

*Data: Linke (1958, 1965)*




Antarcticite ($CaCl_2{\cdot}6H_2O$) is the stable hydrate of $CaCl_2$ at room temperatures. At higher temperatures, Sinjarite ($CaCl_2{\cdot}2H_2O$) is stable. A variety of eutectic points, reaction points are present in this system. The azeotropic point only occurs if the β and γ modifications of $CaCl_2{\cdot}4H_2O$ are present. Otherwise, a reaction point occurs (with the α modification). These modifications can be metastably present with ice at low temperatures.

## Raman Spectra

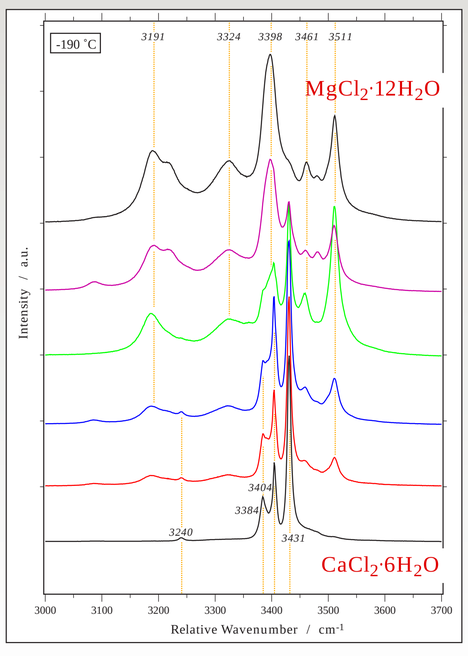
Is this a mechanical mixture of two types of $CaCl_2$ hydrates? Or, is this a relative crystal orientation effect, in which hidden peaks appear or disappear in specific orientations?




Acknowledgement

This study is finacially supported by FWF, project nr. P18209 - B06

## Ternary $CaCl_2$ - $MgCl_2$ - $H_2O$ System




mechanical mixture

Intensity Spectrum
=
$x$·(Int. $CaCl_2{\cdot}6H_2O$)
+
(1-$x$)*(Int. $MgCl_2{\cdot}12H_2O$)