Optical cells with fused silica windows for the study of geological fluids

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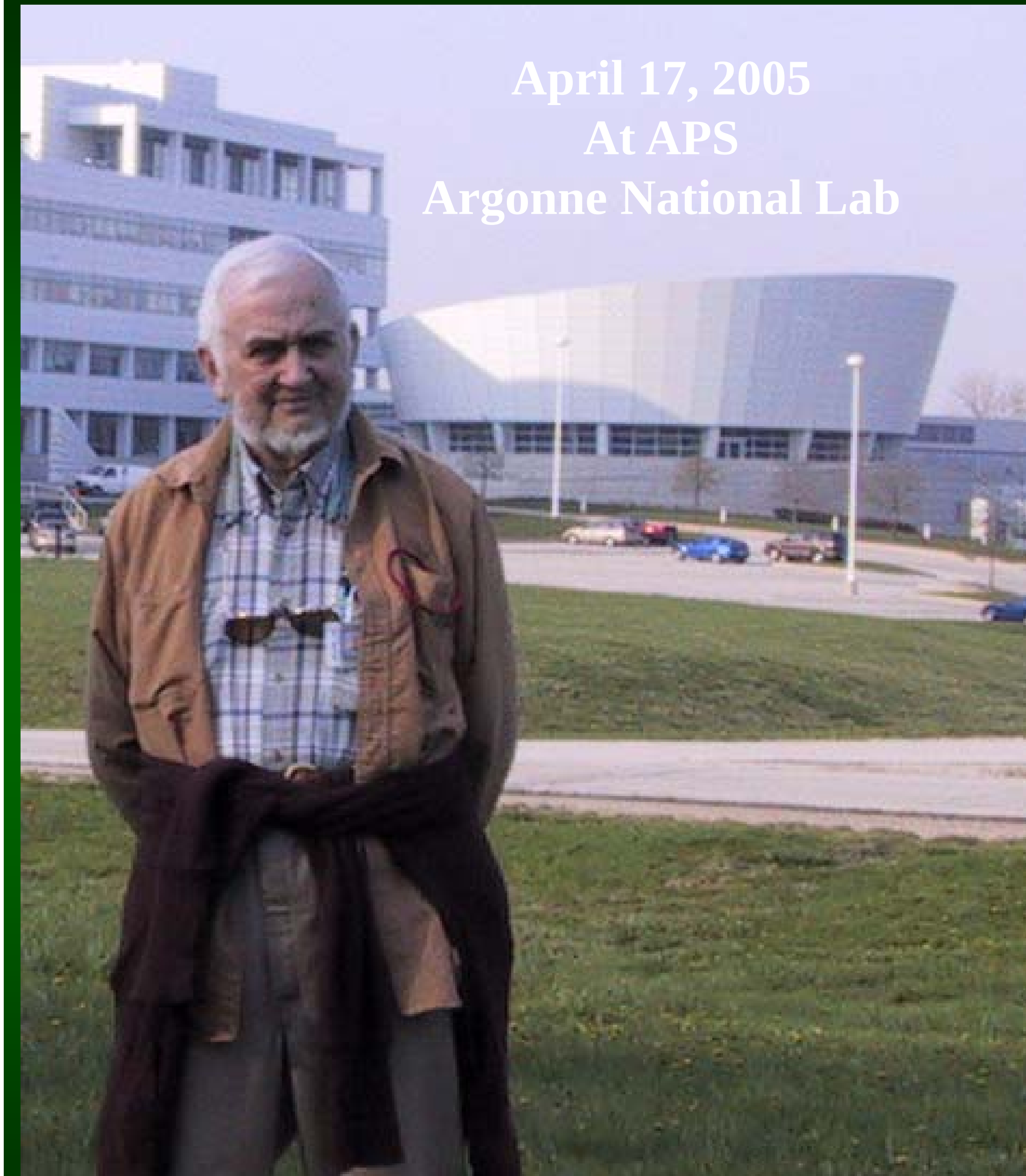
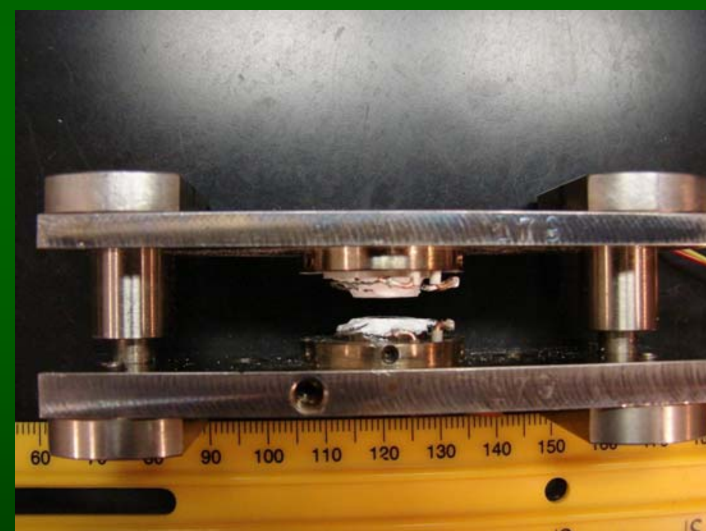
Outline

- HDAC vs FSCC
- Two types of optical cells with fused silica windows for the study of geologic fluids (C-O-H-N-S-salts) at *P-T* conditions up to 100 MPa and 600 ºC:
  – (1) High pressure optical cell (HPOC) for samples with known compositions and adjustable pressures for in-situ experiments
  – (2) Fused silica capillary capsule (FSCC) for samples with mostly uncertain composition and pressure, and suitable for long term (days or weeks) experiments
- Constructions of these optical cells and applications
- Summary



April 17, 2005
At APS
Argonne National Lab

Bassett et al. (1993)



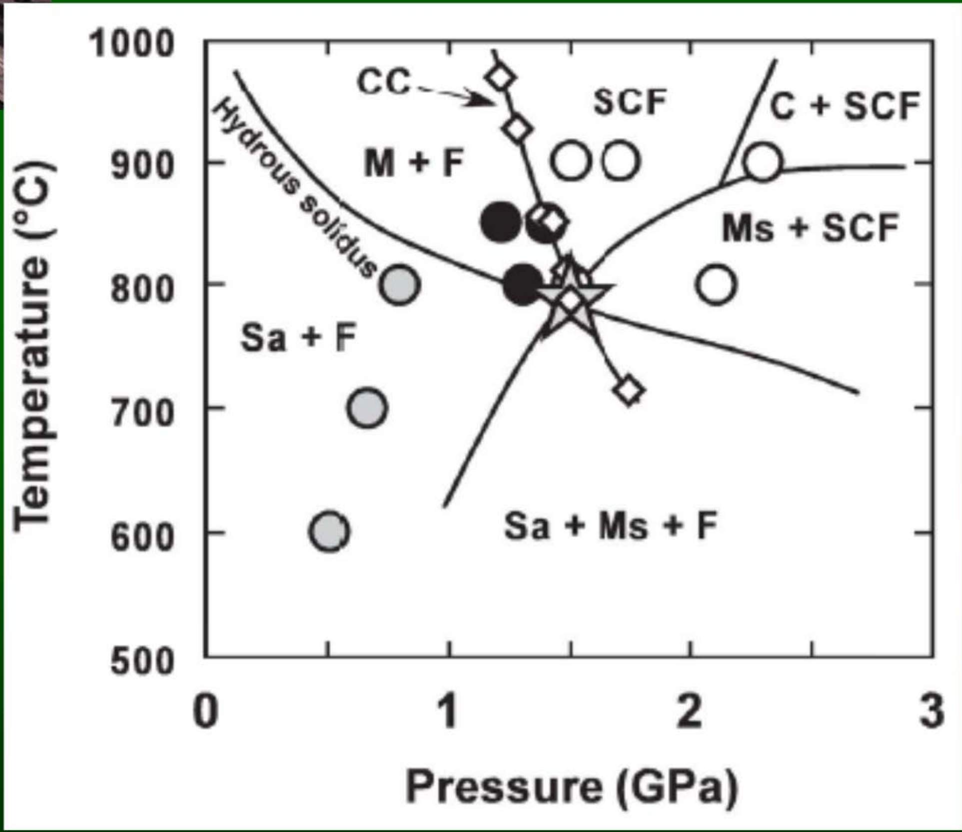
HDAC type V

Raman study of synthetic subduction-zone fluids ($KAlSi_3O_8$-H_2O) system

Mibe, Chou, & Bassett
JGR, 113 (2008)

Kenji Mibe
Earthquake Research Institute
University of Tokyo, Japan

- SCF: supercritical fluid
- F: aqueous fluid
- Sa: sanidine
- M: hydrous melt
- Ms: muscovite
- C: corundum



Sanidine
$KAlSi_3O_8$

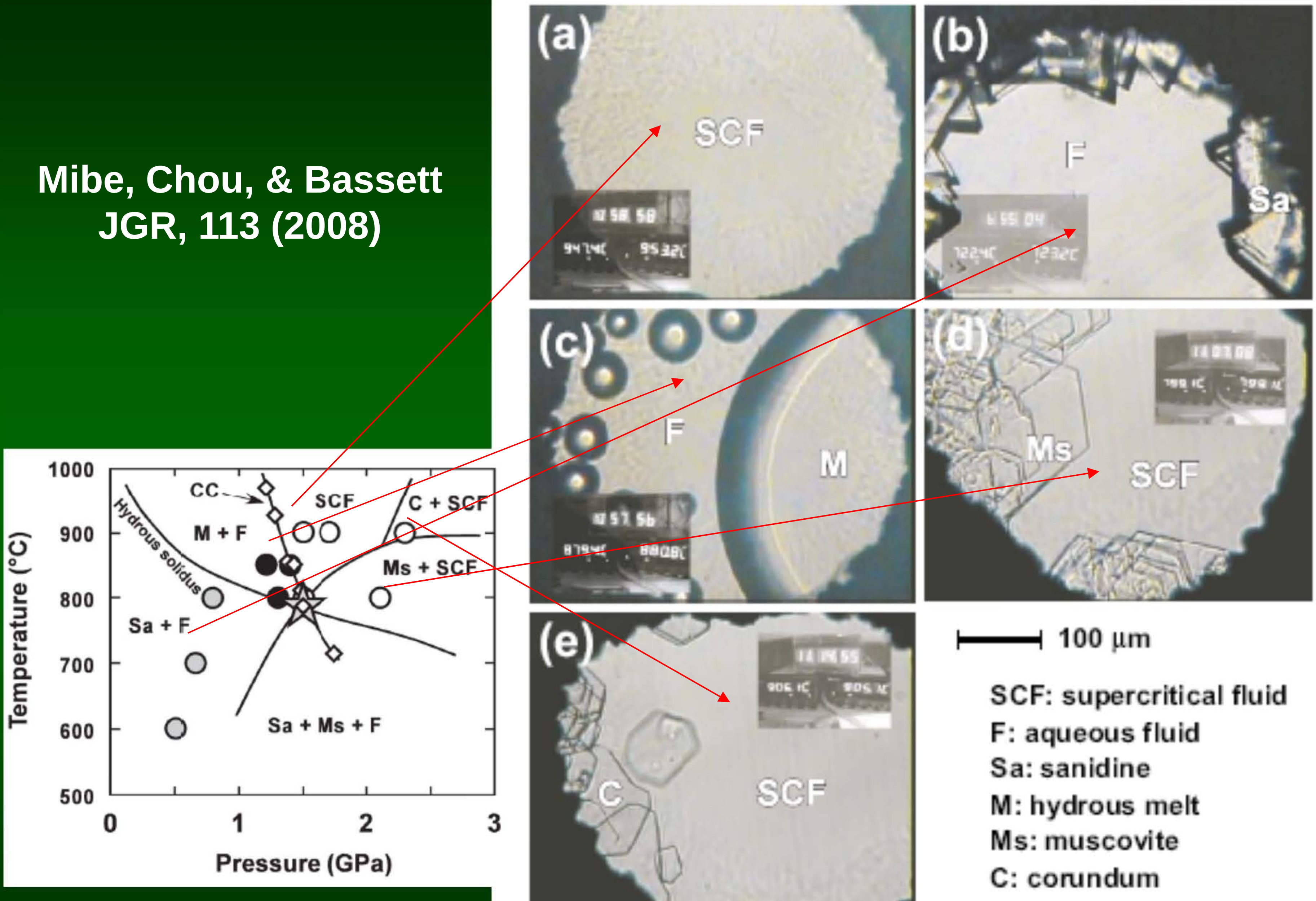
Muscovite
$KAl_2(Si_3Al)O_{10}(OH)_2$

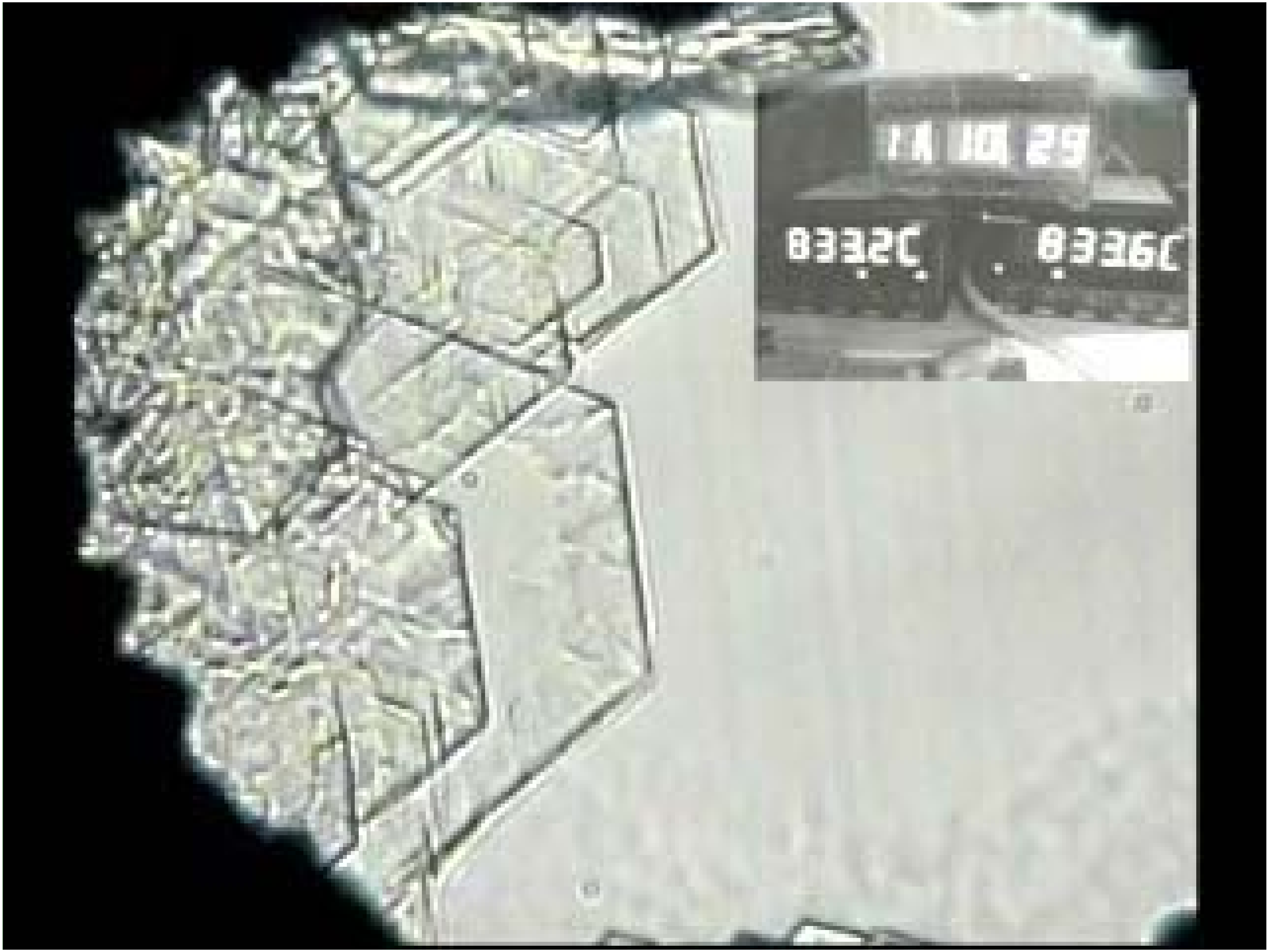
Some minerals in the system:

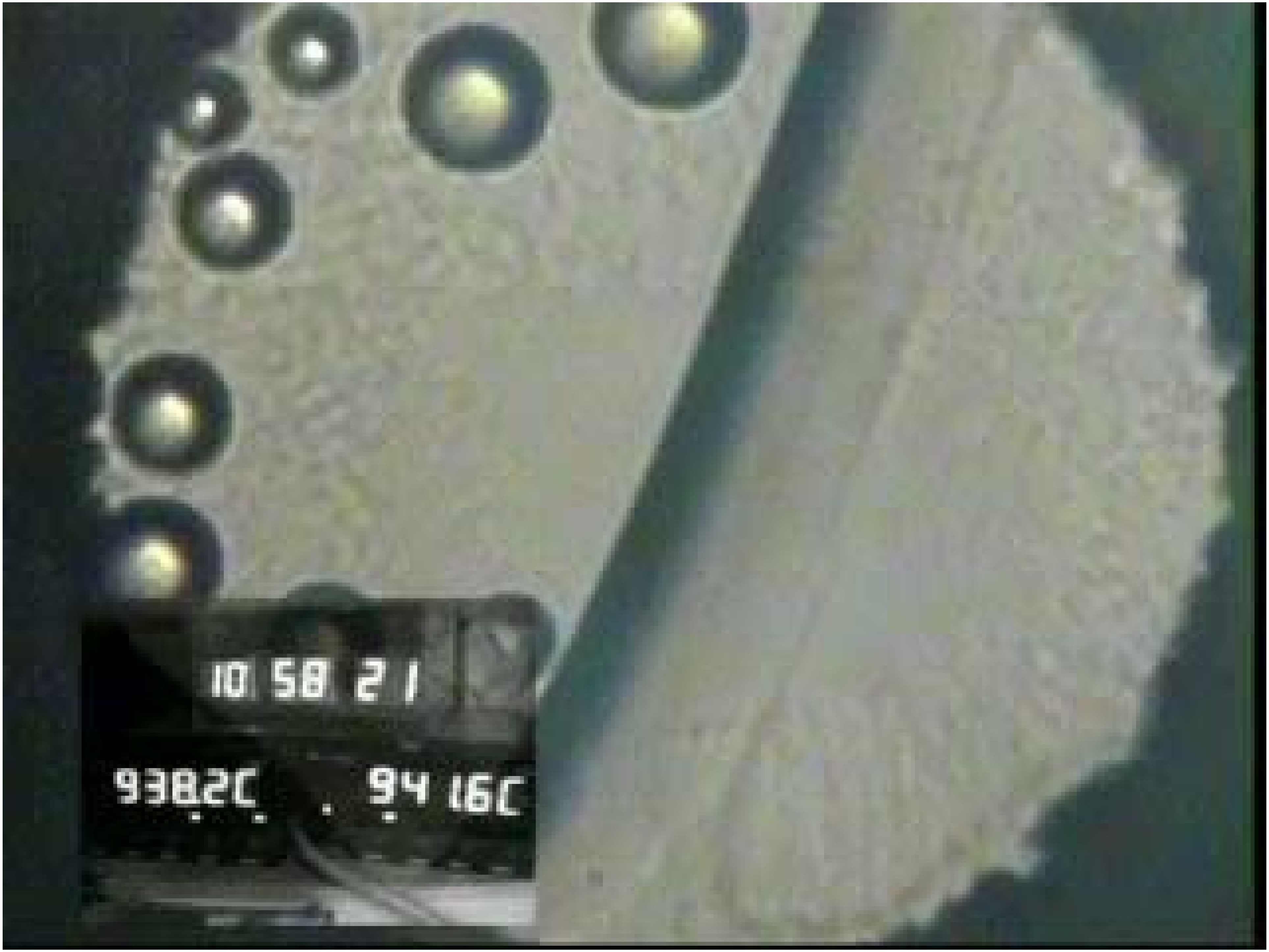
$KAlSi_3O_8$ - H_2O

Corundum
Al_2O_3

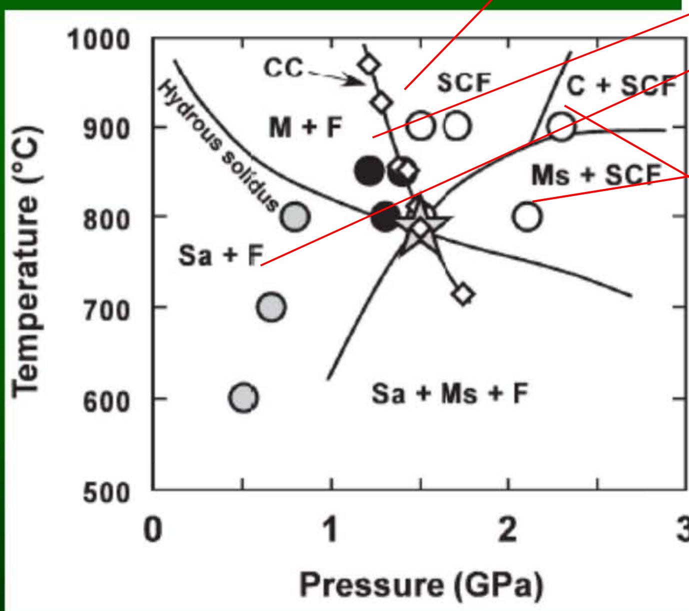
Mibe, Chou, & Bassett
JGR, 113 (2008)

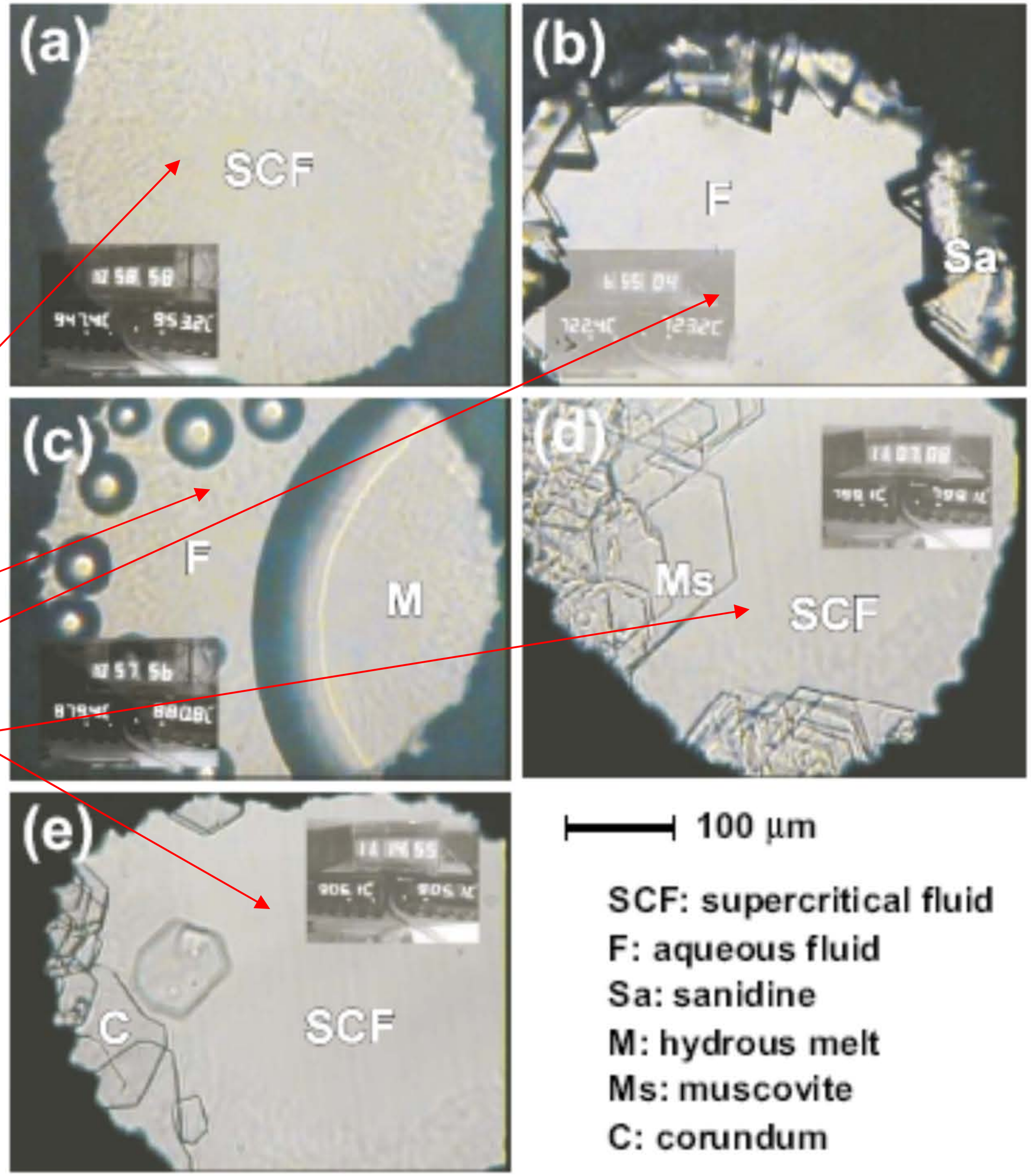



8332C
8336C


10 58 21
9382C
9416C

Mibe, Chou, & Bassett
JGR, 113 (2008)

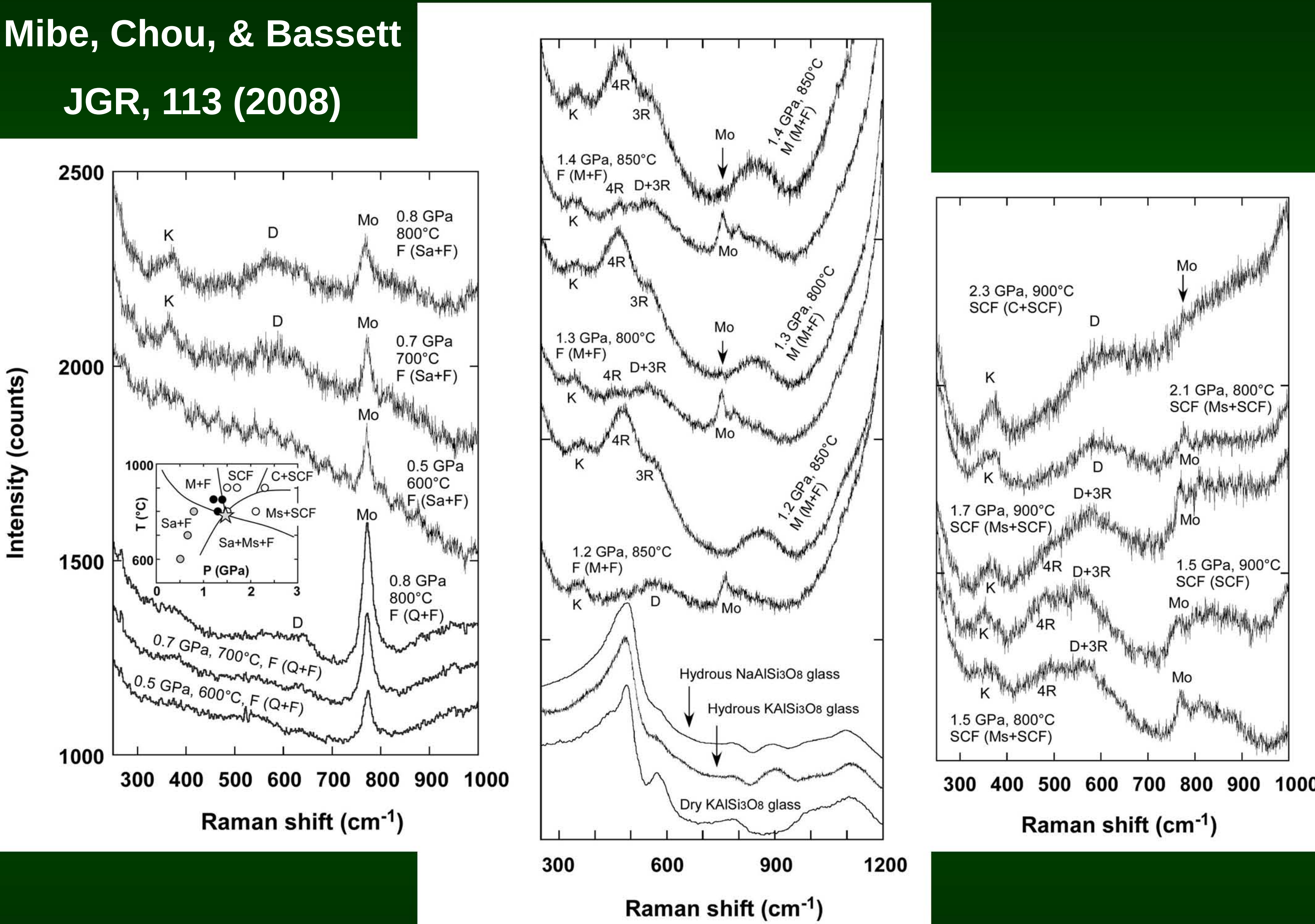




Molecule[a]	Frequency (cm^{-1})[b]	Motion[j]
H_4SiO_4 (Mo)	783 (calc)[c], 785 (exp)[d], 788 (calc)[e]	n(Si-O)
KH_3SiO_4 (Mo)	748 (calc)[f]	n(Si-O)
$H_6Si_2O_7$ (D)	620 (calc)[e], 631 (calc)[c], 638 (calc)[g]	n(Si-O), d(Si-O-Si)
$H_6SiAlO_7^{1-}$ (D)	585 (calc)[g]	n(T[k]-O), d(Si-O-Al)
$H_4SiAlO_7^{3-}$ (D)	574 (exp)[d]	n(T-O), d(Si-O-Al)
$H_6Si_3O_9$ (3R)	629 (calc)[e]	n(Si-O-Si)
$H_6Si_2AlO_9^{1-}$ (3R)	574 (calc)[h]	n(T-O-T)
$H_8Si_4O_{12}$ (4R)	490 (calc)[h]	n(Si-O-Si)
$H_8Si_3AlO_{12}^{1-}$ (4R)	488 (calc)[h]	n(T-O-T)
$Al(OH)_4^{1-}$	616 (calc)[i], 620 (exp)[d]	n(Al-O)
$KAl(OH)_4$	619 (calc)[f]	n(Al-O)
KH_2AlO_3	691 (calc)[f]	n(Al-O)
$Al(OH)_3H_2O$	438 (calc)[i]	n(Al-OH_2)
KOH	361 (calc)[f]	d(K-O-H)

Mibe, Chou, & Bassett

JGR, 113 (2008)



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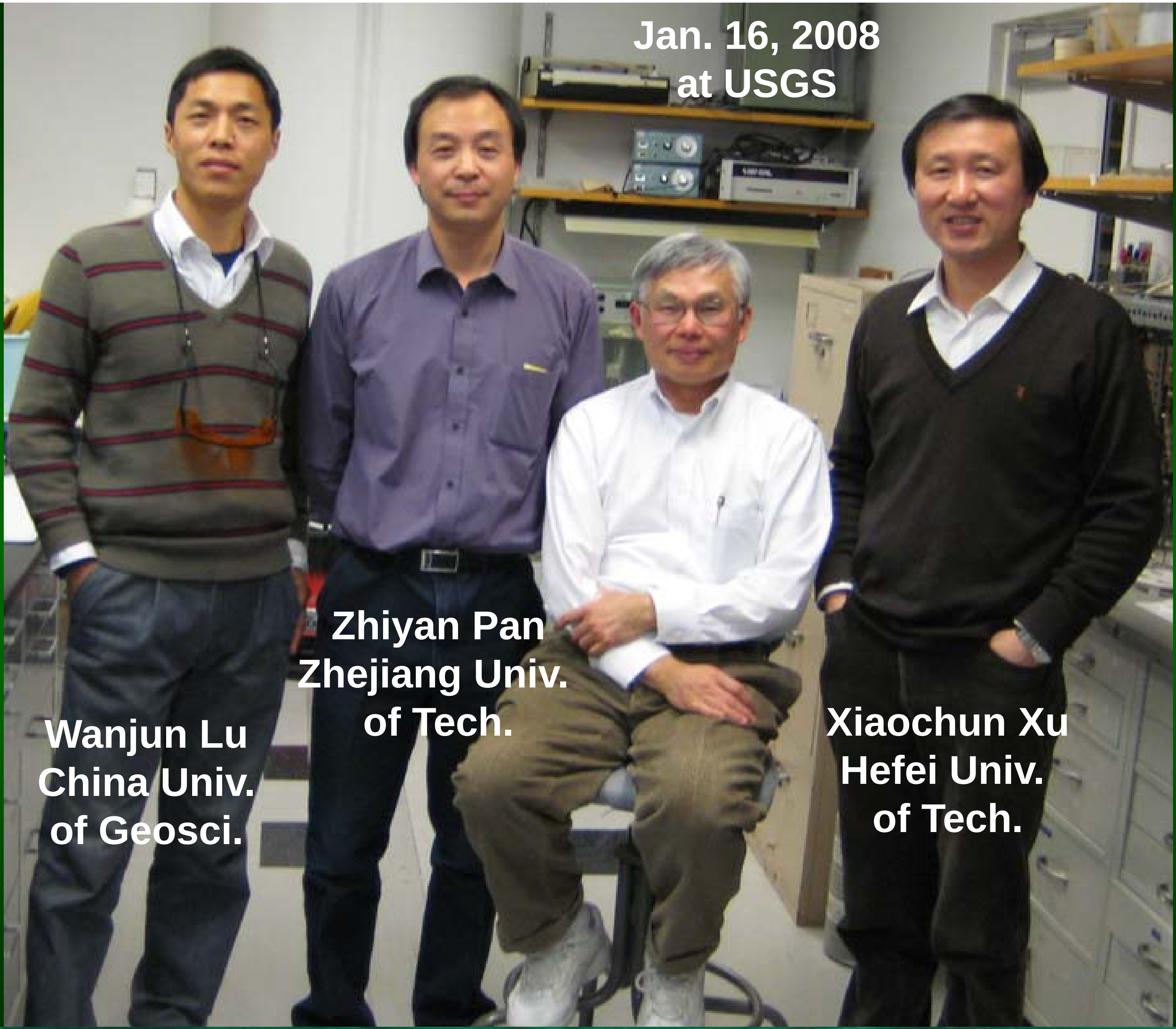
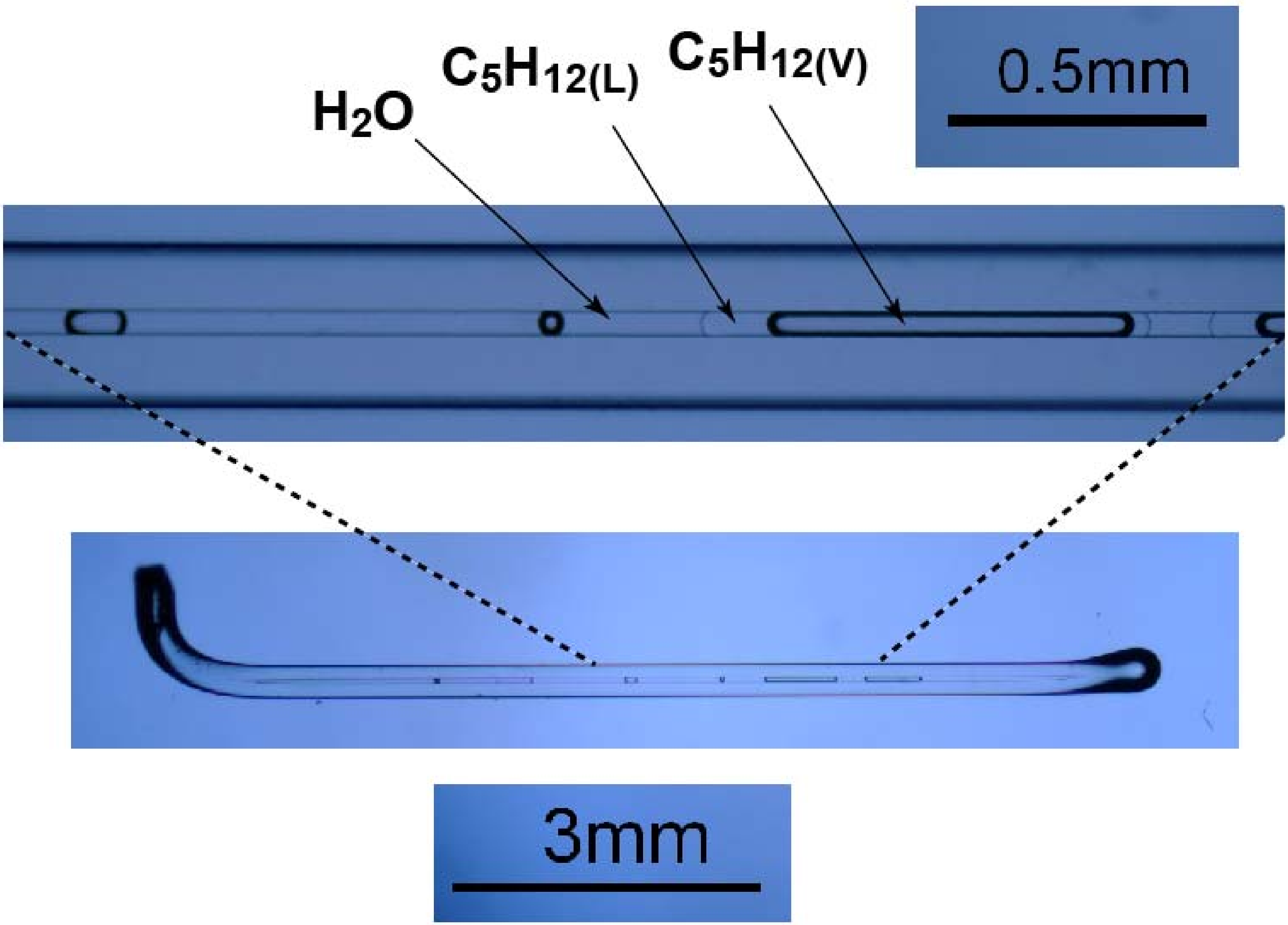

Jan. 16, 2008
at USGS
Zhiyan Pan
Zhejiang Univ.
of Tech.
Wanjun Lu
China Univ.
of Geosci.
Xiaochun Xu
Hefei Univ.
of Tech.

USGS



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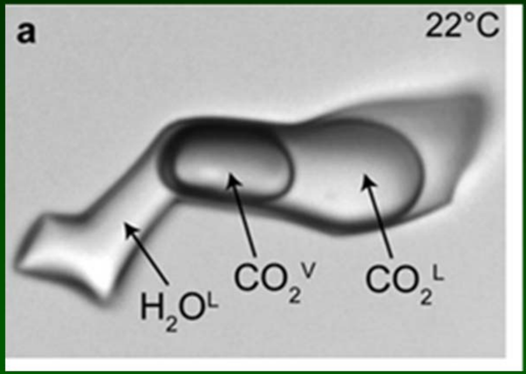
Synthetic Fluid Inclusions in Quartz (Sterner & Bodnar, 1984)

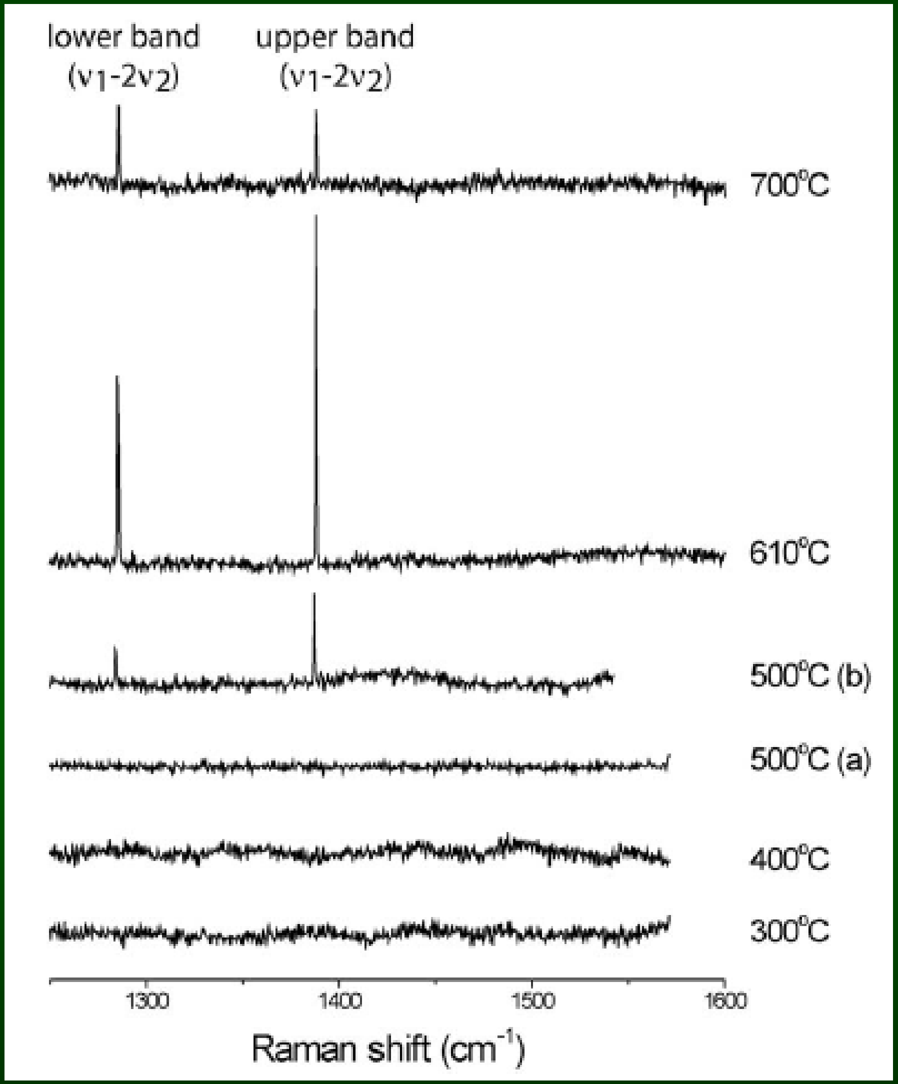


- Pre-fractured quartz core or prism, together with sample fluid and silica powder, were sealed in a precious-metal capsule.
- The fractures in quartz were healed at a fixed P-T condition in a pressure vessel and captured sample fluid as inclusions.
- To heal the fractures requires high T (> 300 ºC) and time (days and weeks).

Lin (2005)

- **Synthesized CH_4-H_2O fluid inclusions in quartz in Pt capsules at 300 to 700 °C and 1, 3, and 5 kbars**
- **$Al_4C_3 + 12\ H_2O = 3\ CH_4 +$**
  $4\ Al(OH)_3$
- **All inclusions formed at and above 600 °C contain CO_2**

$CH_4 + H_2O = CO_2 + H_2$



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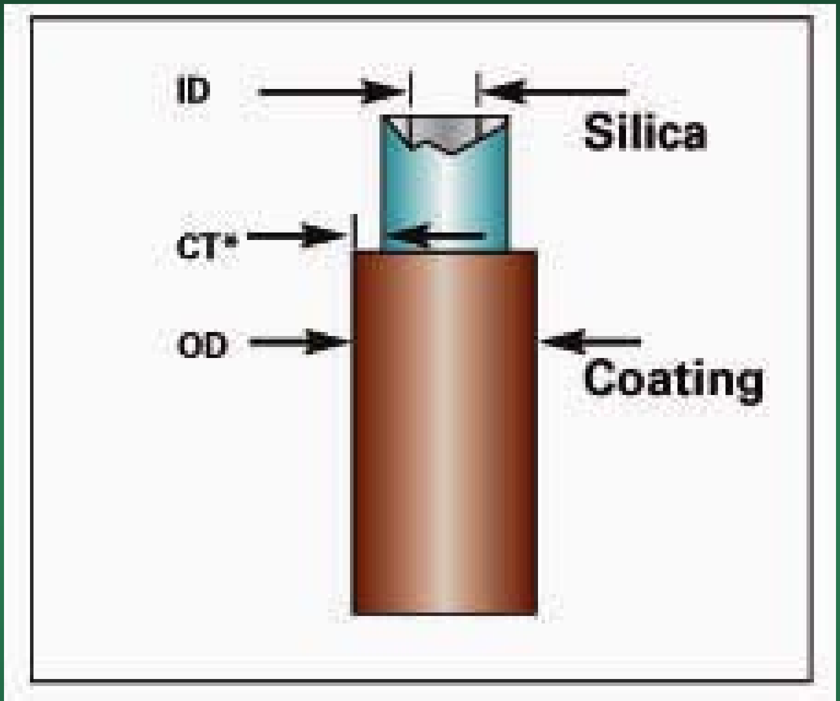
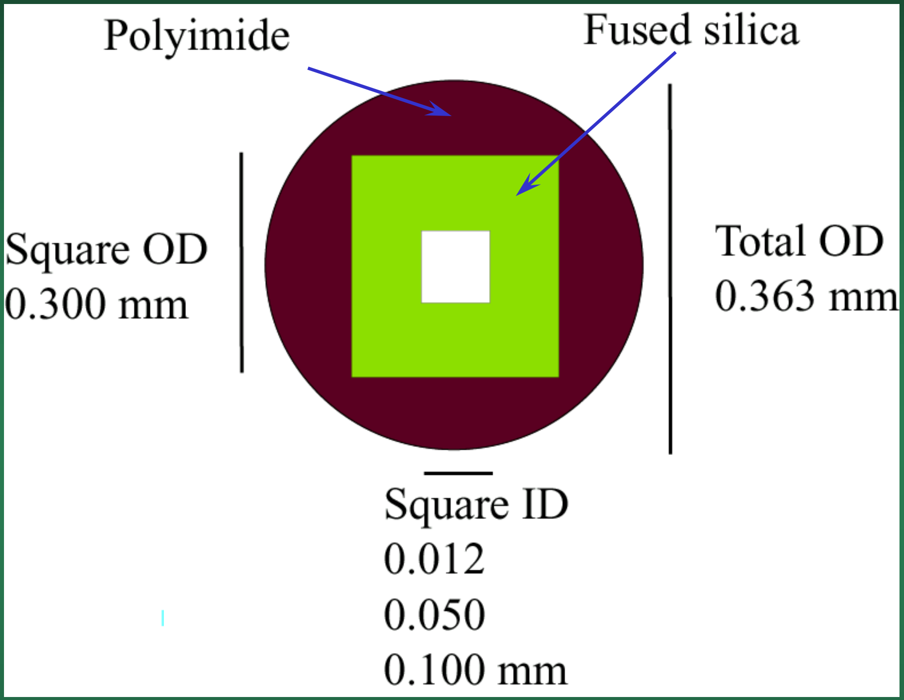
Fused Silica Capillary Tube





Round-sectioned tube

Square-sectioned tube

Polymicro Technologies, LLC (www.polymicro.com).

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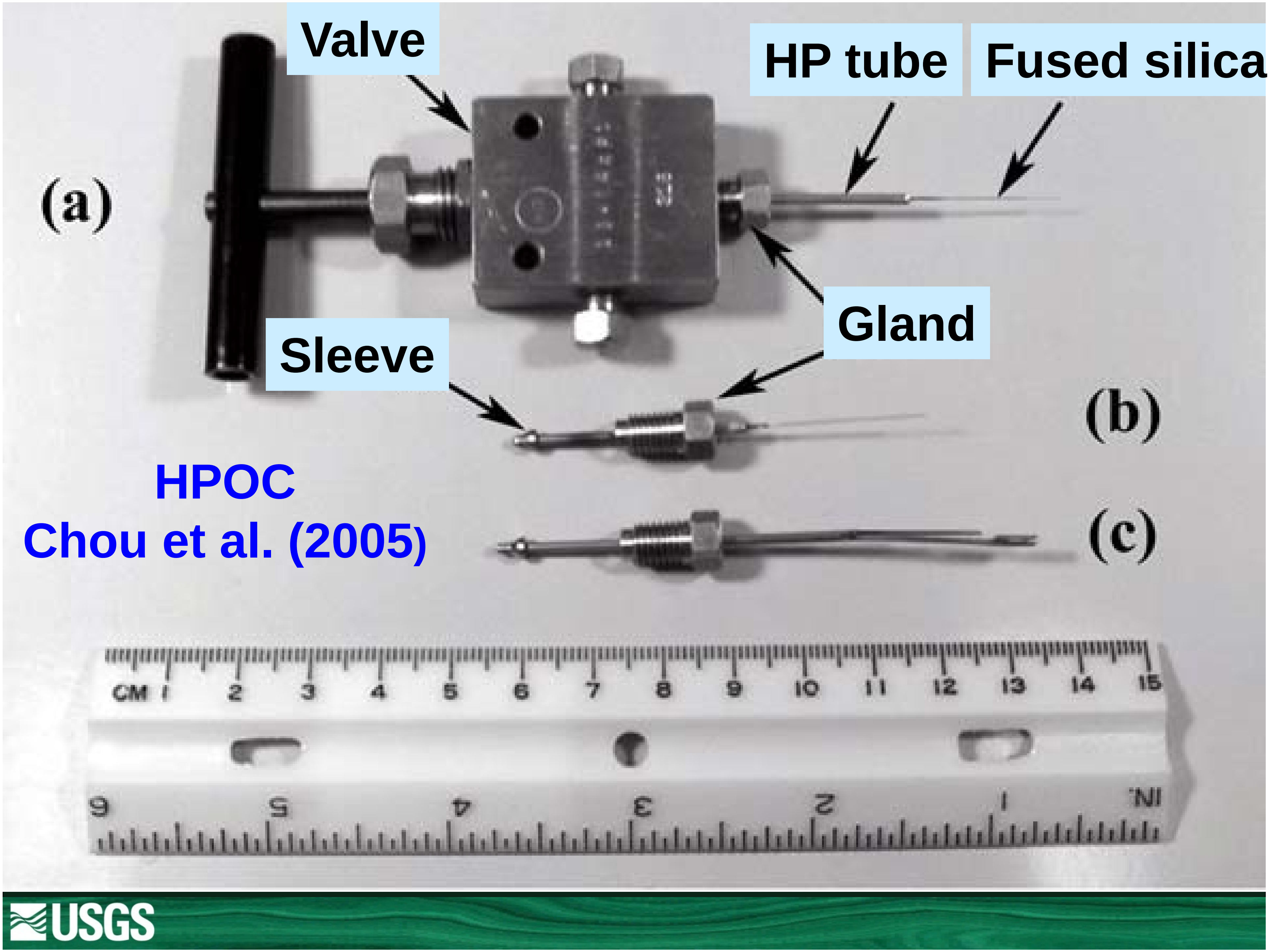
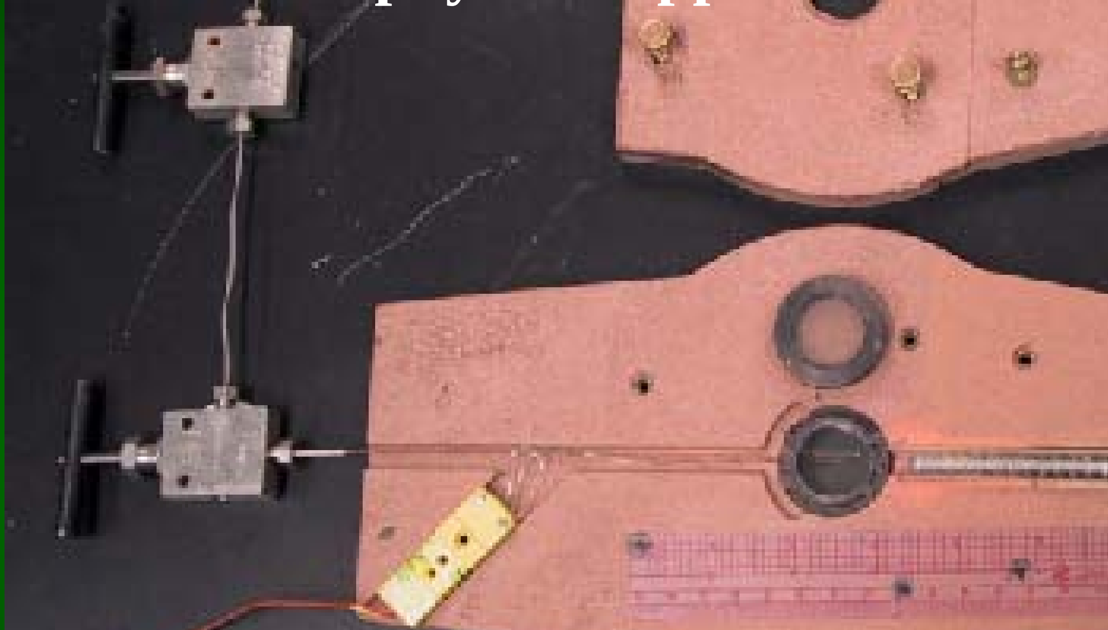
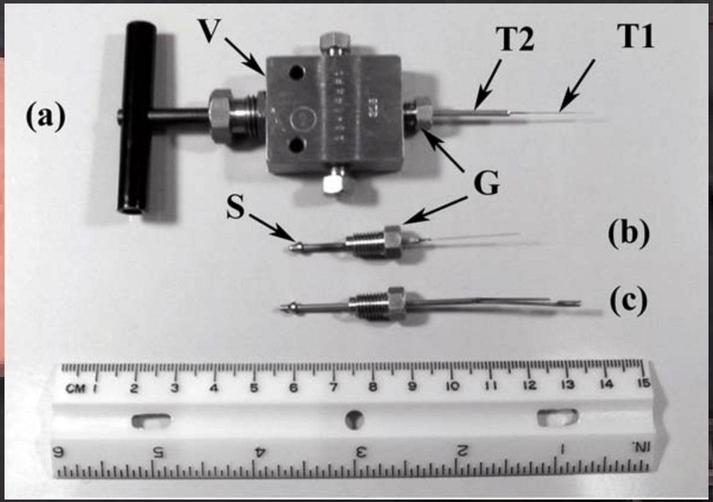
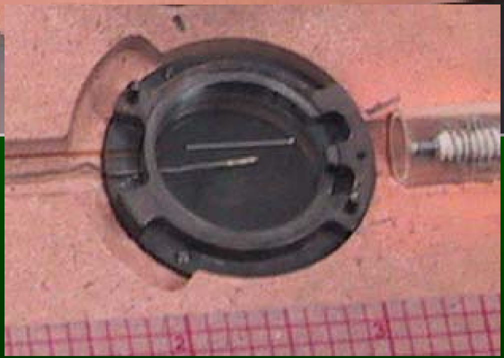


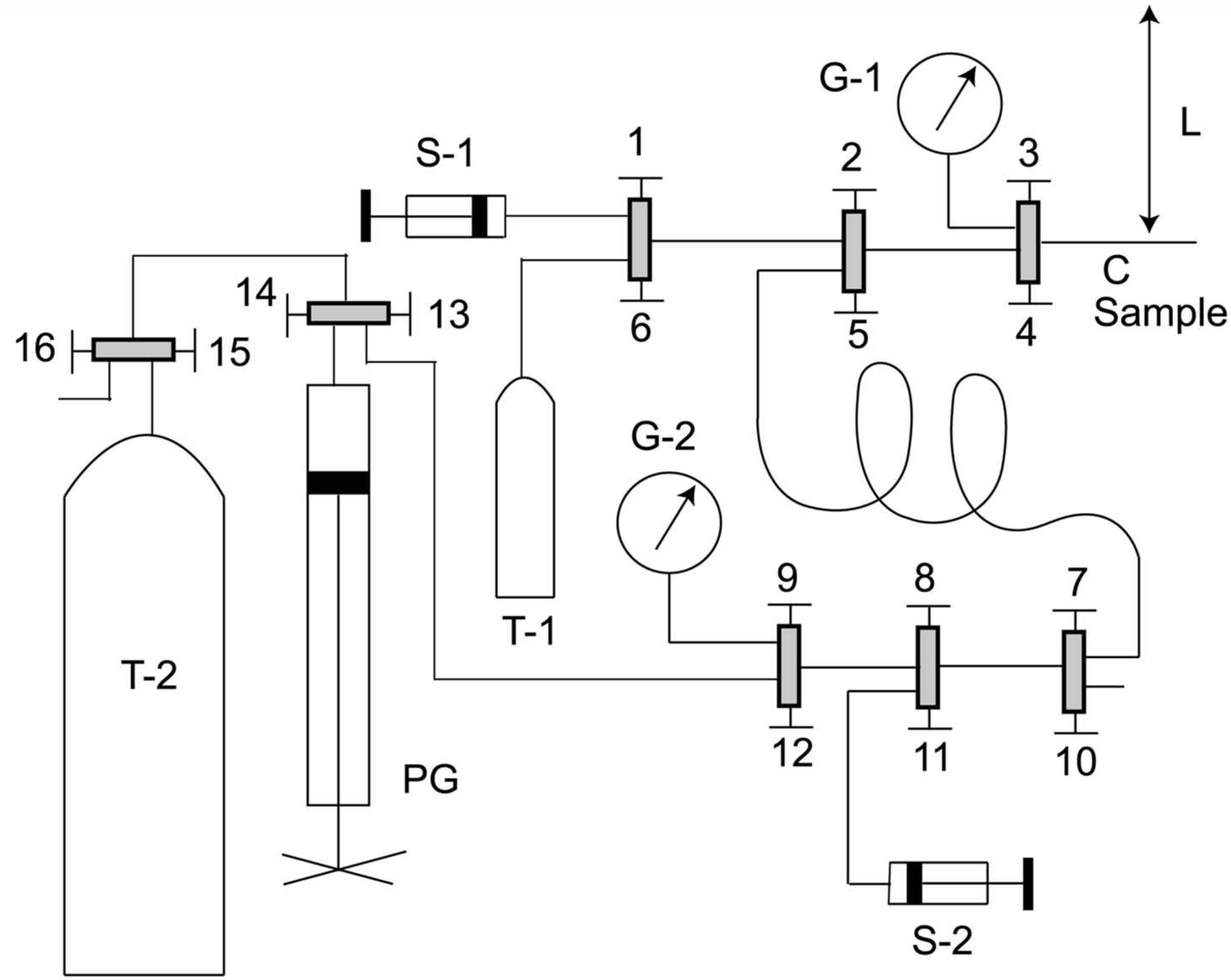
Valve
HP tube
Fused silica
(a)
Gland
Sleeve
(b)
HPOC
Chou et al. (2005)
(c)
CM 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
IN. 1 2 3 4 5 6
USGS

Chou, Burruss, Lu (2005)
Chapter 24 in
Advances in High-Pressure Technology for Geophysical Applications



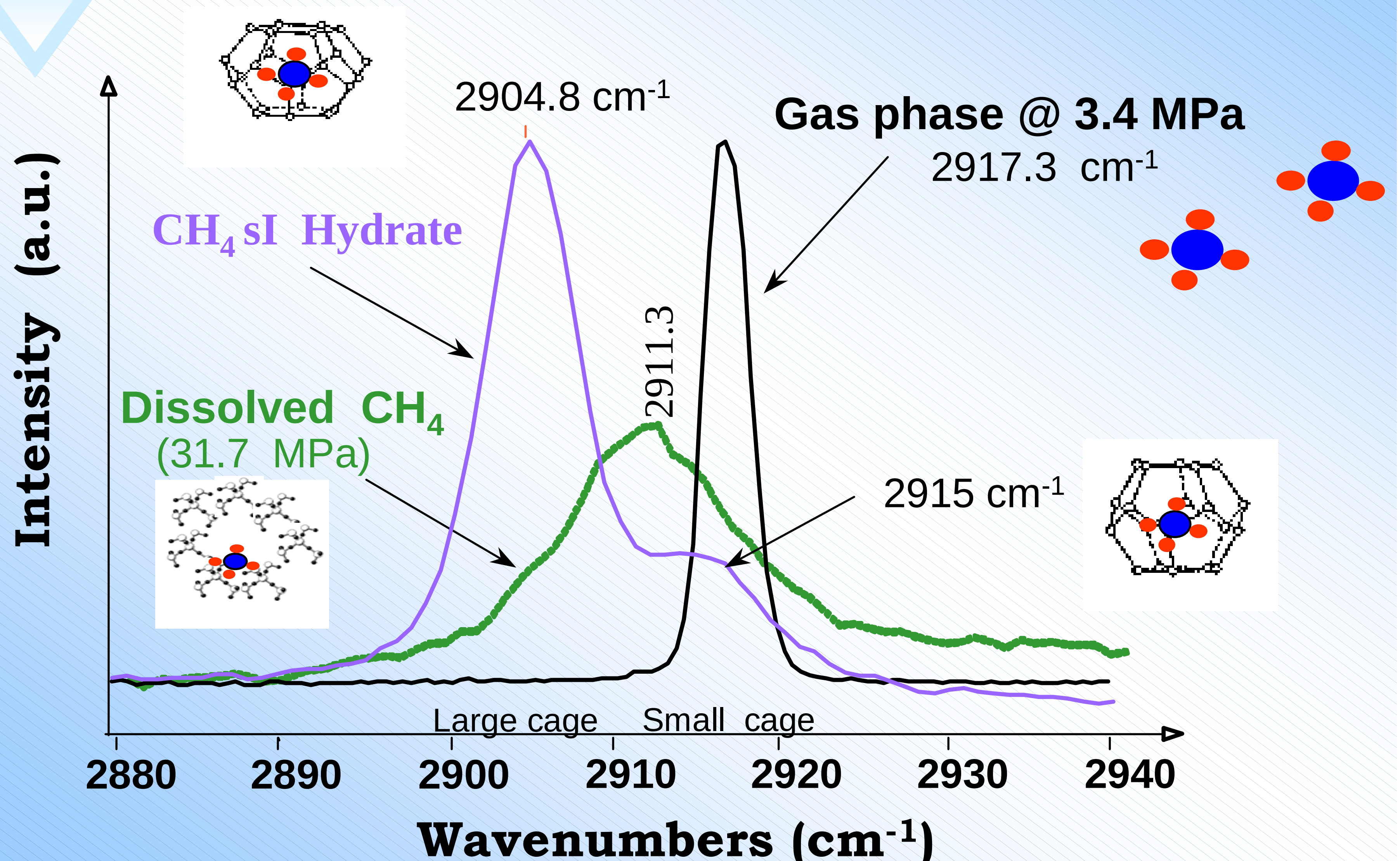






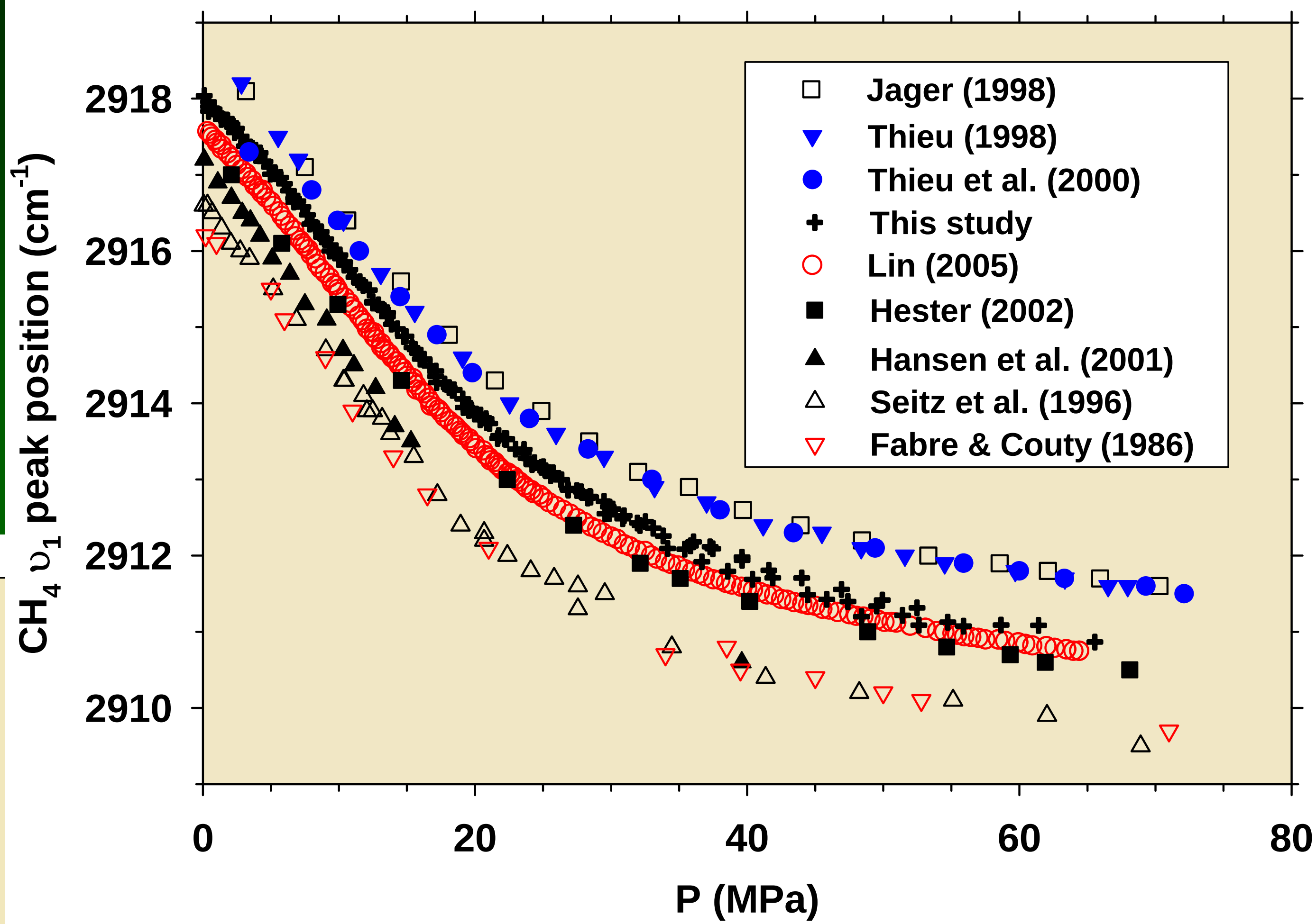
G-1 Low-P gauge	C Capillary tubing	L Laser beam (downward)
G-2 High-P gauge	T-1 Sample fluid tank	Raman scattered
S-1 & S-2 Syringes	T-2 High pressure fluid tank	light (upward)
1 to 16 Pressure valves	PG Pressure generator	

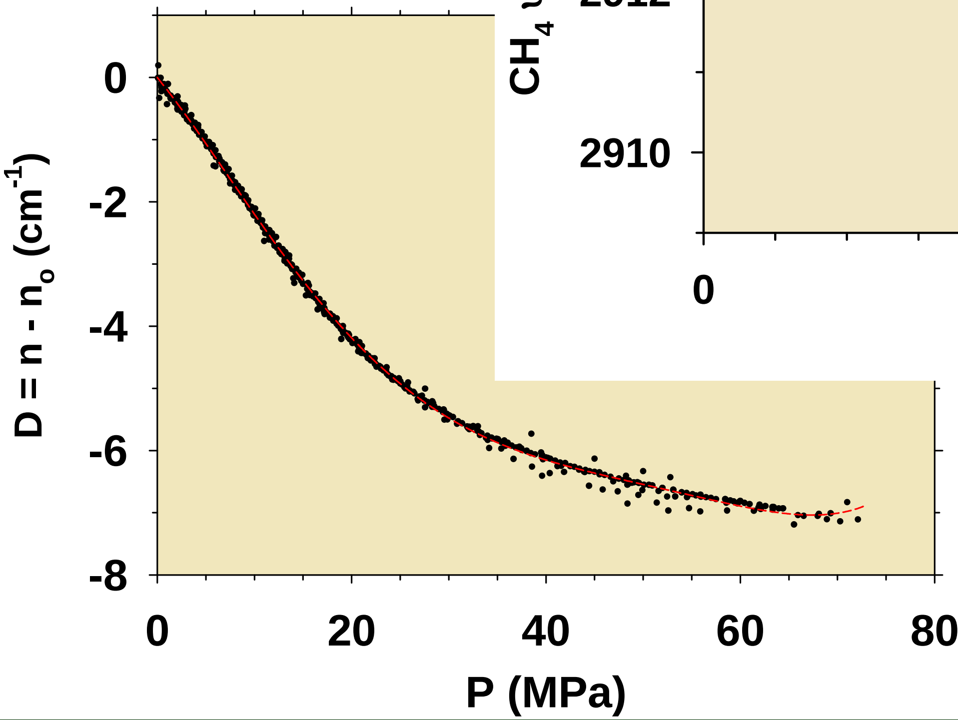
Raman Spectra for CH_4 in Different Phases



n_o = p.p. near 0 P

n = p.p. at high P





Lu, Chou, Burruss, Song
GCA (2007)

$$P\ (MPa) = -\ 0.0148\ D^5 - 0.1791\ D^4 - 0.8479\ D^3 - 1.765\ D^2 - 5.876\ D$$

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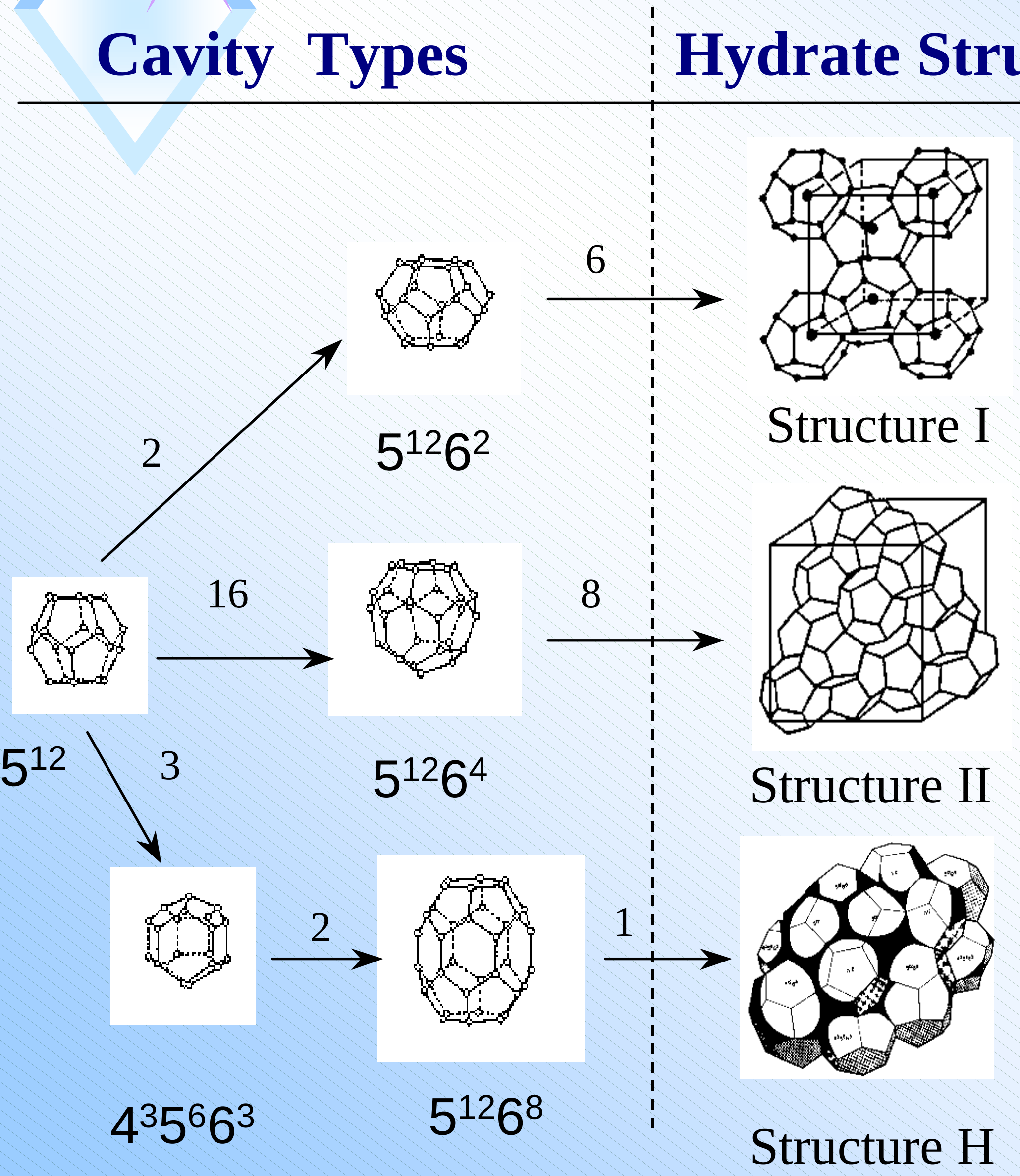
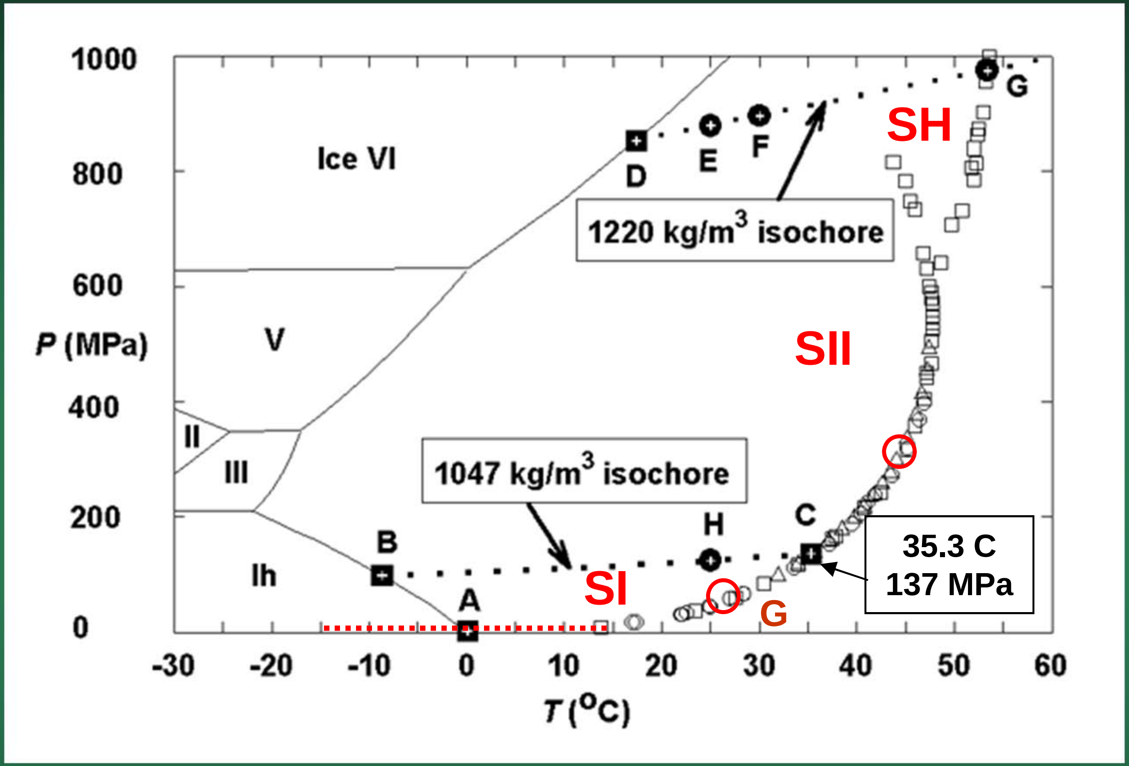
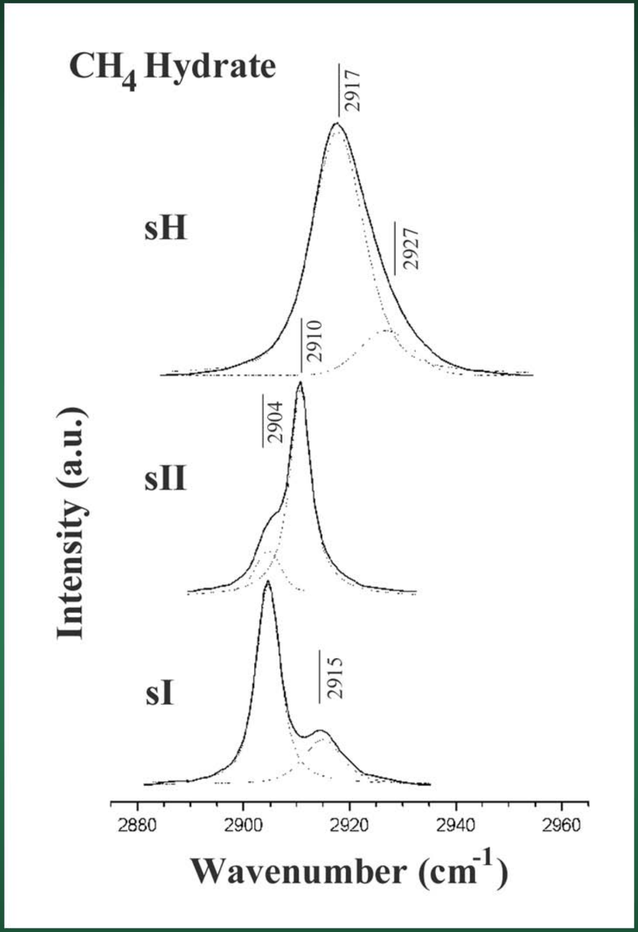
What Are Gas Hydrates ?



Hydrate Structure		'Guest' Molecules
Structure I	46 H_2O	Methane, Ethane, Carbon dioxide, etc.
Structure II	136 H_2O	Propane, Iso-butane, etc.
Structure H	34 H_2O	Methane + Neohexane, Methane + Cycloheptane, etc.

Chou et al. (2000) *PNAS, v. 97, 13484-13487*





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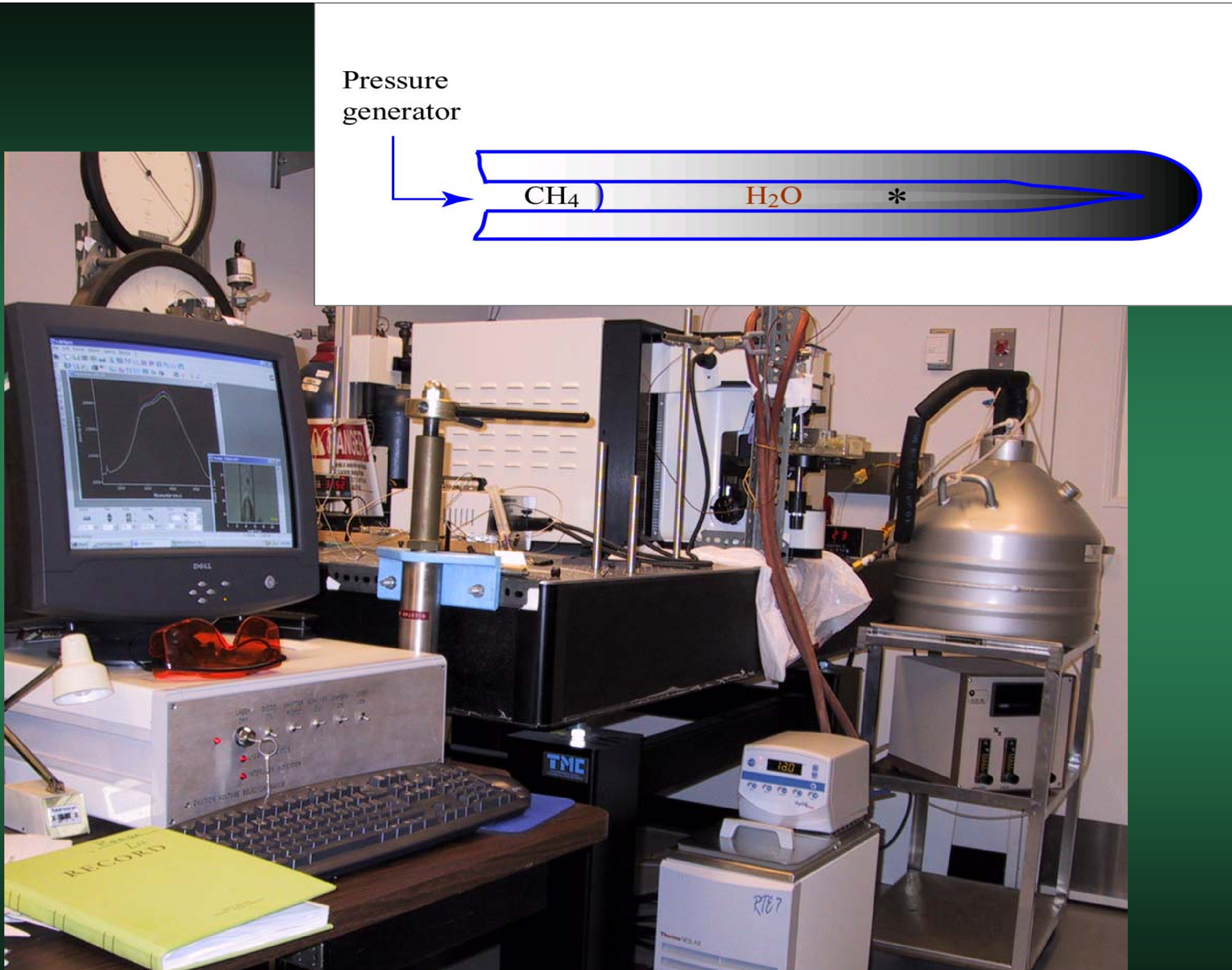
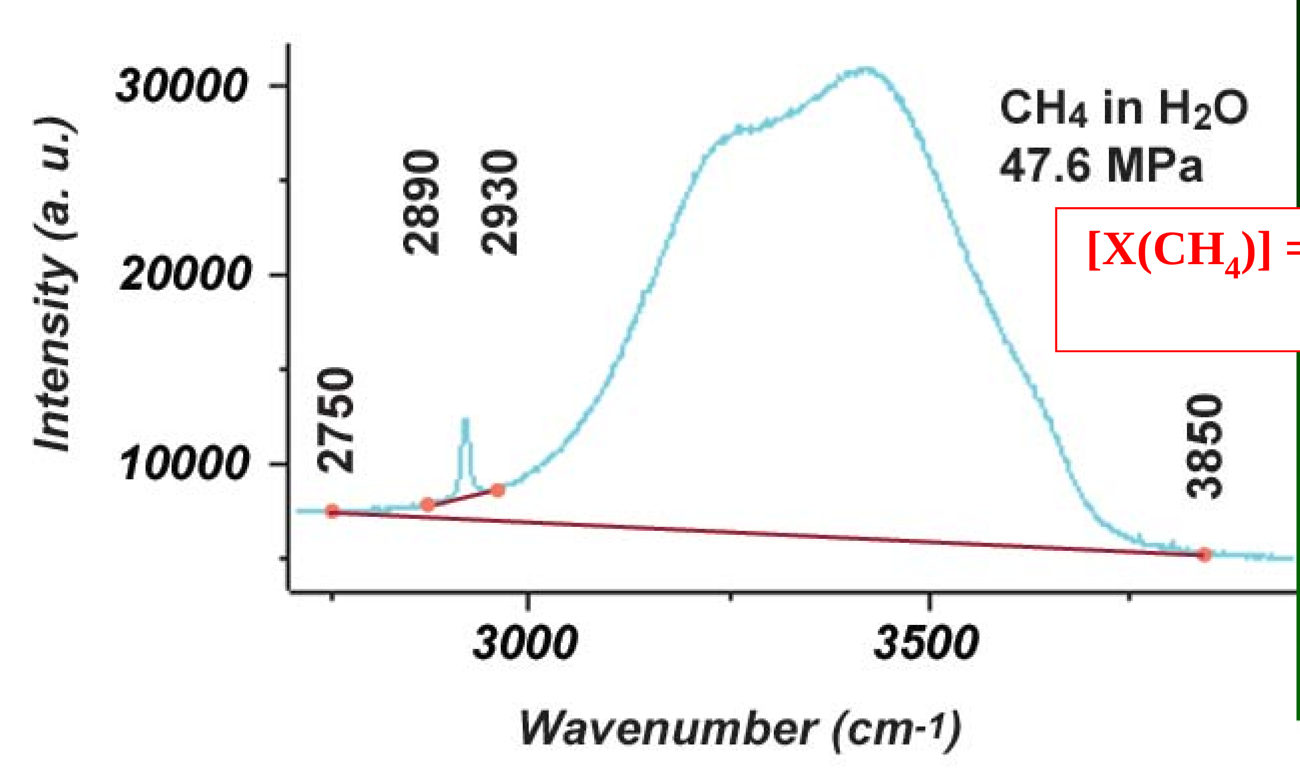
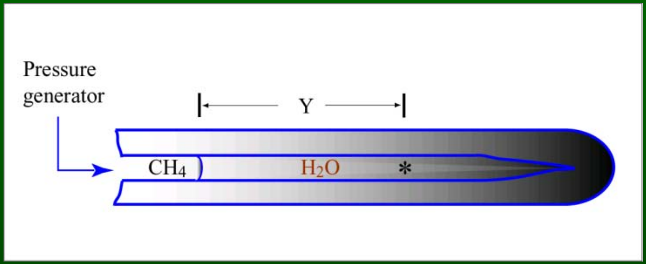
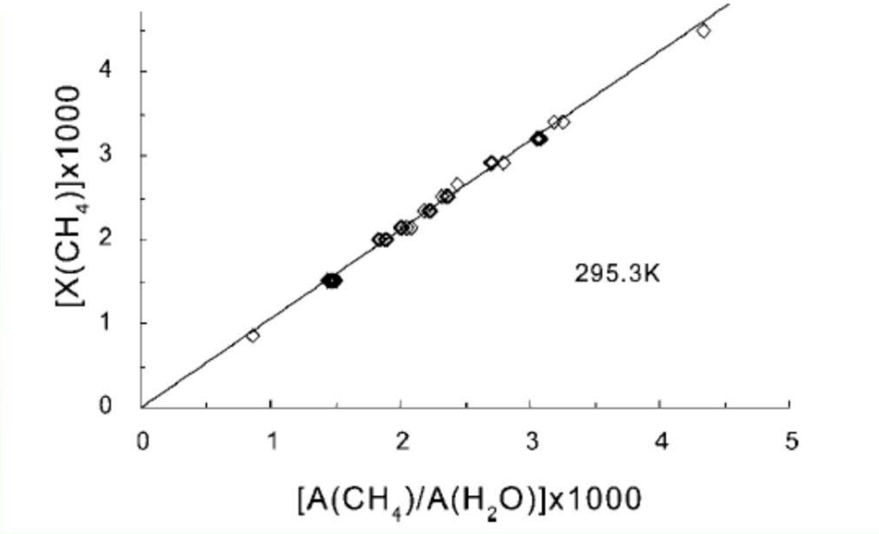

Pressure generator
CH_4
H_2O
*
DANGER
DELL
TMC
RECORD



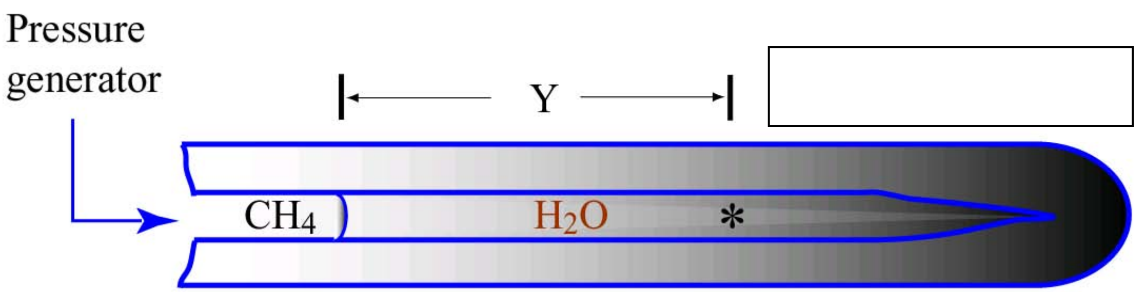
$$[X(CH_4)] = 1.0563\ [A(CH_4)_{aq}/A(H_2O)]$$



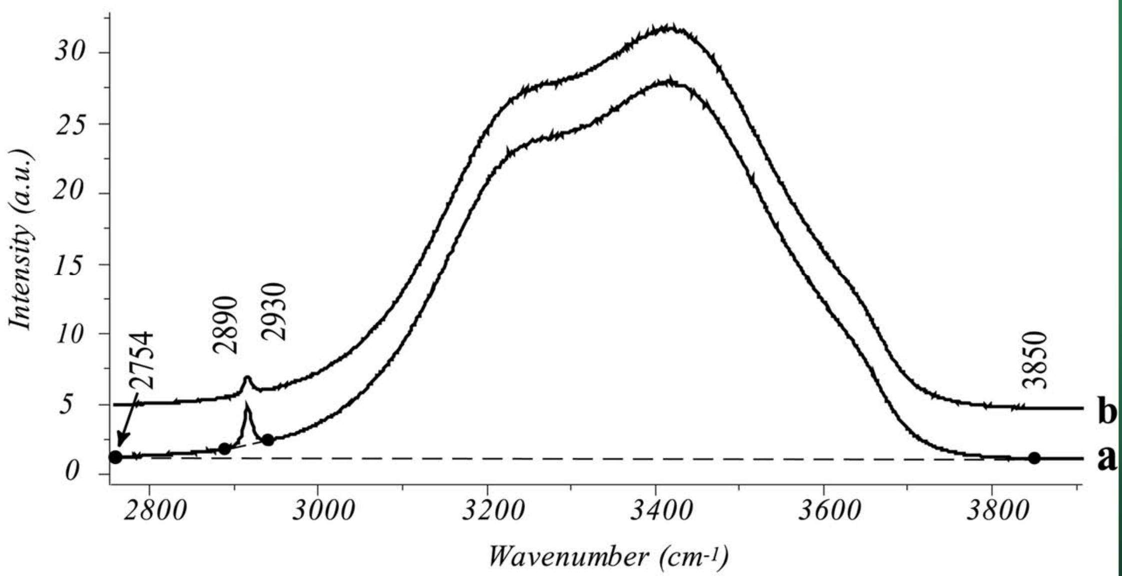


Lu, Chou, Burruss, Yang (2006)
Applied Spectroscopy

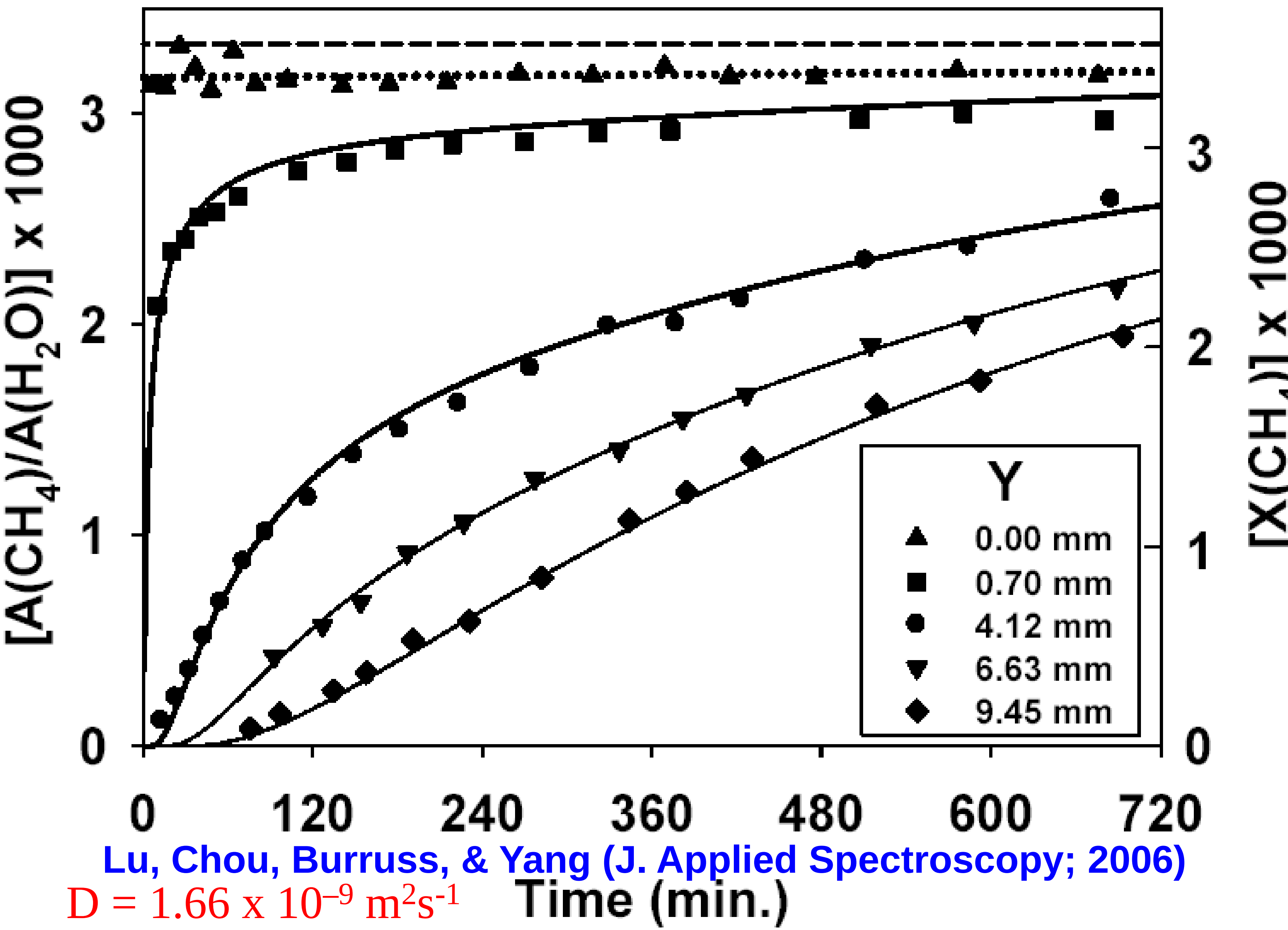
Diffusion of Methane in Water



115 minutes after being pressurized by CH_4 at 24.47 MPa



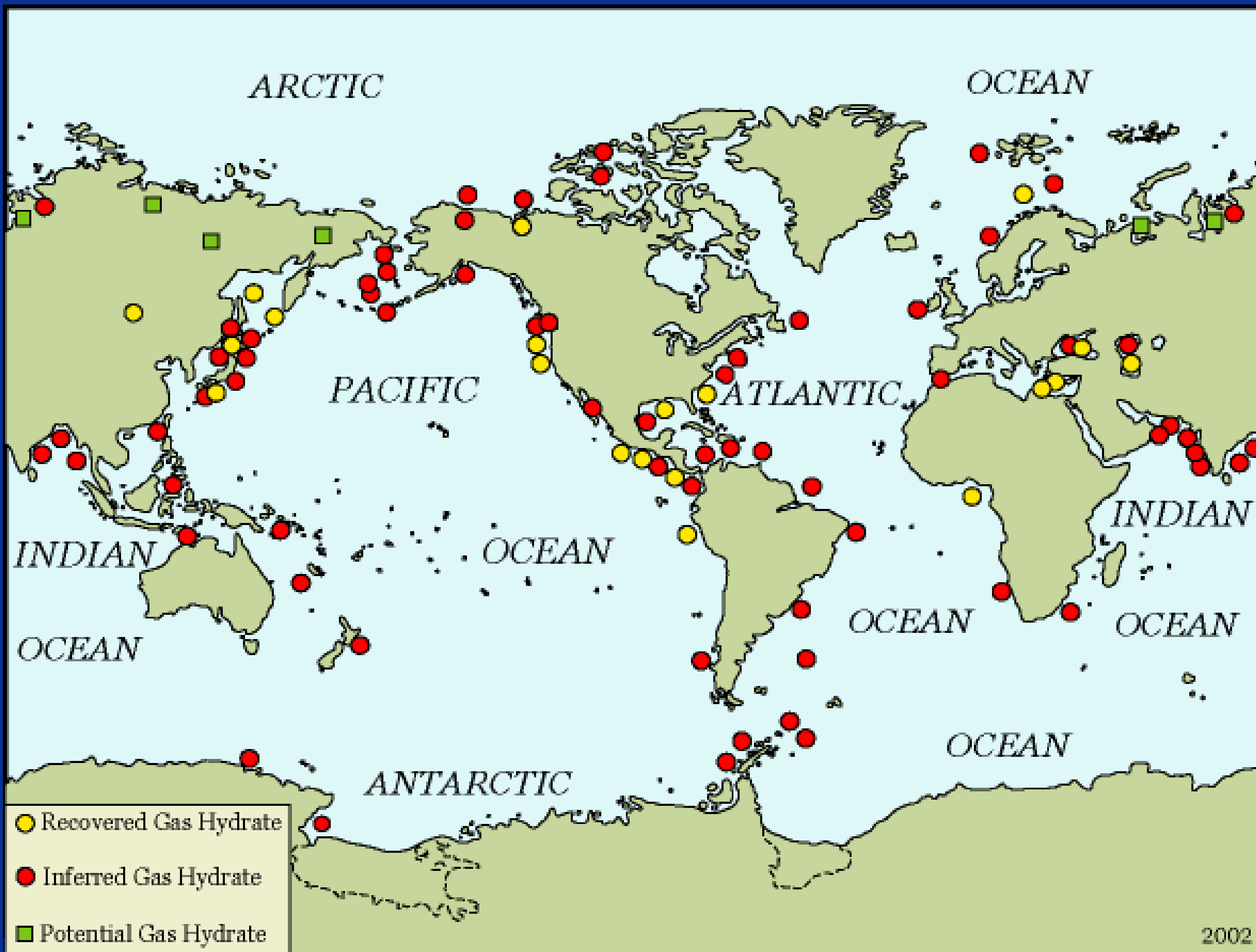
$[X(CH_4)] = 1.0563\ [A(CH_4)_{aq}/A(H_2O)]$



Lu, Chou, Burruss, & Yang (J. Applied Spectroscopy; 2006)

$D = 1.66 \times 10^{-9}\ m^2s^{-1}$

WORLD GAS HYDRATE



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Keith Kvenvolden

CH_4 conc. in equilib. with methane hydrate

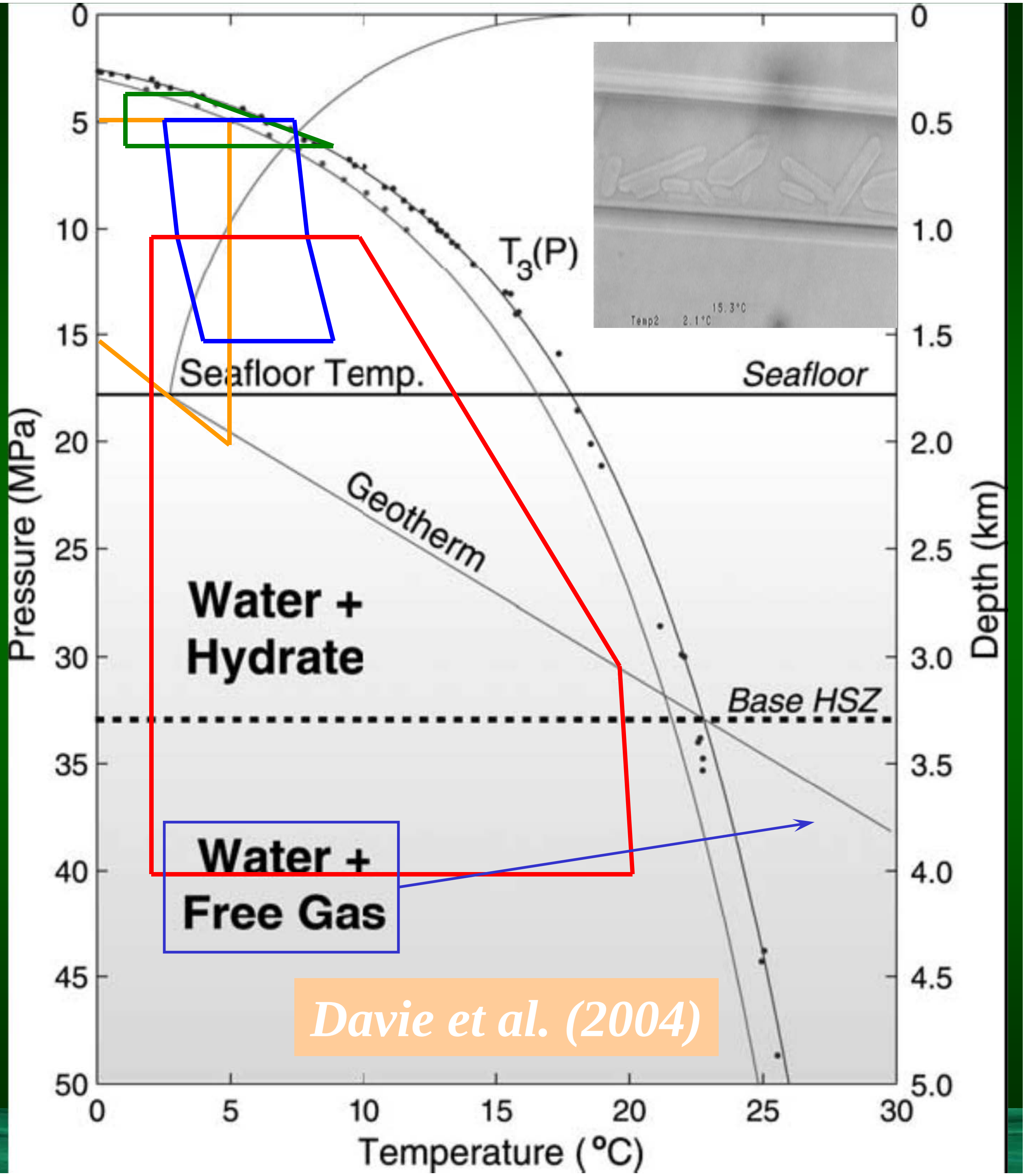
Previous studies

Servio & Englezos (2002)

Yang et al. (2001)

Kim et al. (2003)

This study
Lu, Chou, Burruss
GCA (2008)



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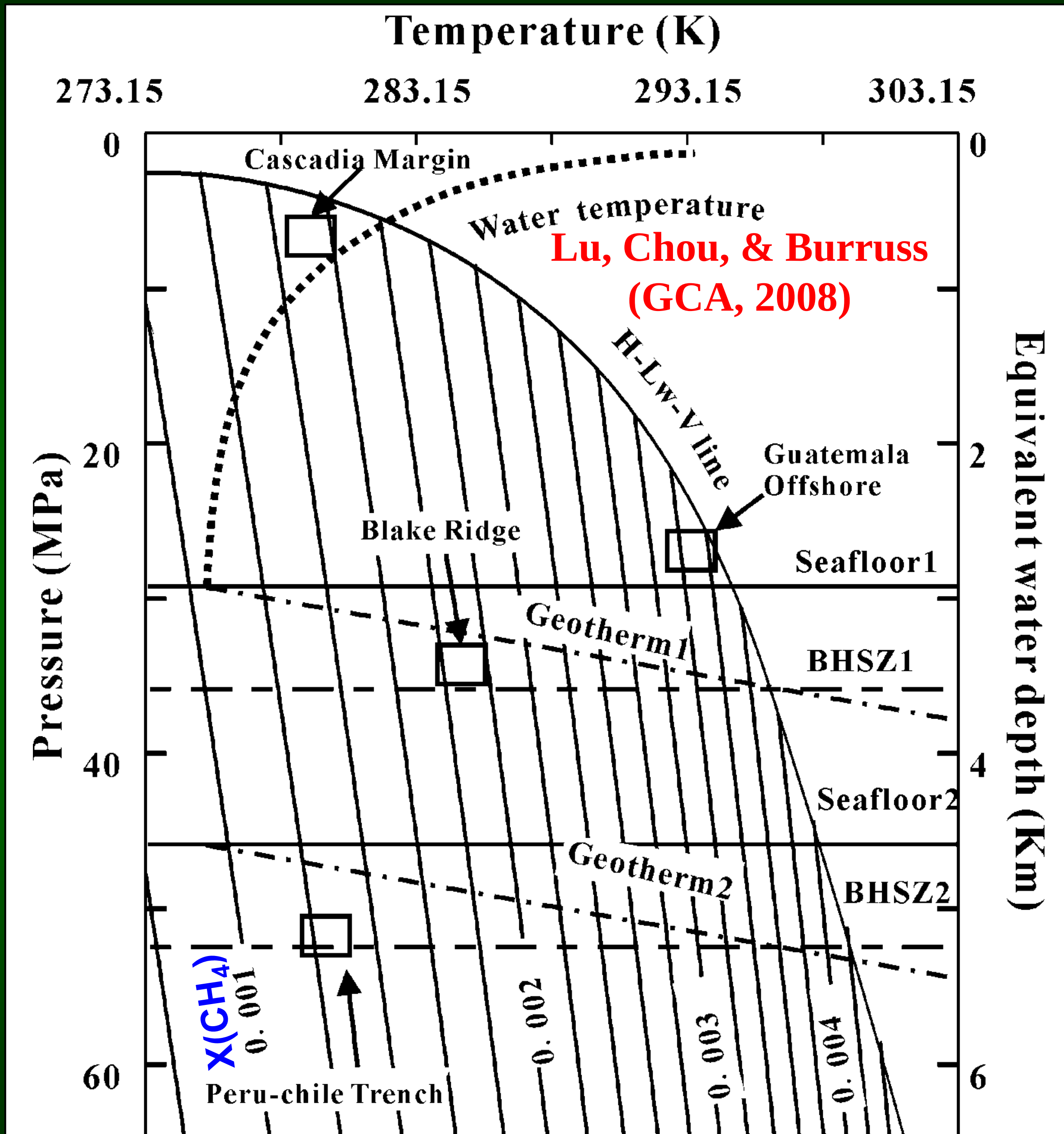

Temperature (K)
273.15
283.15
293.15
303.15
0
20
40
60
Pressure (MPa)
0
2
4
6
Equivalent water depth (Km)
Cascadia Margin
Water temperature
Lu, Chou, & Burruss
(GCA, 2008)
H-Lw-V line
Guatemala
Offshore
Blake Ridge
Seafloor1
Geotherm1
BHSZ1
Seafloor2
Geotherm2
BHSZ2
X(CH4)
0. 001
0. 002
0. 003
0. 004
Peru-chile Trench

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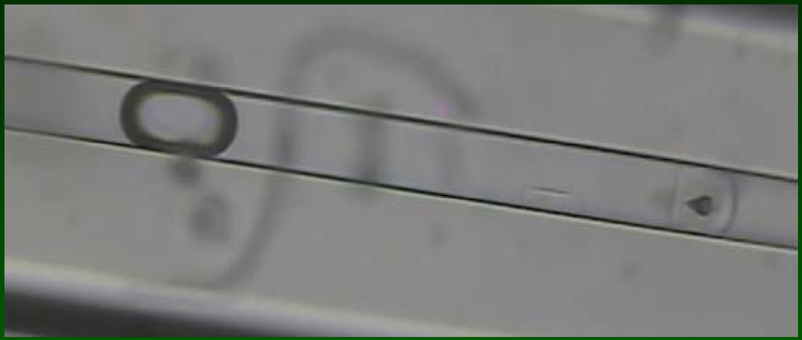
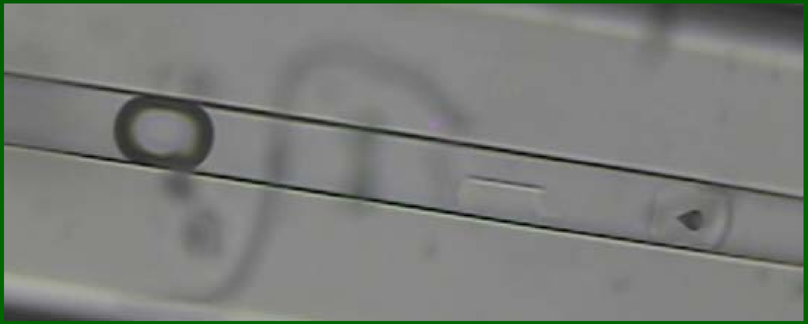
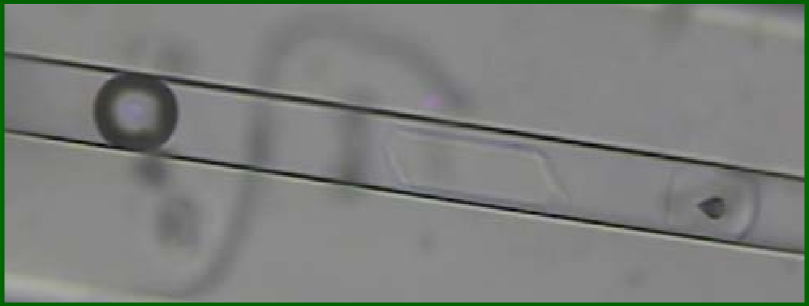
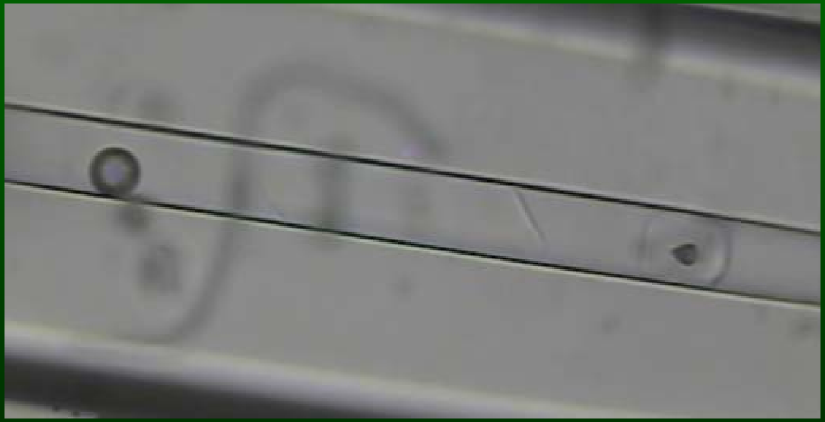
Growth of methane hydrate in 2 wt% Na_2SO_4 aqueous solution near room temperature







T dropped from ~23°C to ~22°C in one hour



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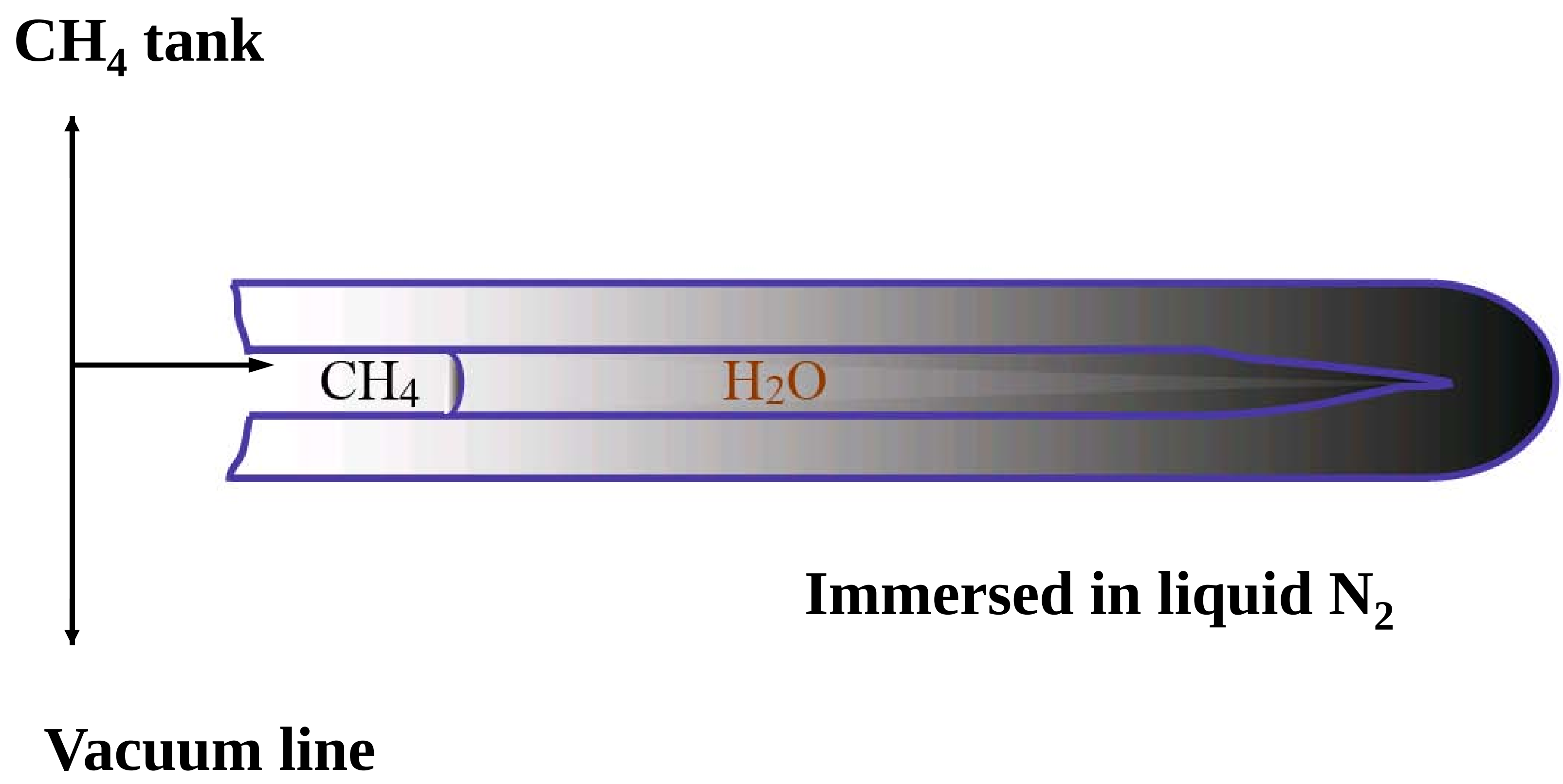
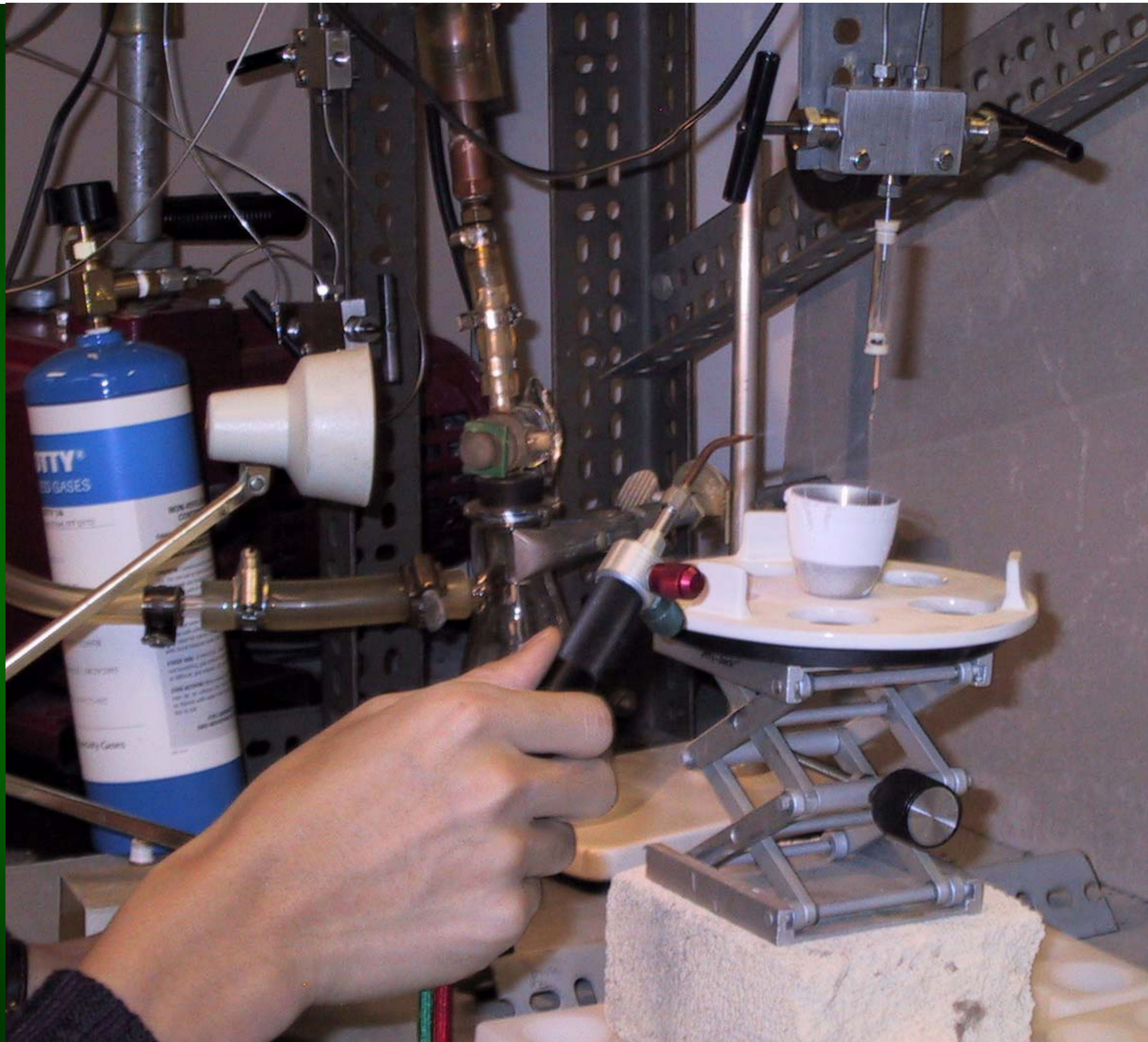
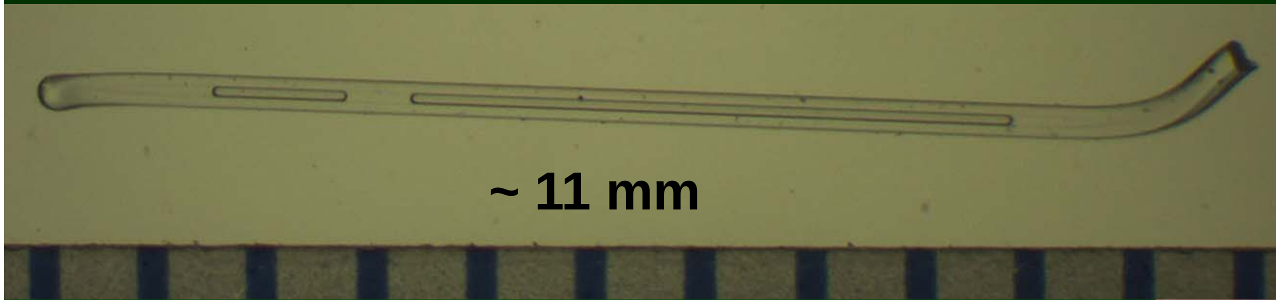
14:56:03:09
1X Lens
2% Na2SO4+H2O+CH4+HYDRATE
DVD-Video
X70
Created with a non-activated version www.avs4you.com
17.3°C
Temp2 21.0°C

Sample loading system for a capillary capsule

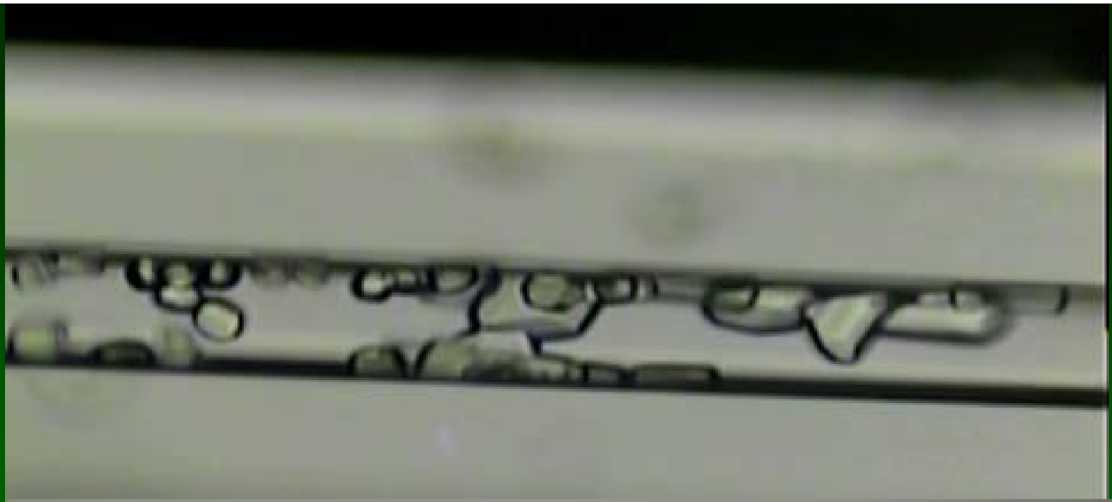




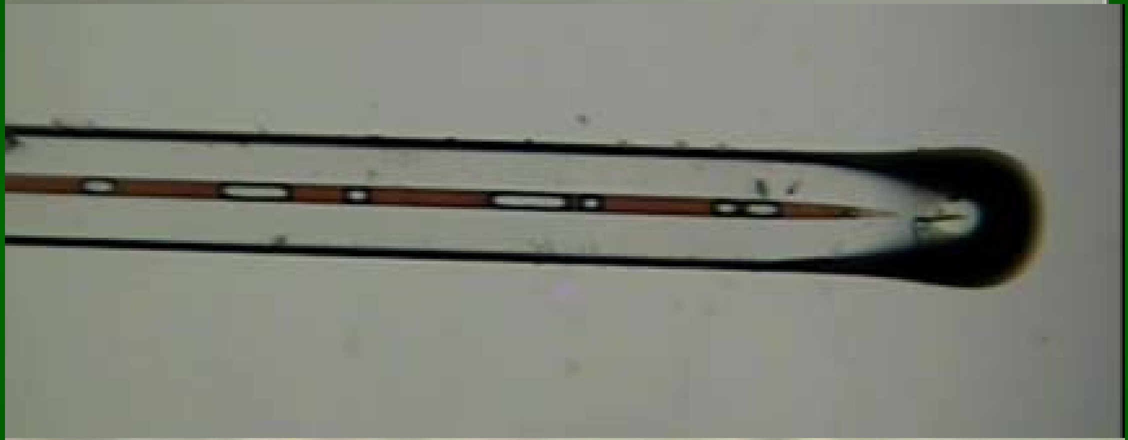

~ 11 mm

Room T
(50 µm ID)

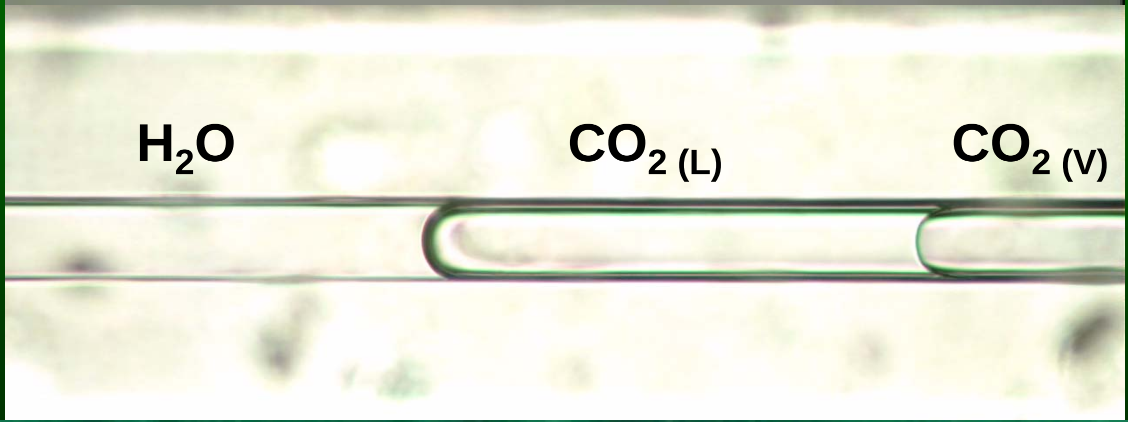
Methane Hydrate



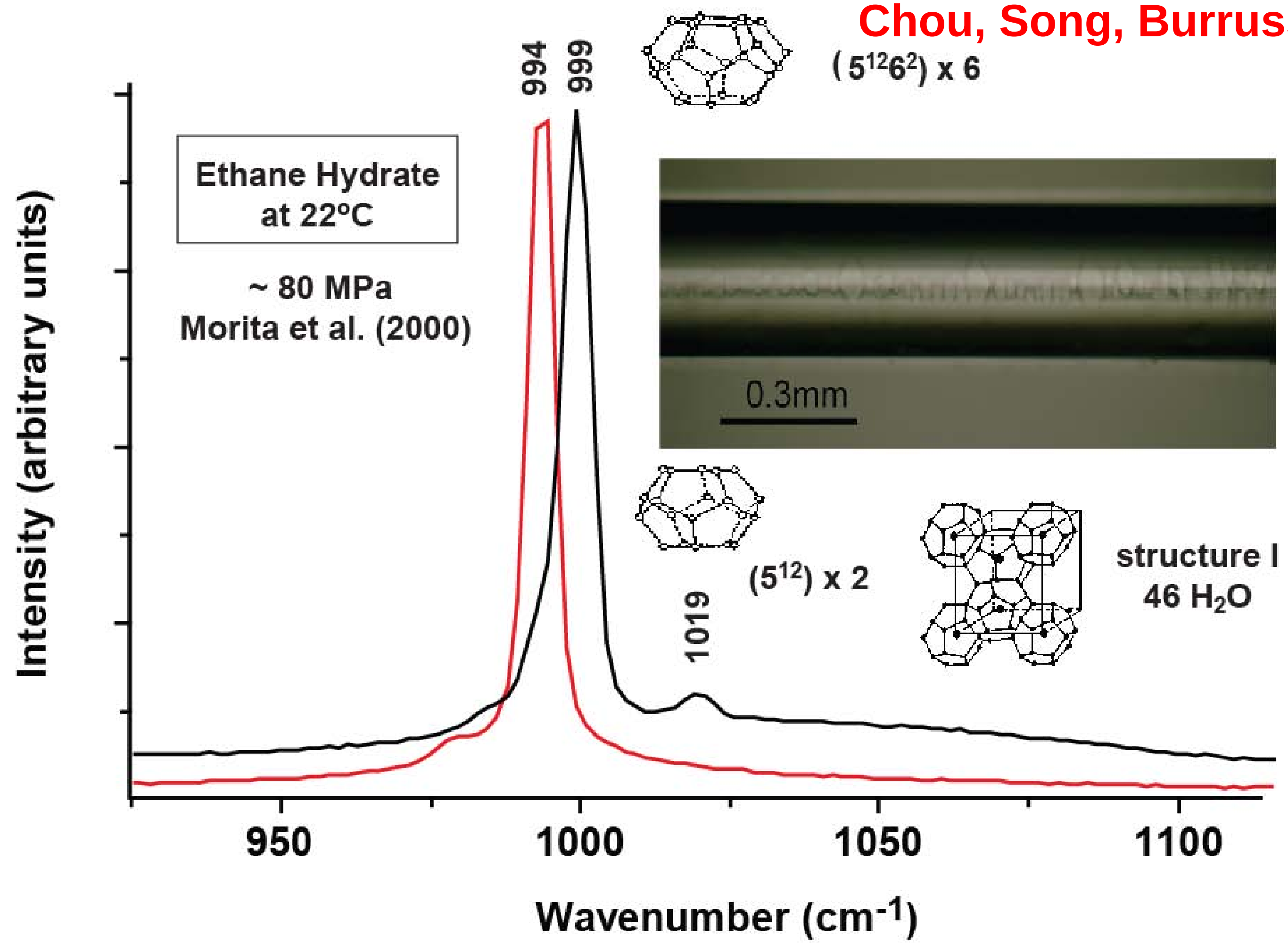
Smackover Oil
(50 µm ID)

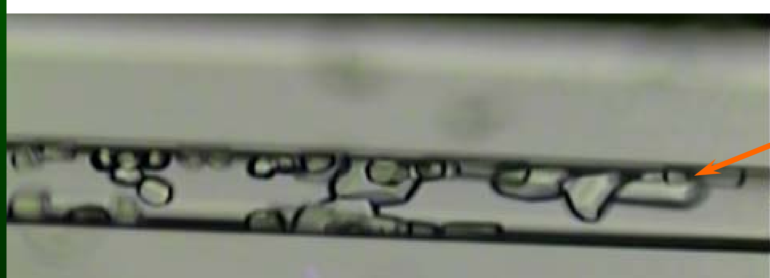


CO_2-H_2O



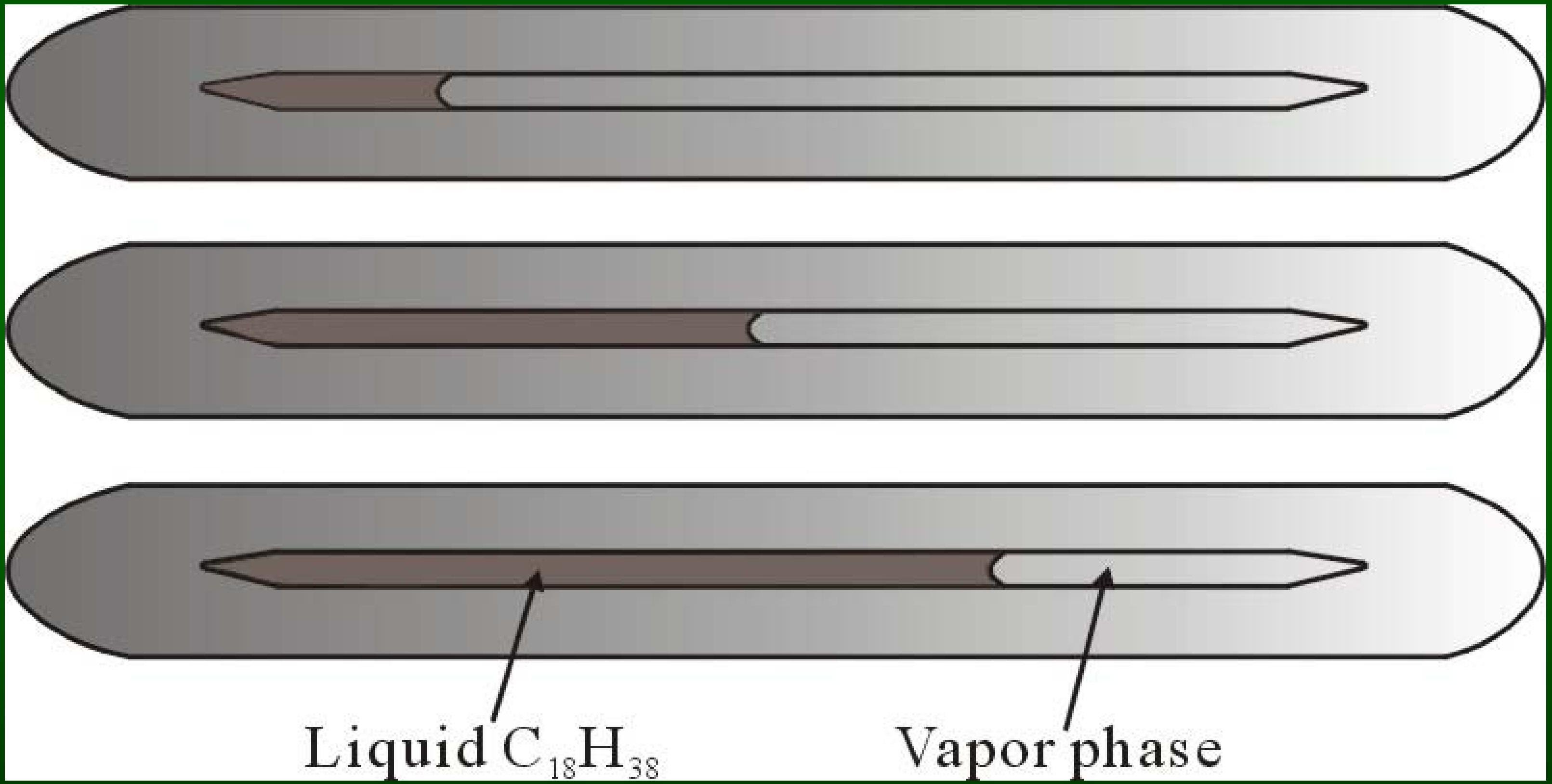
Chou, Song, Burruss (GCA, 2008)

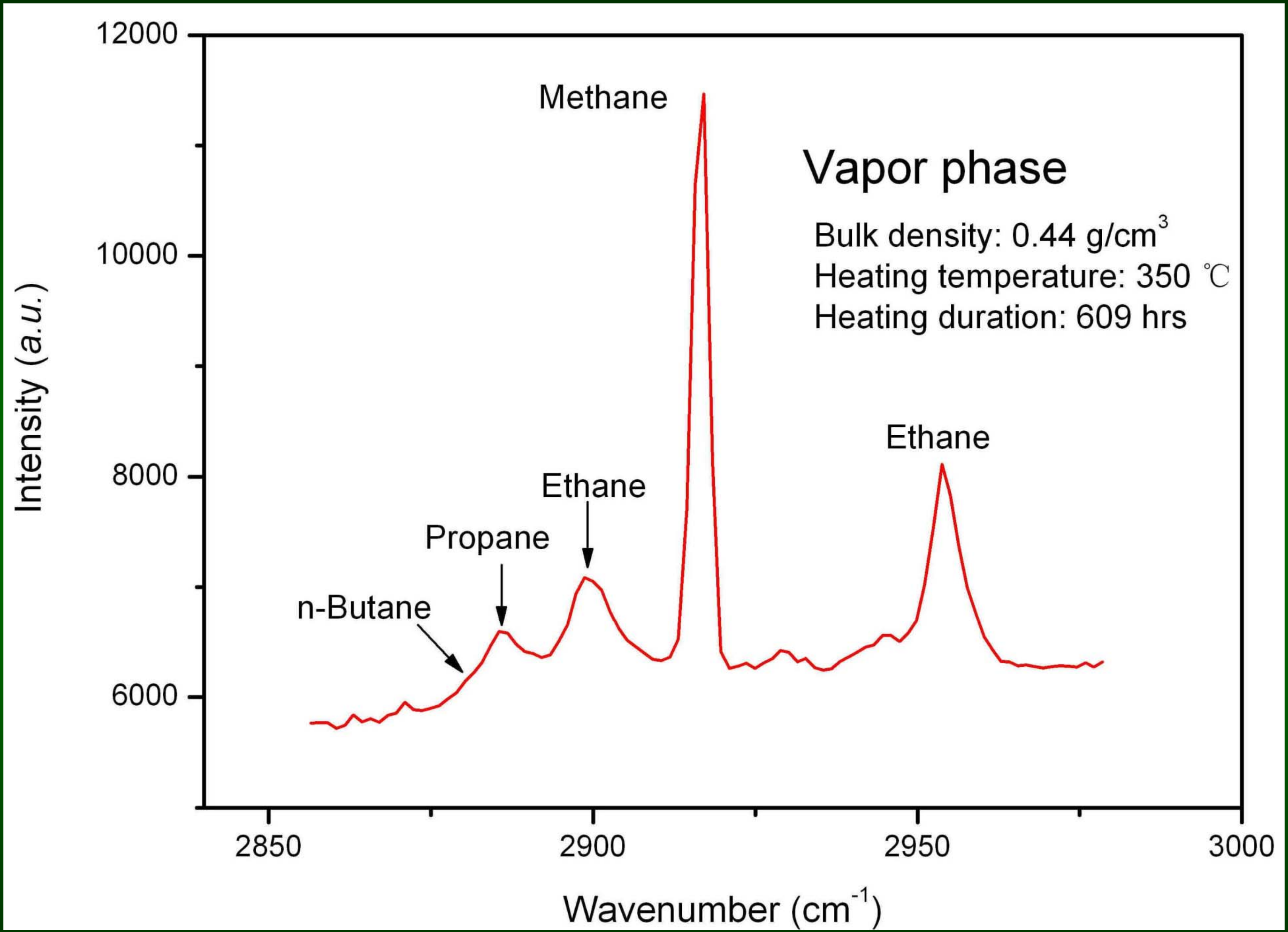




Methane hydrate
at 22°C
~ 40 MPa

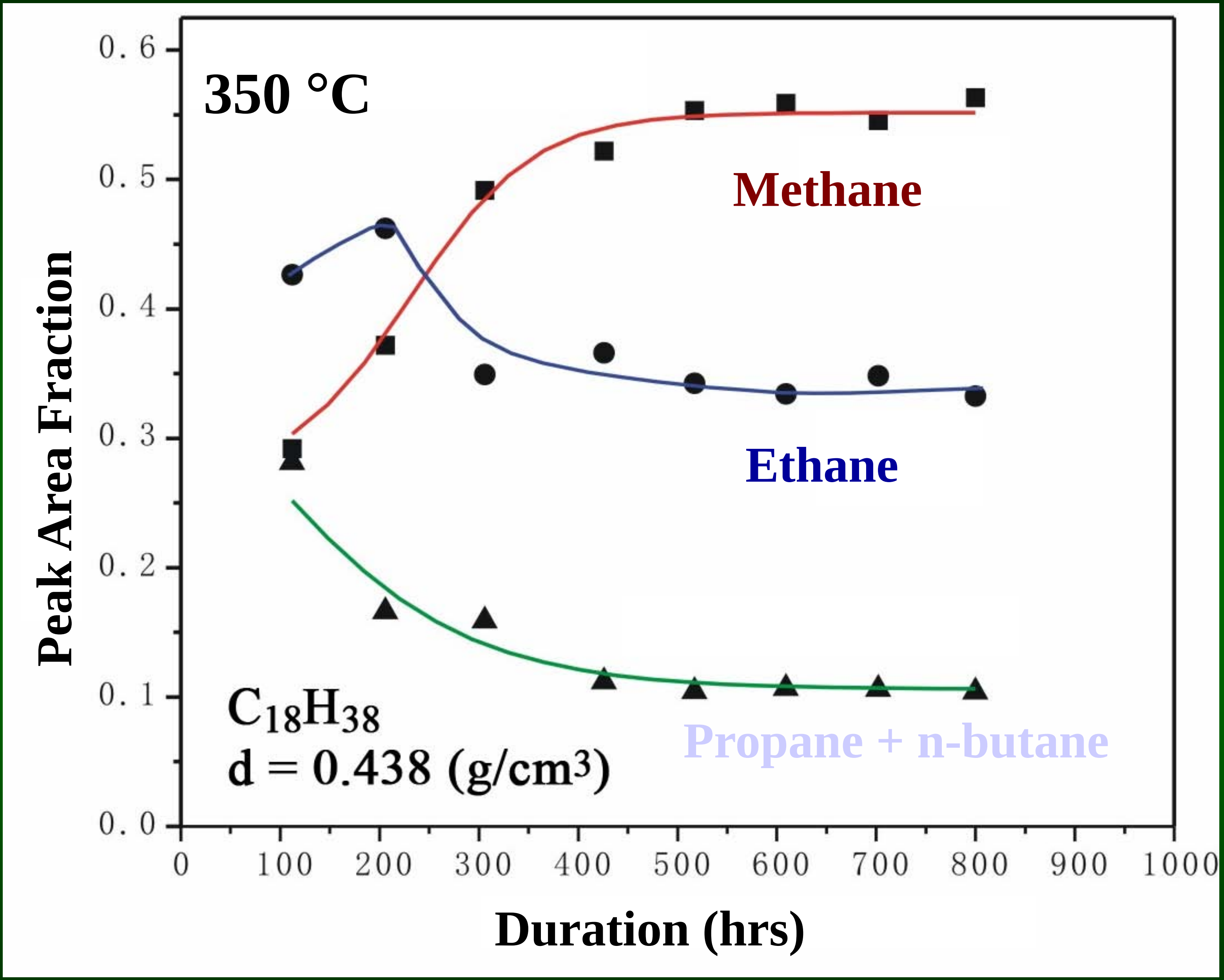
Cracking of octadecane ($C_{18}H_{38}$) with various densities at 350, 375, and 400 ℃





Intensity (a.u.)
12000
10000
8000
6000
2850
2900
2950
3000
Wavenumber (cm-1)
Methane
Vapor phase
Bulk density: 0.44 g/cm3
Heating temperature: 350 ℃
Heating duration: 609 hrs
Ethane
Ethane
Propane
n-Butane

USGS


350 °C
Methane
Ethane
Propane + n-butane
$C_{18}H_{38}$
d = 0.438 (g/cm3)
Peak Area Fraction
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
100
200
300
400
500
600
700
800
900
1000
Duration (hrs)

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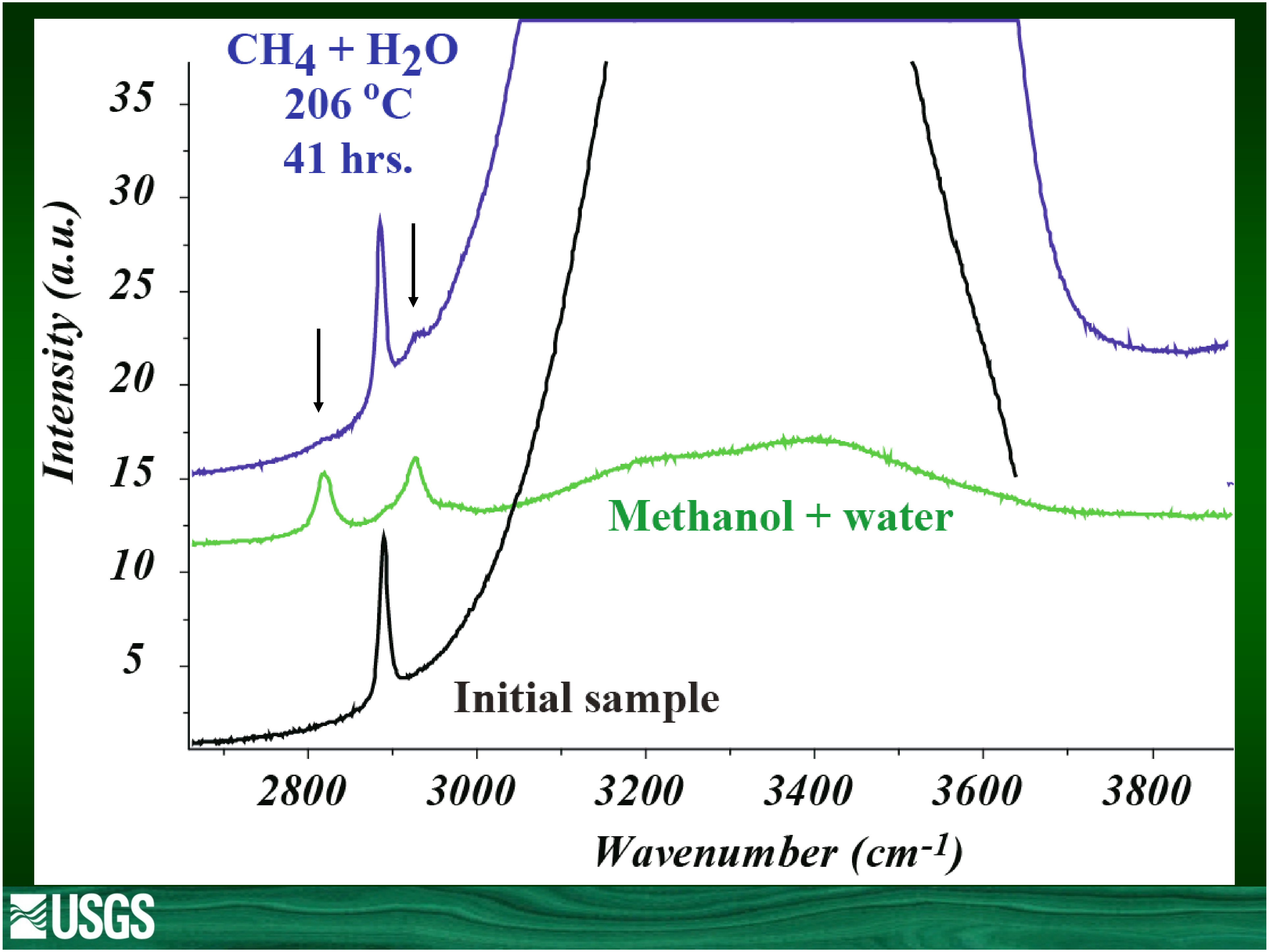
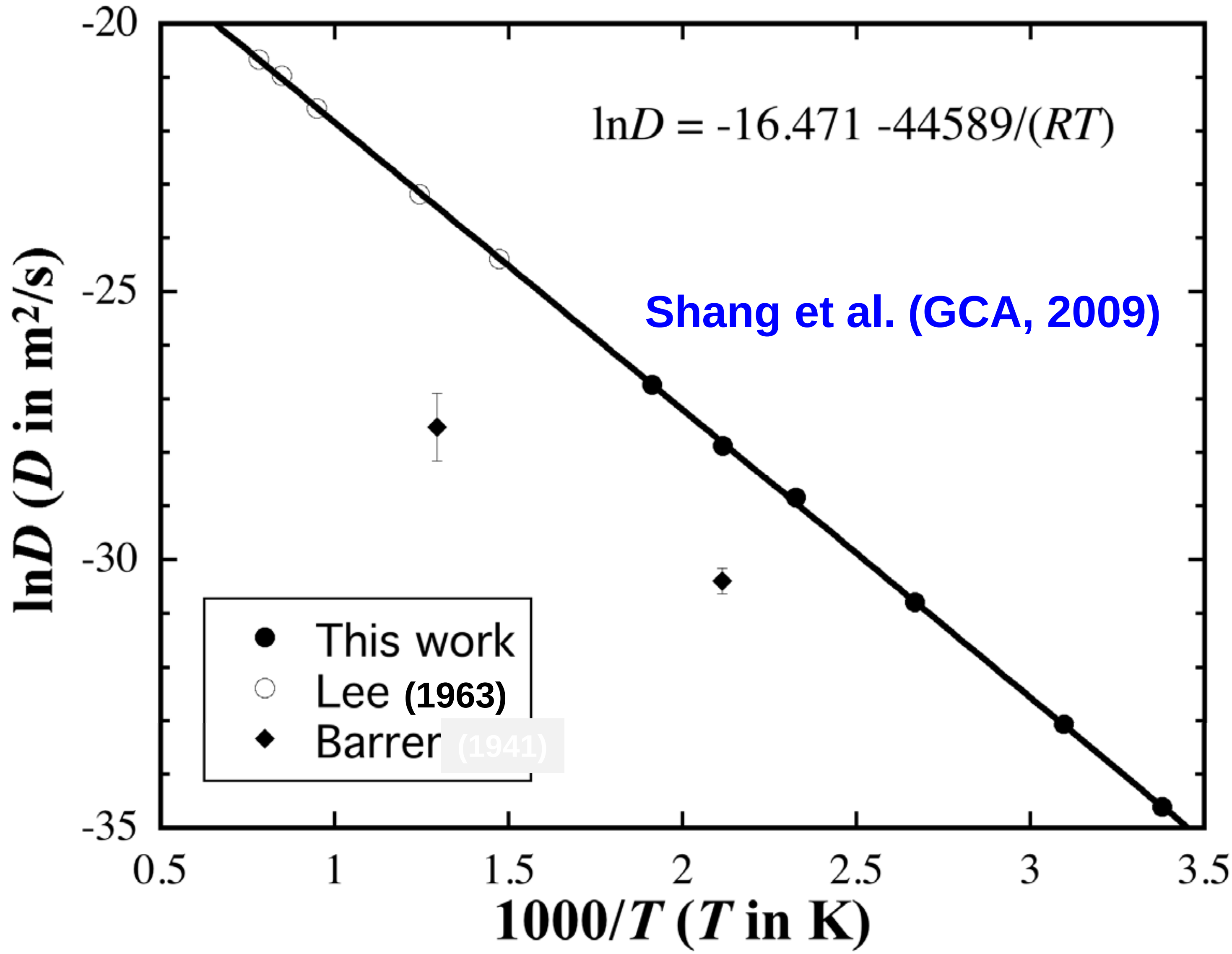
- **Our understanding of the reaction pathways and decomposition of organic compounds in the presence of water is limited.**
- **Raman spectroscopic analysis for the following reactions at 206 ˚C for 41 hours:**
  - $CH_4 + H_2O = CH_3OH + H_2$
  - $C_2H_6 + H_2O = C_2H_5OH + H_2$
  - $C_2H_6 + 2\ H_2O = CH_3CO_2H + 3\ H_2$

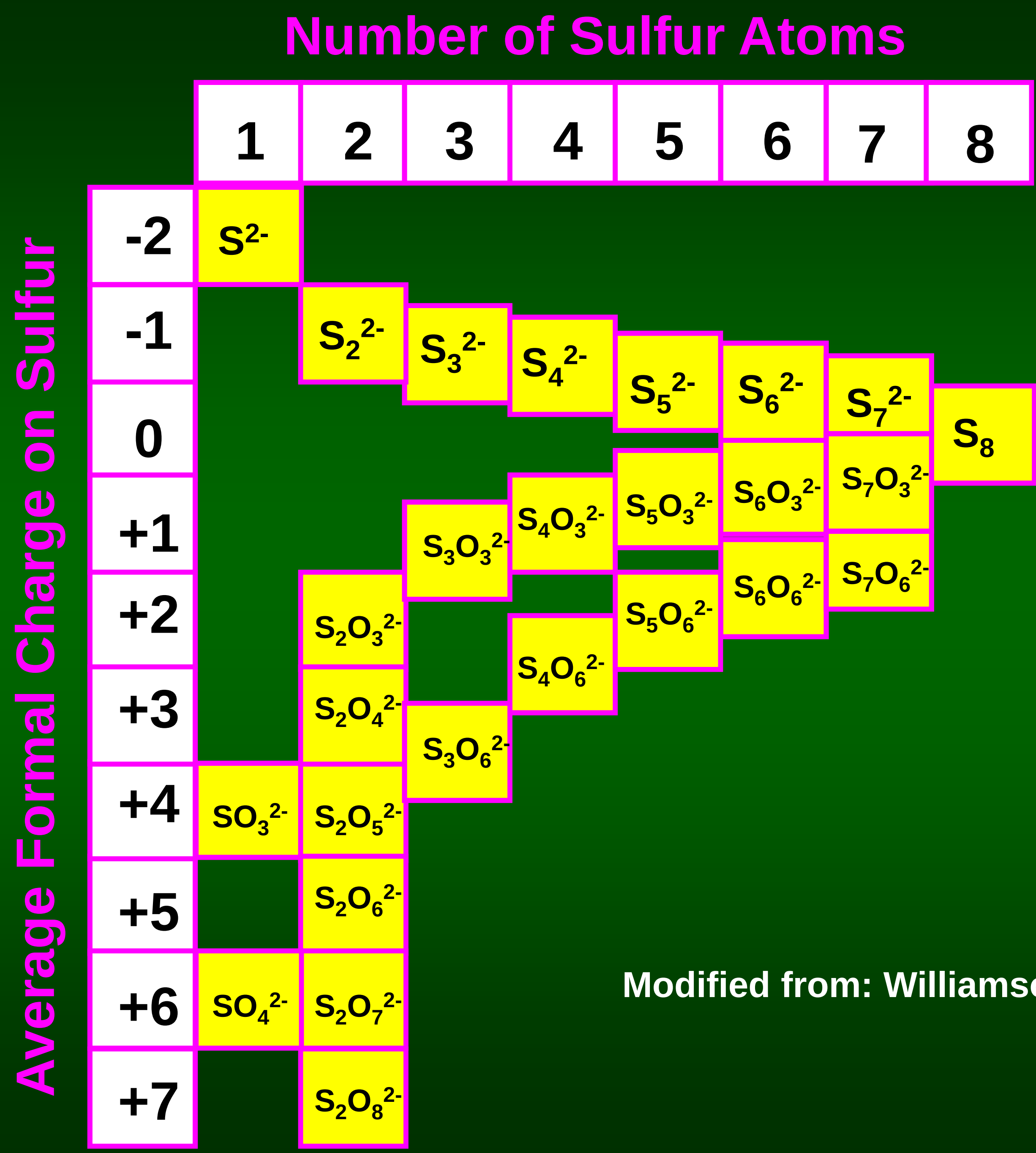
USGS



CH4 + H2O
206 °C
41 hrs.
Methanol + water
Initial sample
Intensity (a.u.)
Wavenumber (cm-1)
5
10
15
20
25
30
35
2800
3000
3200
3400
3600
3800
USGS

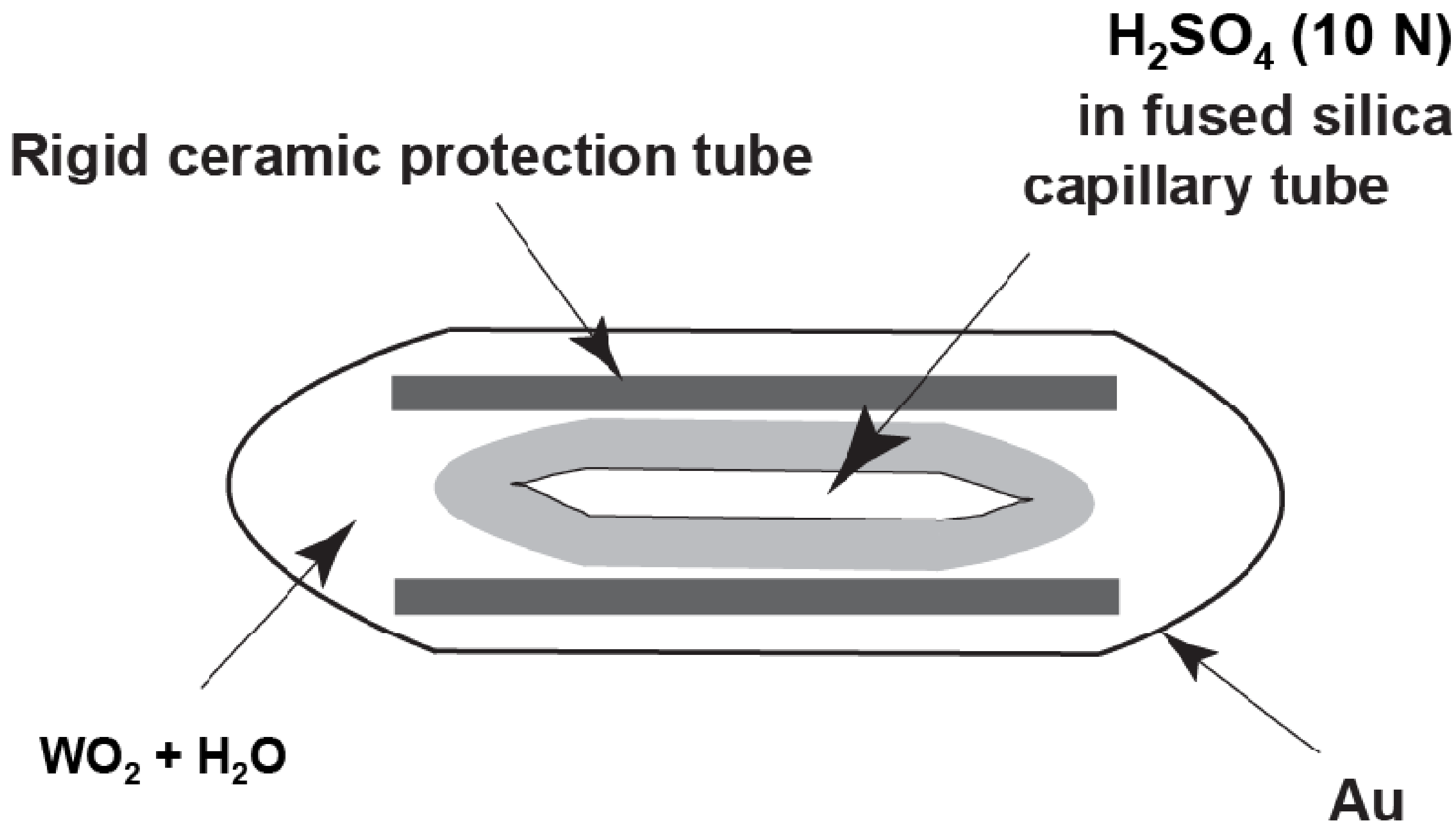


lnD = -16.471 -44589/(RT)
Shang et al. (GCA, 2009)
This work
Lee (1963)
Barrer (1941)
-20
-25
-30
-35
0.5
1
1.5
2
2.5
3
3.5
lnD (D in m²/s)
1000/T (T in K)

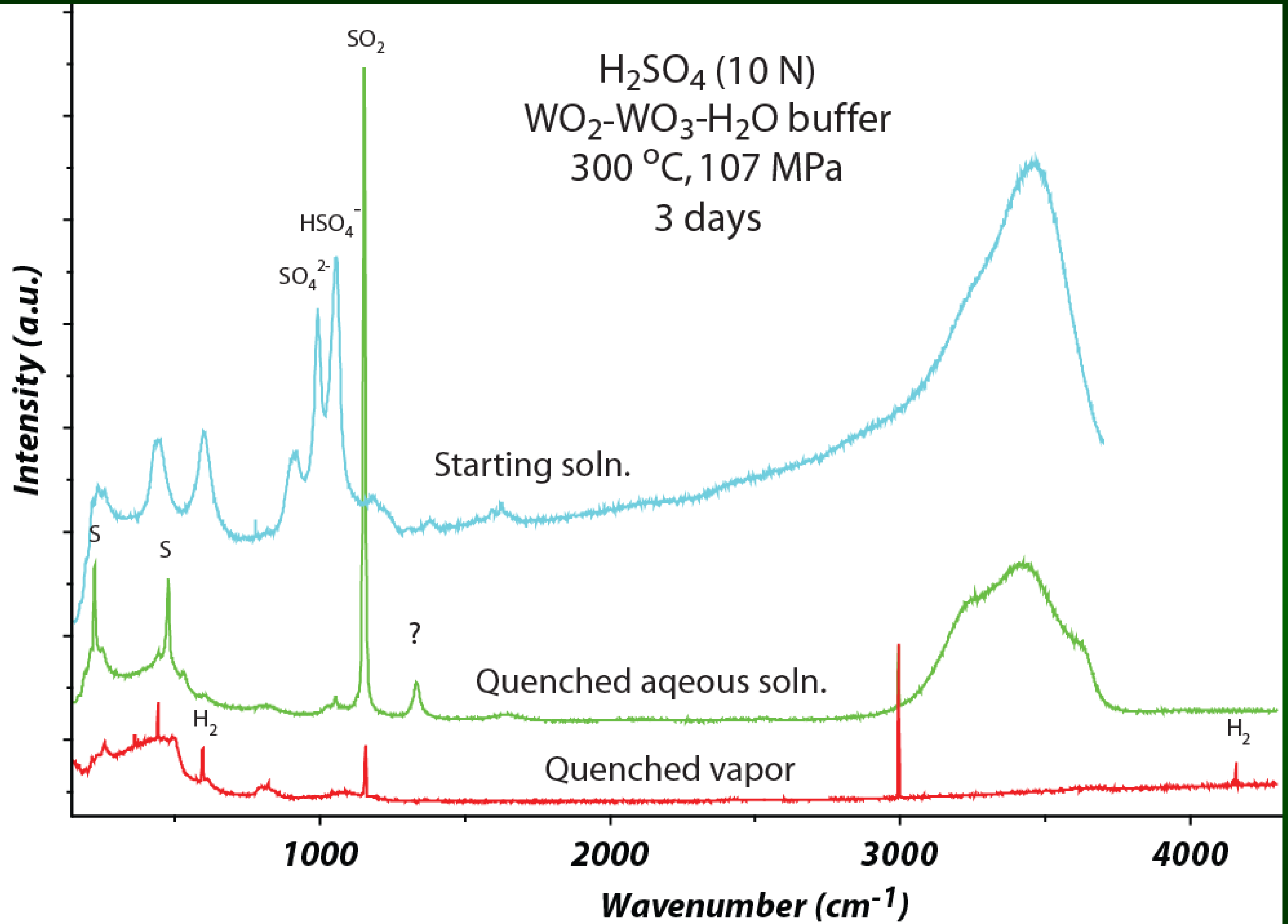


Modified from: Williamson & Rimstidt (1992)

TSR by H_2

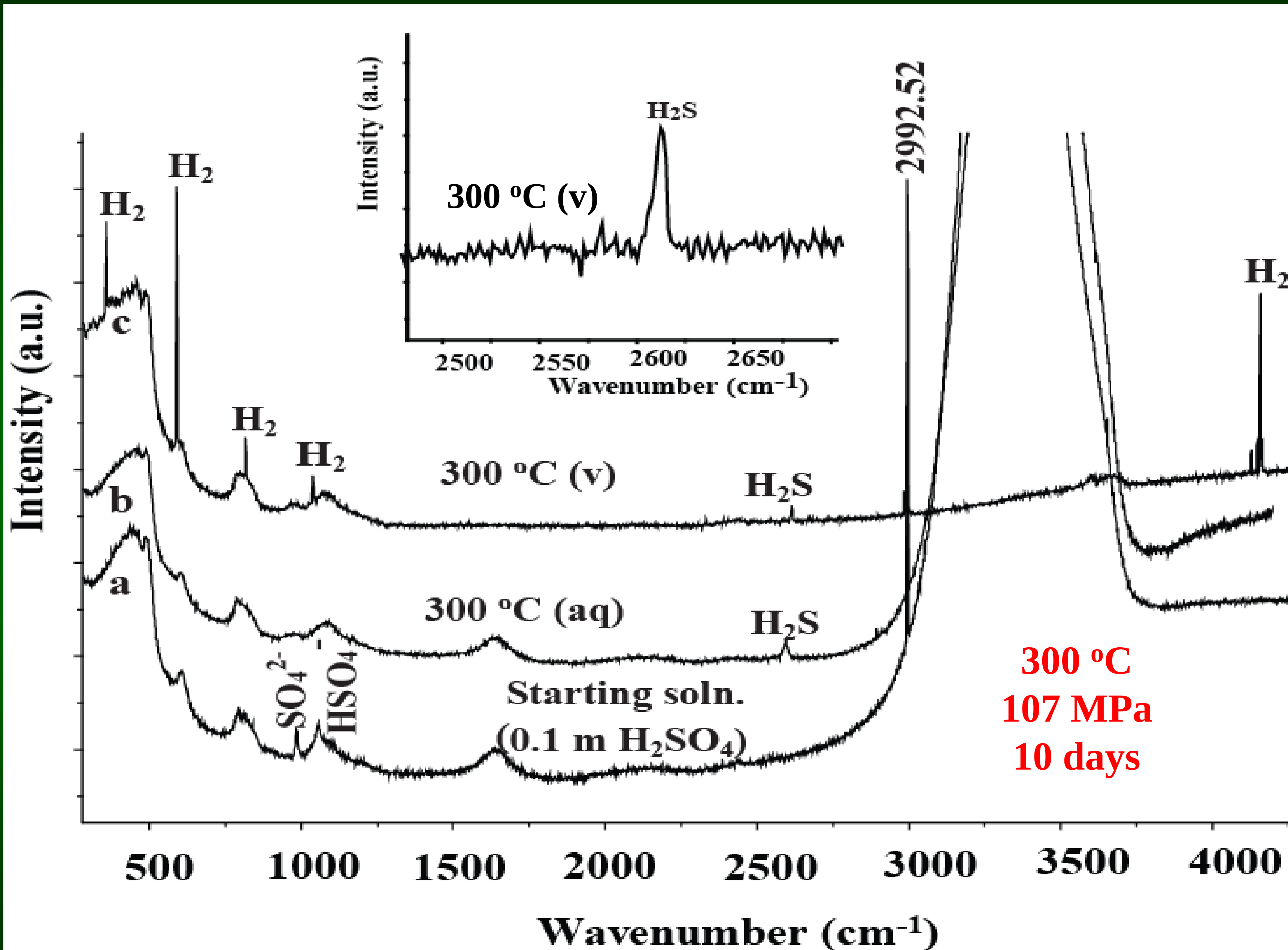


$$WO_2 + H_2O \rightarrow WO_3 + H_2$$



H_2SO_4 (10 N)
WO_2-WO_3-H_2O buffer
300 °C, 107 MPa
3 days
SO_2
HSO_4^-
SO_4^{2-}
Starting soln.
S
S
?
Quenched aqeous soln.
H_2
H_2
Quenched vapor
Intensity (a.u.)
1000
2000
3000
4000
Wavenumber (cm^{-1})

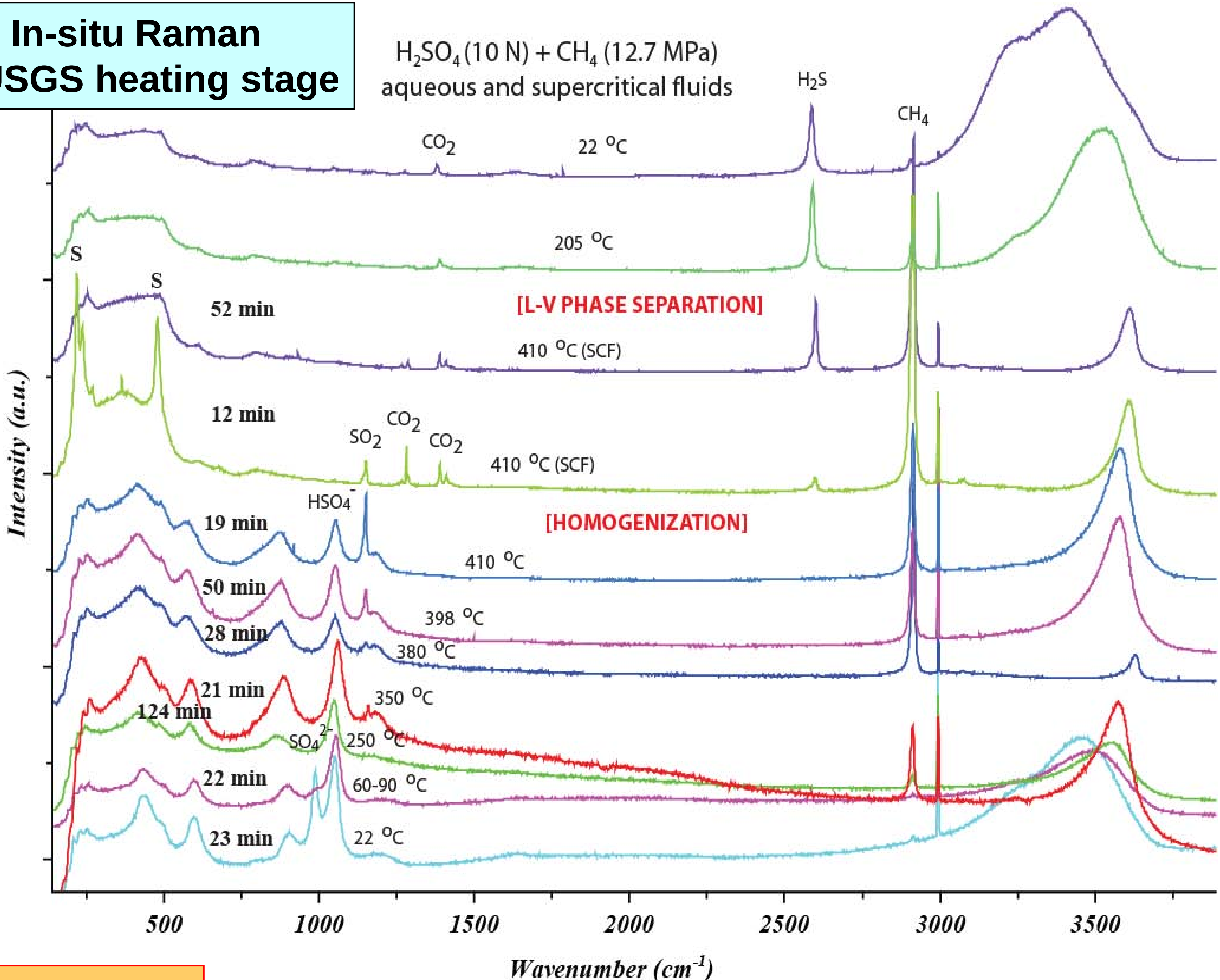
USGS



Intensity (a.u.)
H2
H2
c
b
a
H2
H2
300 °C (v)
H2S
300 °C (aq)
H2S
SO4 2-
HSO4 -
Starting soln.
(0.1 m H2SO4)
2992.52
H2
Intensity (a.u.)
H2S
300 °C (v)
2500
2550
2600
2650
Wavenumber (cm-1)
500
1000
1500
2000
2500
3000
3500
4000
Wavenumber (cm-1)
300 °C
107 MPa
10 days

USGS

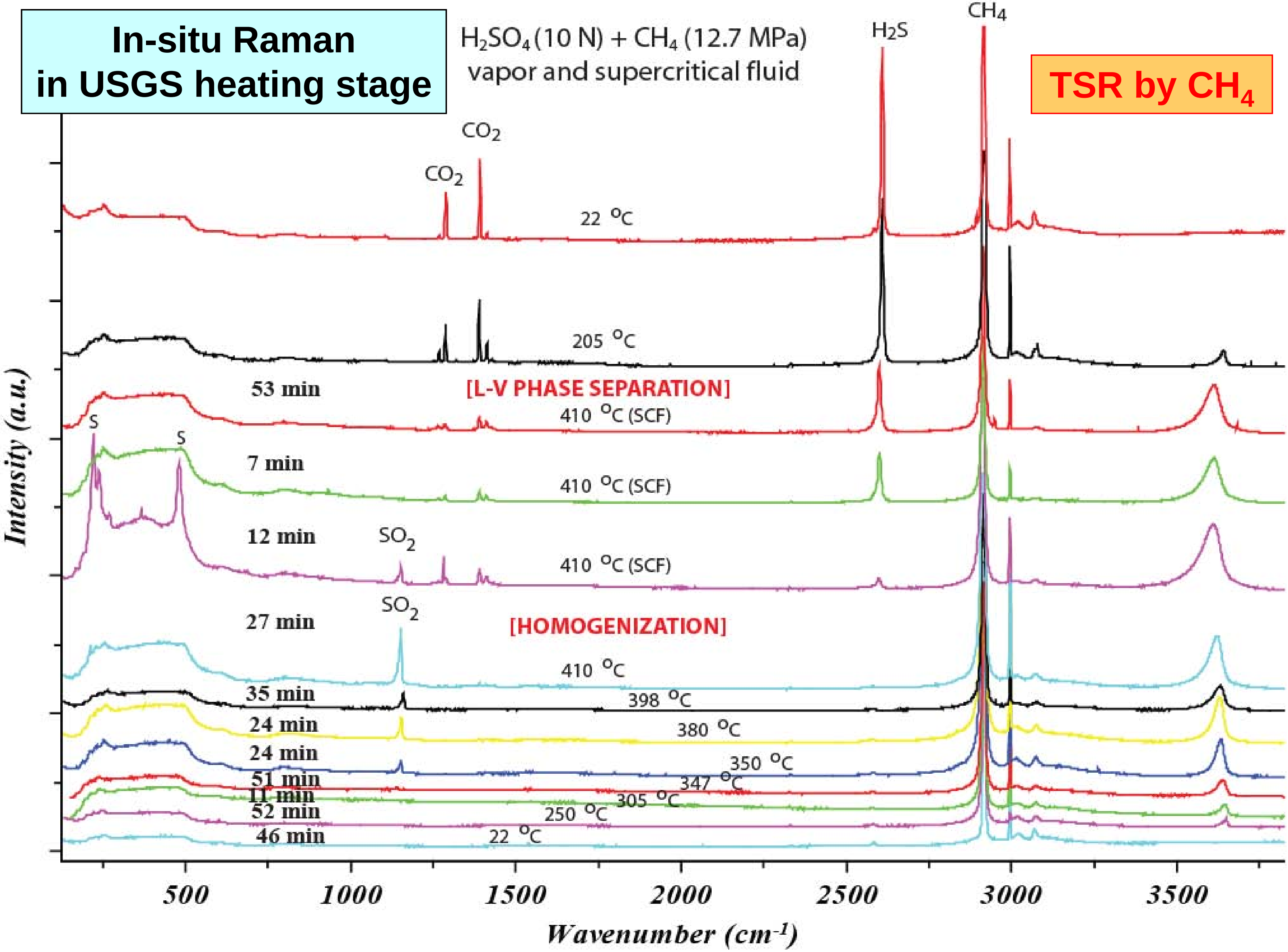
In-situ Raman in USGS heating stage

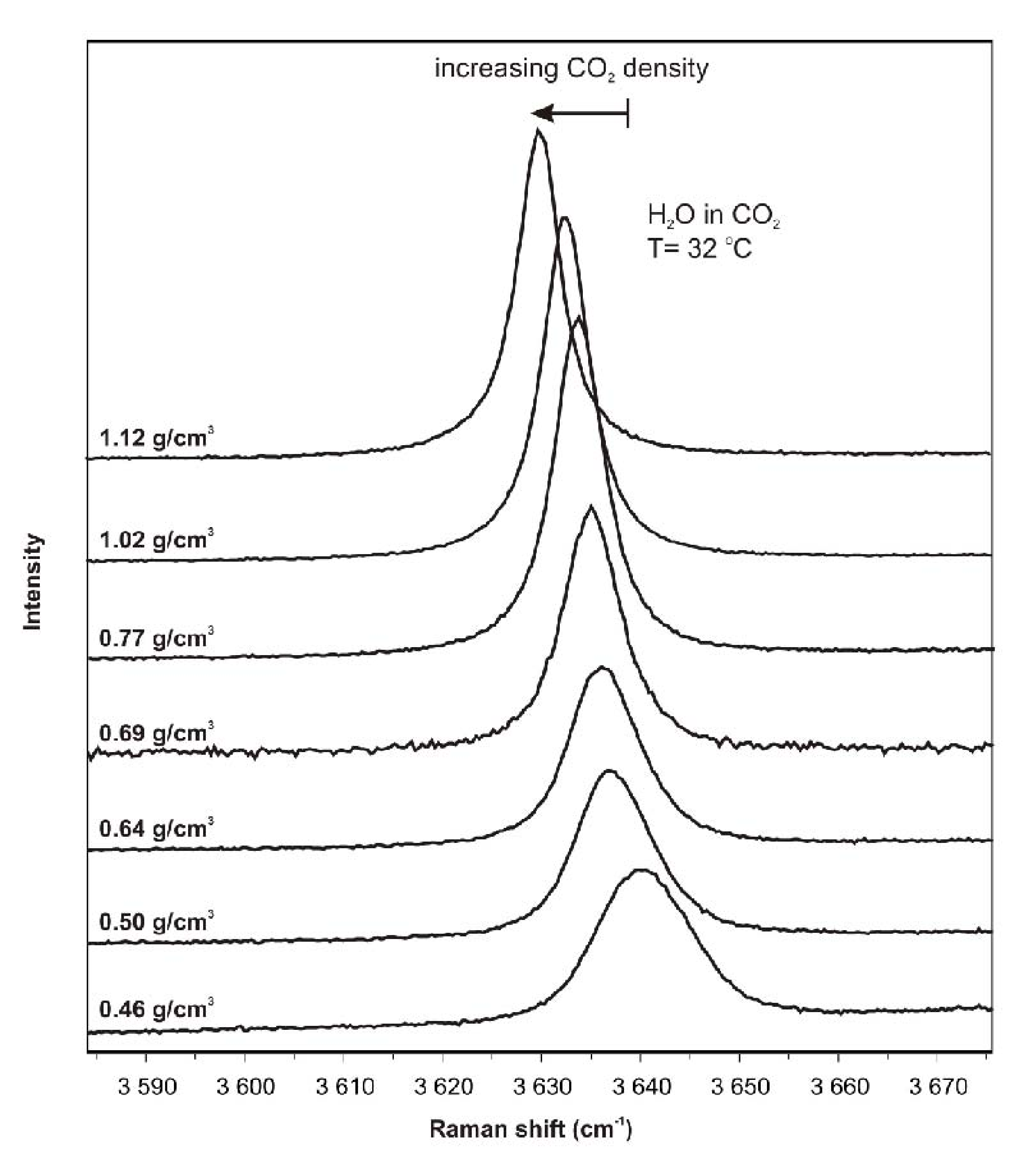


TSR by CH_4

In-situ Raman in USGS heating stage

TSR by CH_4

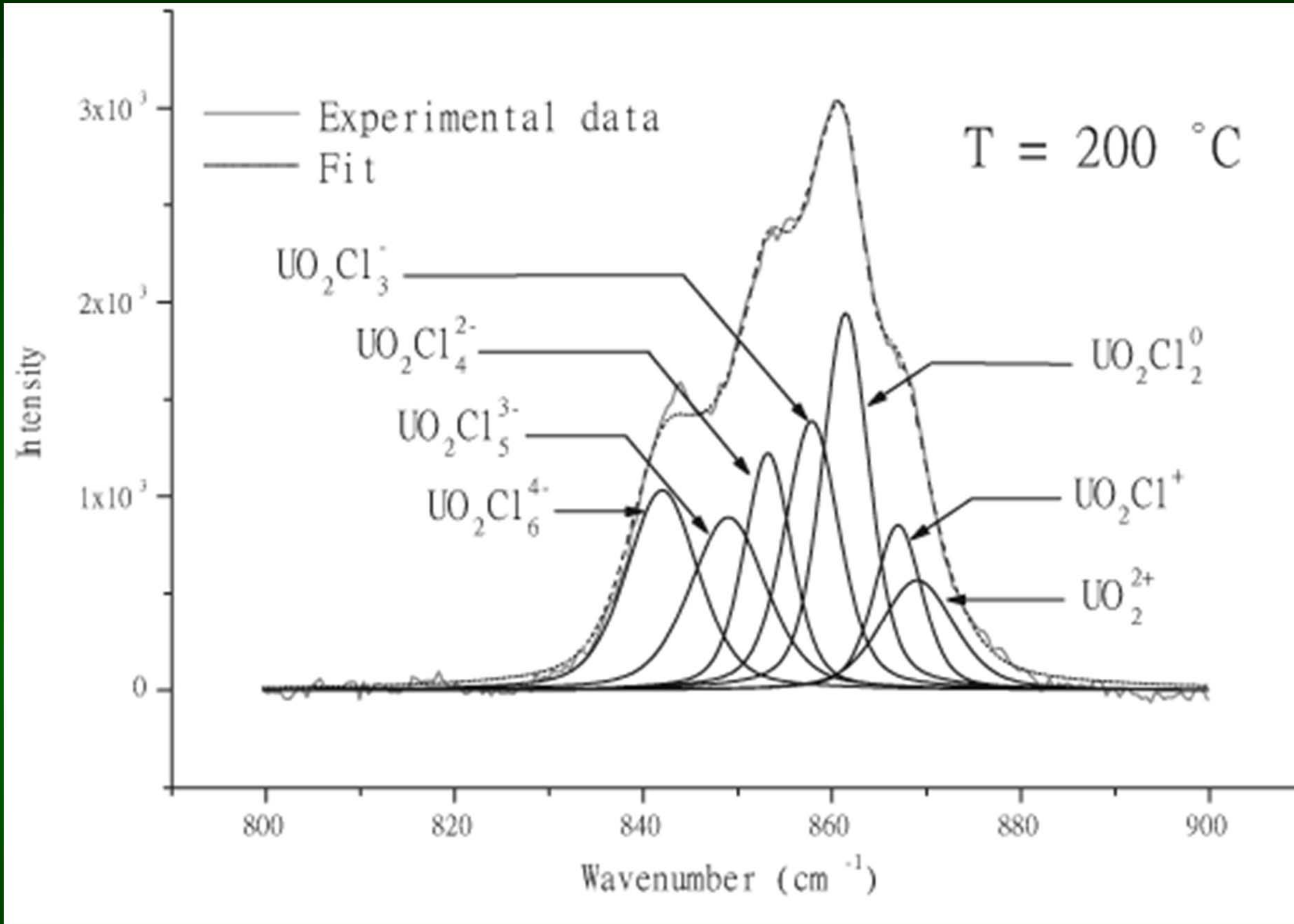




Stretching frenquency of water dissolved in CO_2 at 32 ºC as a function of CO_2 density

Berkesi et al. (2009)

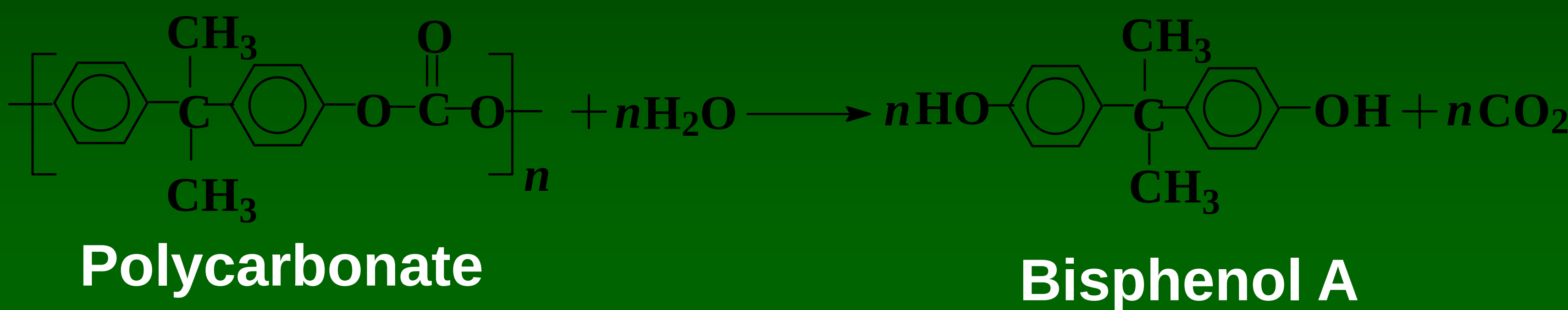
USGS

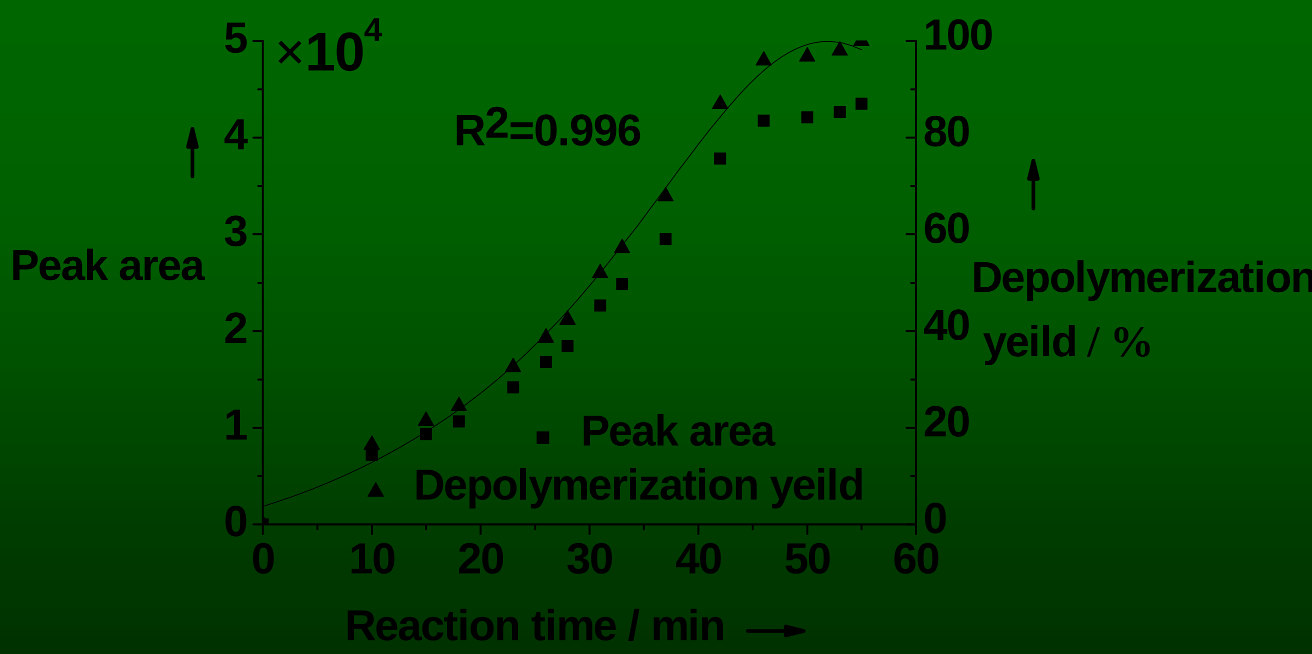


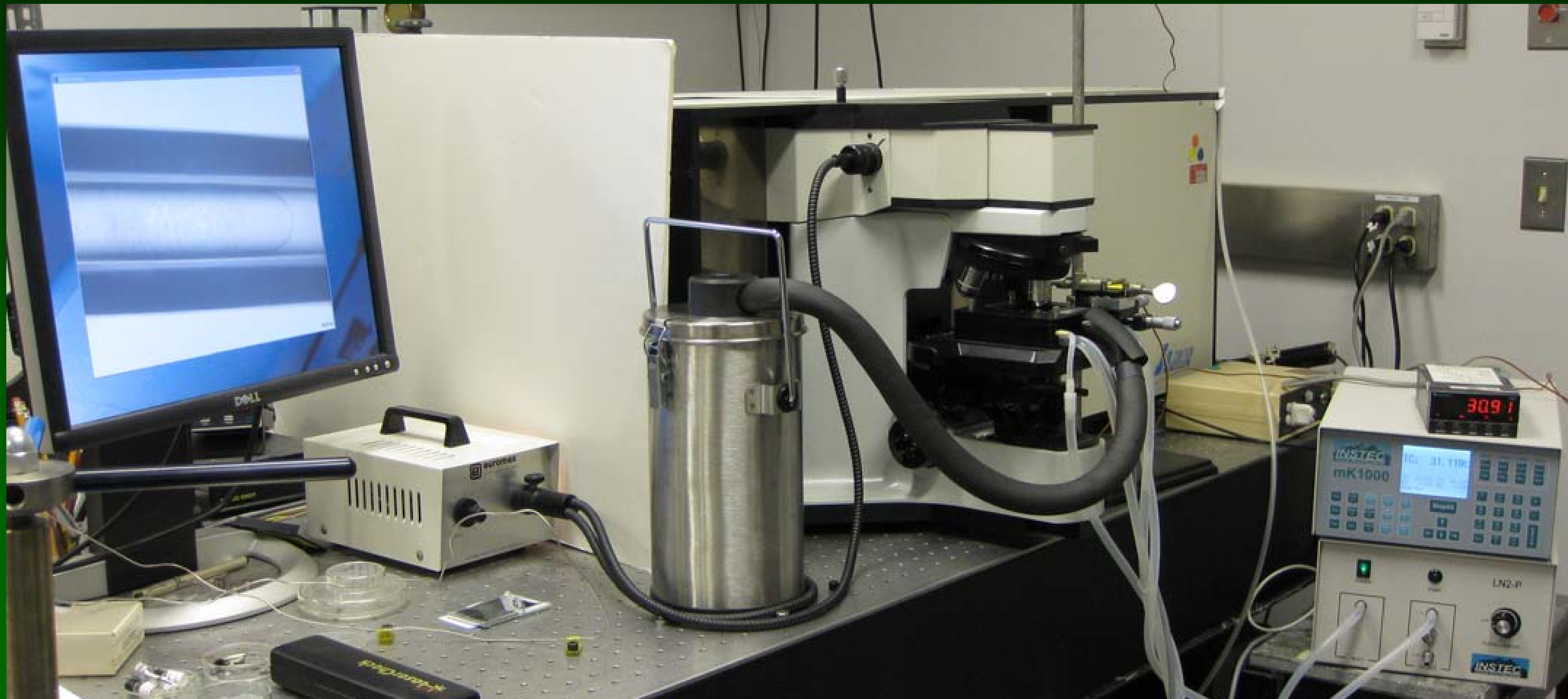
Uranyl chloride complexes in LiCl solution (1.5 molal) at 200 ºC at vapor satrated (Dargent et al., 2012)

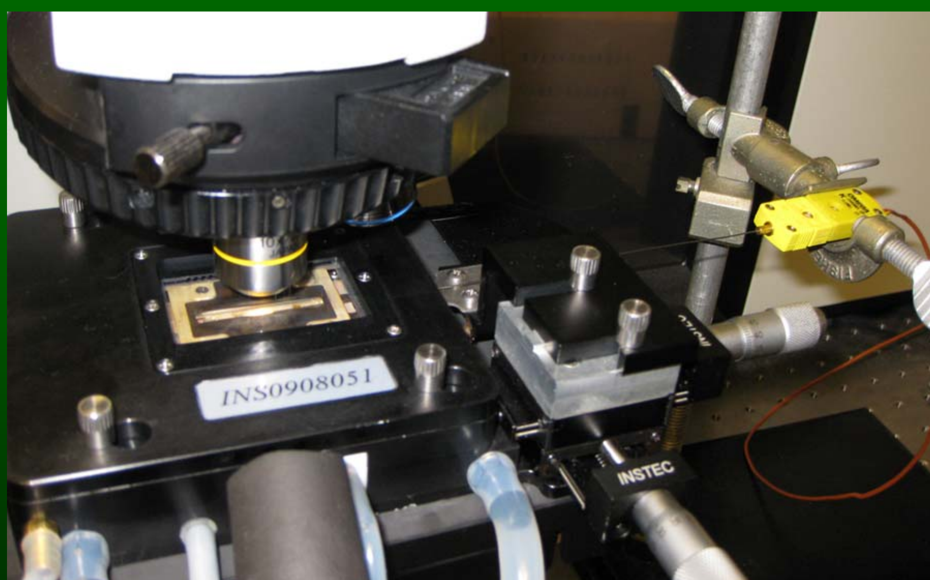
USGS

Hydrolysis of Polycarbonate in sub-critical water (280 ºC)
Pan, Chou & Burruss (Green Chem., 2009)



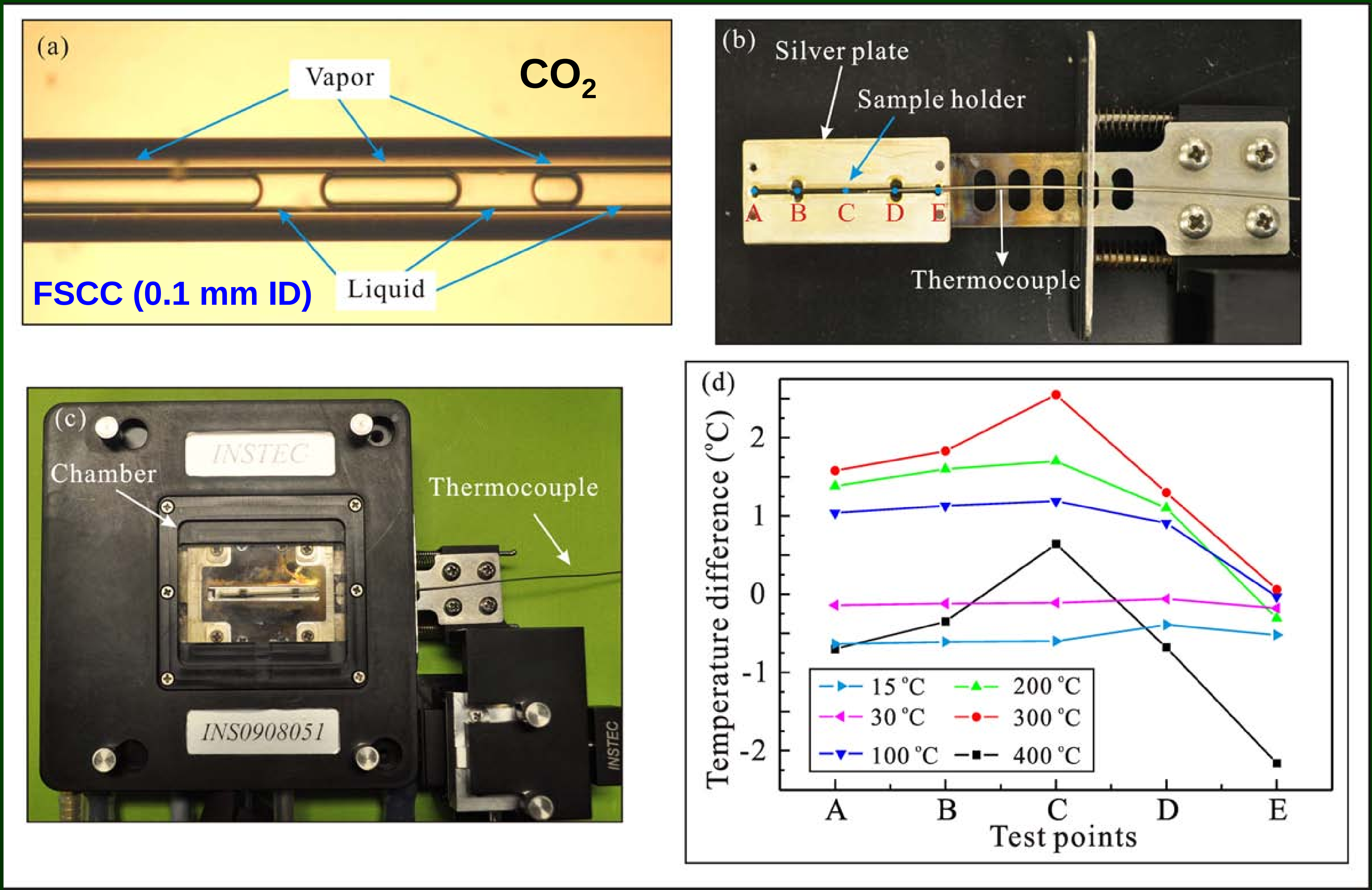



DELL
euromex
INSTEC
mK1000
30.91
LN2-P
INSTEC

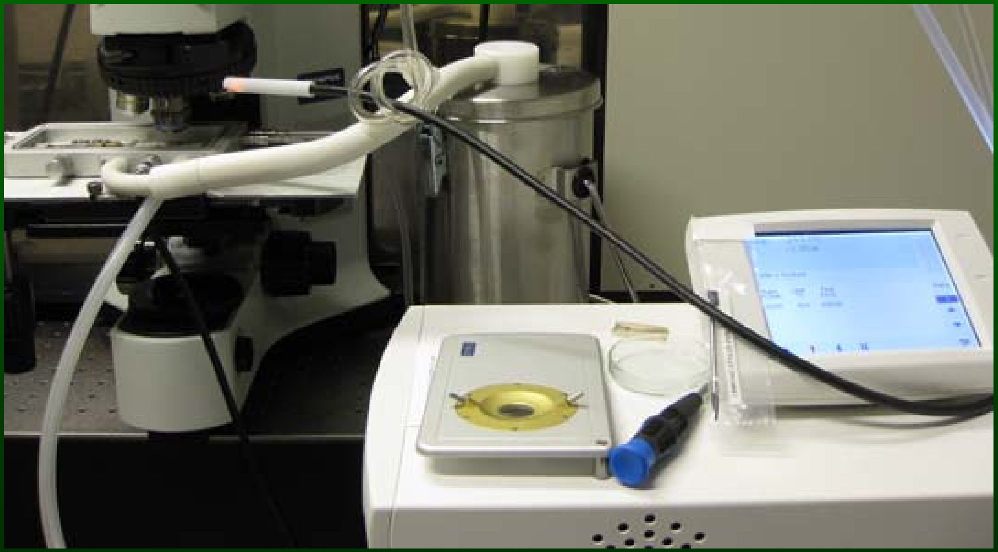

INS0908051
INSTEC

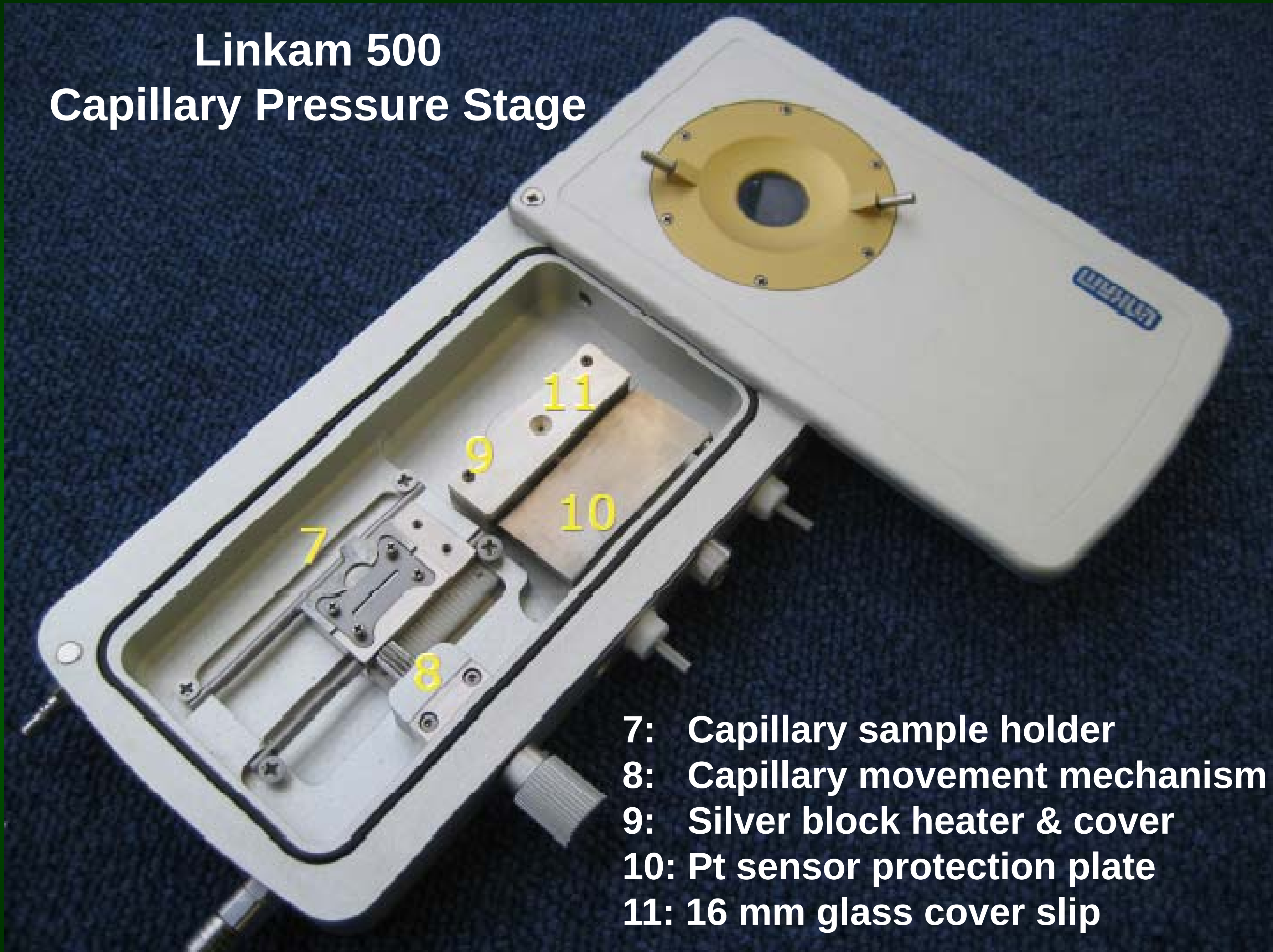

30.38
INSTEC
mK1000
TC: 30.622C
StopAll
POWER
PUMP
LN2-P
PURGE/DEFROST
INLET
INSTEC

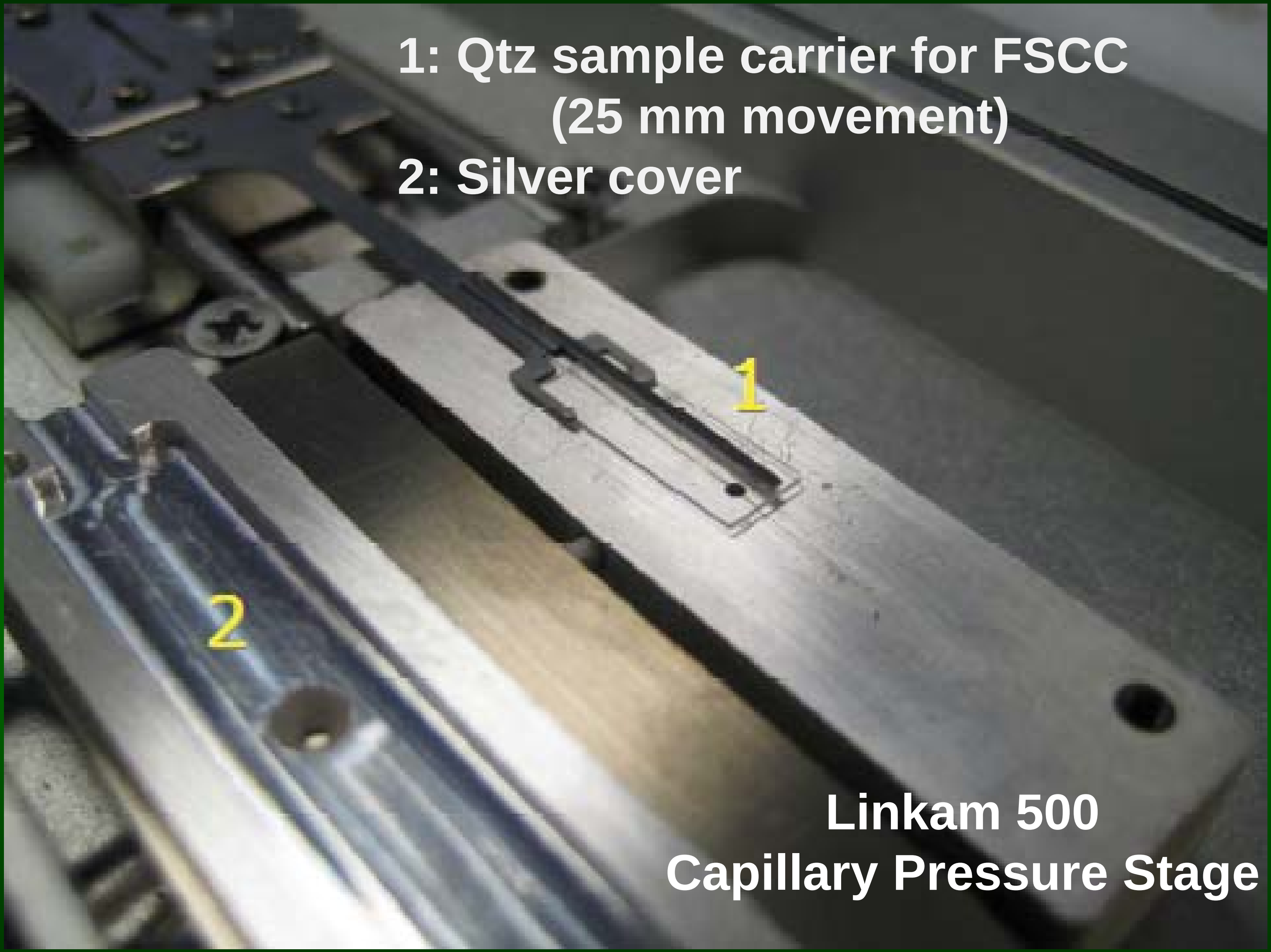
INSTEC Heating-Cooling Stage



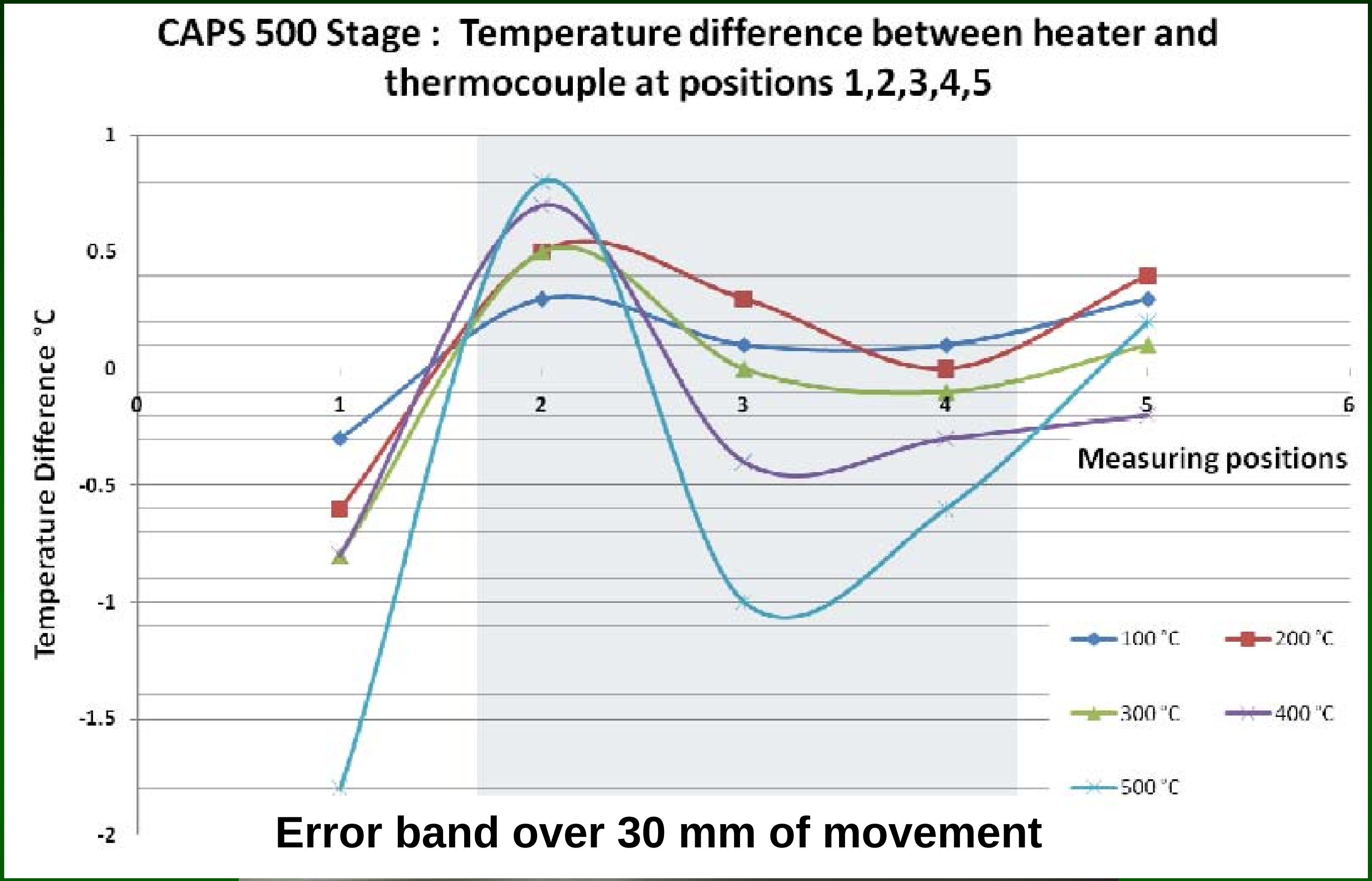

Linkam 500
Capillary Pressure Stage

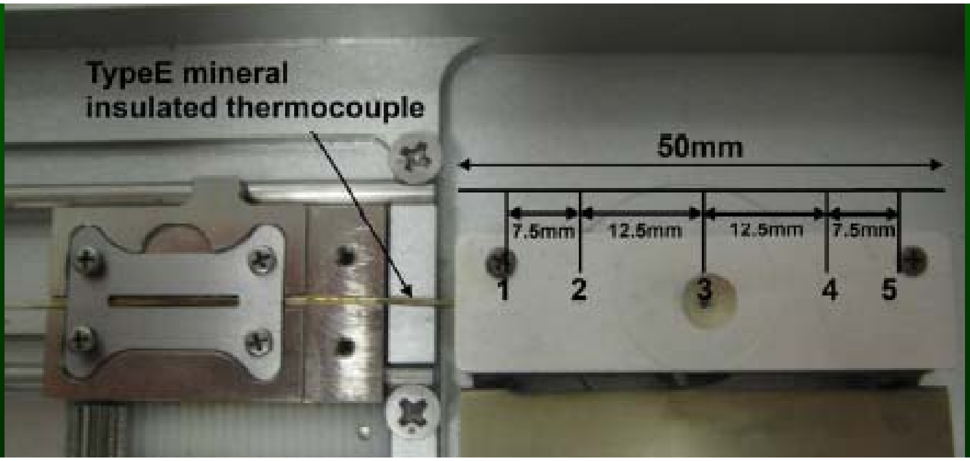



Linkam 500
Capillary Pressure Stage
11
9
10
7
8
linkam
7: Capillary sample holder
8: Capillary movement mechanism
9: Silver block heater & cover
10: Pt sensor protection plate
11: 16 mm glass cover slip


1: Qtz sample carrier for FSCC
(25 mm movement)
2: Silver cover
1
2
Linkam 500
Capillary Pressure Stage

USGS


CAPS 500 Stage : Temperature difference between heater and thermocouple at positions 1,2,3,4,5
Temperature Difference °C
Measuring positions
100 °C
200 °C
300 °C
400 °C
500 °C
Error band over 30 mm of movement


TypeE mineral insulated thermocouple
50mm
7.5mm
12.5mm
12.5mm
7.5mm
1
2
3
4
5

Summary

- **Optical cells with fused silica windows, such as HPOC and FSCC, were designed for experiments at pressures up to 100 MPa and temperatures up to 600 ºC, such as the *P-T* conditions of sedimentary basins, hydrothermal systems, and low-grade metamorphism.**

- **These types of cells are particularly suitable for the study of organic compounds and also for the systems containing S.**

USGS

Summary

- **When compared with the conventional synthetic fluid inclusion method, in which fluid inclusions were formed by healing fractures in quartz chips at elevated *P-T* conditions, the new FSCC method has the following advantages: (1) simple; (2) large and uniform inclusions can be formed; (3) suitable for the studies of organic material and/or S with/without water, and (5) allowing redox control when needed, especially for TSR experiments.**

- **The HPOC & FSCC have a great potential for studying geologic fluids at various *P-T* conditions, as demonstrated by many examples.**