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

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Reston, Virginia
USA
• 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
Raman study of synthetic subduction-zone fluids (KAlSi$_3$O$_8$-H$_2$O) system

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

Dec. 6, 2006 at USGS

Kenji Mibe
Earthquake Research Institute
University of Tokyo, Japan

SCF: supercritical fluid
F: aqueous fluid
Sa: sanidine
M: hydrous melt
Ms: muscovite
C: corundum
Some minerals in the system:

Sanidine
$\text{KAlSi}_3\text{O}_8$

Muscovite
$\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$

Corundum
$\text{Al}_2\text{O}_3$

$\text{KAlSi}_3\text{O}_8 - \text{H}_2\text{O}$
Mibe, Chou, & Bassett

JGR, 113 (2008)

SCF: supercritical fluid
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M: hydrous melt
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<table>
<thead>
<tr>
<th>Moleculea</th>
<th>Frequency (cm⁻¹)b</th>
<th>Motioni</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₄SiO₄ (Mo)</td>
<td>783 (calc)c, 785 (exp)d, 788 (calc)e</td>
<td>n(Si-O)</td>
</tr>
<tr>
<td>KH₃SiO₄ (Mo)</td>
<td>748 (calc)f</td>
<td>n(Si-O)</td>
</tr>
<tr>
<td>H₆Si₂O₇ (D)</td>
<td>620 (calc)e, 631 (calc)c, 638 (calc)g</td>
<td>n(Si-O), d(Si-O-Si)</td>
</tr>
<tr>
<td>H₆SiAlO₇¹⁻ (D)</td>
<td>585 (calc)g</td>
<td>n(Tk-O), d(Si-O-Al)</td>
</tr>
<tr>
<td>H₄SiAlO₇³⁻ (D)</td>
<td>574 (exp)d</td>
<td>n(T-O), d(Si-O-Al)</td>
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<tr>
<td>H₆Si₃O₉ (3R)</td>
<td>629 (calc)e</td>
<td>n(Si-O-Si)</td>
</tr>
<tr>
<td>H₆Si₂AlO₉¹⁻ (3R)</td>
<td>574 (calc)h</td>
<td>n(T-O-T)</td>
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<tr>
<td>H₈Si₄O₁₂ (4R)</td>
<td>490 (calc)h</td>
<td>n(Si-O-Si)</td>
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<tr>
<td>H₈Si₃AlO₁₂¹⁻ (4R)</td>
<td>488 (calc)h</td>
<td>n(T-O-T)</td>
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<tr>
<td>Al(OH)₄¹⁻</td>
<td>616 (calc)i, 620 (exp)d</td>
<td>n(Al-O)</td>
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<tr>
<td>KAl(OH)₄</td>
<td>619 (calc)f</td>
<td>n(Al-O)</td>
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<tr>
<td>KH₂AlO₃</td>
<td>691 (calc)f</td>
<td>n(Al-O)</td>
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<tr>
<td>Al(OH)₃H₂O</td>
<td>438 (calc)i</td>
<td>n(Al-OH₂)</td>
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<tr>
<td>KOH</td>
<td>361 (calc)f</td>
<td>d(K-O-H)</td>
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</table>
Jan. 16, 2008
at USGS

Wanjun Lu
China Univ. of Geosci.

Zhiyan Pan
Zhejiang Univ. of Tech.

Xiaochun Xu
Hefei Univ. of Tech.
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 °C) and time (days and weeks).
Lin (2005)

- Synthesized CH$_4$-H$_2$O fluid inclusions in quartz in Pt capsules at 300 to 700 $^\circ$C and 1, 3, and 5 kbars
- $\text{Al}_4\text{C}_3 + 12 \text{H}_2\text{O} = 3 \text{CH}_4 + 4 \text{Al(OH)}_3$
- All inclusions formed at and above 600 $^\circ$C contain CO$_2$
- $\text{CH}_4 + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$
Fused Silica Capillary Tube

Round-sectioned tube

Square-sectioned tube

Polymicro Technologies, LLC
(www.polymicro.com).
HPOC
Chou et al. (2005)
G-1  Low-P gauge
G-2  High-P gauge
S-1 & S-2  Syringes
1 to 16  Pressure valves
C   Capillary tubing
T-1  Sample fluid tank
T-2  High pressure fluid tank
PG  Pressure generator
L   Laser beam (downward)
     Raman scattered light (upward)
Raman Spectra for CH$_4$ in Different Phases

- Dissolved CH$_4$ (31.7 MPa)
- Gas phase @ 3.4 MPa
- CH$_4$ sI Hydrate

Wavenumbers (cm$^{-1}$):
- 2904.8 cm$^{-1}$
- 2911.3 cm$^{-1}$
- 2915 cm$^{-1}$
- 2917.3 cm$^{-1}$

Intensity (a.u.)

Large cage vs. Small cage
\[ n_o = \text{p.p. near } 0 \text{ P} \]
\[ n = \text{p.p. at high } P \]

\[ P (\text{MPa}) = -0.0148 D^5 - 0.1791 D^4 - 0.8479 D^3 - 1.765 D^2 - 5.876 D \]

Lu, Chou, Burruss, Song
GCA (2007)

\[ P (\text{MPa}) = -0.0148 D^5 - 0.1791 D^4 - 0.8479 D^3 - 1.765 D^2 - 5.876 D \]
What Are Gas Hydrates?

<table>
<thead>
<tr>
<th>Cavity Types</th>
<th>Hydrate Structure</th>
<th>‘Guest’ Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>5₁²6²</td>
<td>Structure I</td>
<td>Methane, Ethane, Carbon dioxide, etc.</td>
</tr>
<tr>
<td>5₁²6⁴</td>
<td>Structure II</td>
<td>Propane, Iso-butane, etc.</td>
</tr>
<tr>
<td>4³5⁶6³</td>
<td>Structure H</td>
<td>Methane + Neohexane, Methane + Cycloheptane, etc.</td>
</tr>
<tr>
<td>5₁²6⁸</td>
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</tbody>
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<th>Cavity Types</th>
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<tr>
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<tr>
<td>46 H₂O</td>
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<tr>
<td>136 H₂O</td>
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<td></td>
</tr>
<tr>
<td>34 H₂O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ [X(CH_4)] = 1.0563 \ [A(CH_4)/aq/A(H_2O)] \]

Lu, Chou, Burruss, Yang (2006)
Applied Spectroscopy
115 minutes after being pressurized by CH$_4$ at 24.47 MPa

$[X(\text{CH}_4)] = 1.0563 \ [A(\text{CH}_4)_{aq}/A(\text{H}_2\text{O})]$
Lu, Chou, Burruss, & Yang (J. Applied Spectroscopy; 2006)

\[ D = 1.66 \times 10^{-9} \text{ m}^2\text{s}^{-1} \]
Previous studies

- *Servio & Englezos (2002)*
- *Yang et al. (2001)*
- *Kim et al. (2003)*

This study

- *Lu, Chou, Burruss GCA (2008)*

- *Davie et al. (2004)*

**CH$_4$ conc. in equilib. with methane hydrate**

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**Graphical Content:**

- Diagram illustrating pressure, temperature, and depth relationships.
- Sections labeled as 'Water + Hydrate', 'Water + Free Gas', 'Seafloor Temp.', 'Geotherm', 'Base HSZ'.
- Color-coded lines and markers to represent data points and trends.

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**Textual Notes:**

- CH4 concentration in equilibrium with methane hydrate.
- Previous studies and current study contributions.
- USGS logo present.
Lu, Chou, & Burruss
(GCA, 2008)
Growth of methane hydrate in 2 wt% Na$_2$SO$_4$ aqueous solution near room temperature

T dropped from ~23°C to ~22°C in one hour
Sample loading system for a capillary capsule

CH\textsubscript{4} tank

\text{Immersed in liquid N}_2

Vacuum line

CH\textsubscript{4} \quad H\textsubscript{2}O
Methane Hydrate

Smackover Oil

CO$_2$-H$_2$O

Room T
(50 μm ID)

H$_2$O  CO$_2$ (L)  CO$_2$ (V)
Methane hydrate

at 22°C

~ 40 MPa

Chou, Song, Burruss (GCA, 2008)

Ethane Hydrate at 22°C

~ 80 MPa

Morita et al. (2000)

Intensity (arbitrary units)

Wavenumber (cm⁻¹)

Methane hydrate at 22°C

~ 40 MPa
Cracking of octadecane (C_{18}H_{38}) with various densities at 350, 375, and 400 °C
Vapor phase

Bulk density: 0.44 g/cm$^3$
Heating temperature: 350 °C
Heating duration: 609 hrs

Intensities (a.u.)

Wavenumber (cm$^{-1}$)
Methane

Ethane

Propane + n-butane

$\text{C}_{18}\text{H}_{38}$

d = 0.438 (g/cm$^3$)

$350 \, ^\circ\text{C}$

Peak Area Fraction

Duration (hrs)
• 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:

\[- \text{CH}_4 + \text{H}_2\text{O} = \text{CH}_3\text{OH} + \text{H}_2 \]
\[- \text{C}_2\text{H}_6 + \text{H}_2\text{O} = \text{C}_2\text{H}_5\text{OH} + \text{H}_2 \]
\[- \text{C}_2\text{H}_6 + 2 \text{H}_2\text{O} = \text{CH}_3\text{CO}_2\text{H} + 3 \text{H}_2 \]
CH\textsubscript{4} + H\textsubscript{2}O
206 °C
41 hrs.

Intensity (a.u.)

Methanol + water

Initial sample

Wavenumber (cm\textsuperscript{-1})
\[
\ln D = -16.471 - 44589/(RT)
\]

Shang et al. (GCA, 2009)
Modified from: Williamson & Rimstidt (1992)

Number of Sulfur Atoms

1  2  3  4  5  6  7  8

Average Formal Charge on Sulfur

-2  S^{2-}  
-1  S_{2}^{2-}  S_{3}^{2-}  S_{4}^{2-}  S_{5}^{2-}  S_{6}^{2-}  S_{7}^{2-}  S_{8}^{2-}  
0   
+1  S_{3}O_{3}^{2-}  S_{4}O_{3}^{2-}  S_{5}O_{3}^{2-}  S_{6}O_{3}^{2-}  S_{7}O_{3}^{2-}  
+2  S_{3}O_{4}^{2-}  S_{4}O_{4}^{2-}  S_{5}O_{4}^{2-}  S_{6}O_{4}^{2-}  S_{7}O_{4}^{2-}  
+3  S_{4}O_{5}^{2-}  S_{5}O_{5}^{2-}  S_{6}O_{5}^{2-}  S_{7}O_{5}^{2-}  
+4  S_{5}O_{6}^{2-}  S_{6}O_{6}^{2-}  S_{7}O_{6}^{2-}  
+5  S_{6}O_{7}^{2-}  S_{7}O_{7}^{2-}  
+6  S_{7}O_{8}^{2-}  
+7  S_{8}O^{2-}  

Rigid ceramic protection tube

\[ \text{H}_2\text{SO}_4 \ (10 \text{ N}) \] in fused silica capillary tube

\[ \text{WO}_2 + \text{H}_2\text{O} \rightarrow \text{WO}_3 + \text{H}_2 \]
H$_2$SO$_4$ (10 N)
WO$_2$-WO$_3$-H$_2$O buffer
300 °C, 107 MPa
3 days

Starting soln.

Quenched aqueous soln.

Quenched vapor

USGS
300°C
107 MPa
10 days

SO₄²⁻, HSO₄⁻

Starting soln.
(0.1 m H₂SO₄)

300°C (v)

300°C (aq)

H₂S

H₂S

2992.52
In-situ Raman in USGS heating stage

H$_2$SO$_4$ (10 N) + CH$_4$ (12.7 MPa) aqueous and supercritical fluids

TSR by CH$_4$
In-situ Raman in USGS heating stage

H₂SO₄ (10 N) + CH₄ (12.7 MPa) vapor and supercritical fluid

TSR by CH₄
Stretching frequency of water dissolved in CO$_2$ at 32 °C as a function of CO$_2$ density

Berkesi et al. (2009)
Uranyl chloride complexes in LiCl solution (1.5 molal) at 200 °C at vapor satrated (Dargent et al., 2012)
Hydrolysis of Polycarbonate in sub-critical water (280 °C)
Pan, Chou & Burruss (Green Chem., 2009)

Polycarbonate

\[
\begin{array}{c}
\text{O} \\
\text{CH}_3 \\
\text{C} \\
\text{CH}_3 \\
\hline
\end{array}
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O} \\
\text{H}_2\text{O} \\
\hline
\end{array} \rightarrow \begin{array}{c}
\text{O} \\
\text{CH}_3 \\
\text{C} \\
\text{CH}_3 \\
\hline
\end{array}
\begin{array}{c}
\text{HO} \\
\text{OH} \\
\text{CH}_3 \\
\text{OH} \\
\hline
\end{array} + \begin{array}{c}
\text{CO}_2 \\
\text{n} \\
\hline
\end{array}
\]

Bisphenol A

Depolymerization yield

Peak area

\( R^2 = 0.996 \)

Depolymerization yield / %

Reaction time / min

Peak area
Linkam 500
Capillary Pressure Stage
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

Linkam 500
Capillary Pressure Stage
CAPS 500 Stage: Temperature difference between heater and thermocouple at positions 1,2,3,4,5

Error band over 30 mm of movement

Measuring positions

Type E mineral insulated thermocouple

50mm
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.
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.