The hydrothermal diamond anvil cell (HDAC) for Raman spectroscopic studies of geologic fluids at high pressures and temperatures

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Introduction

Hydrous fluids/melts in crust and mantle are crucial for element cycling.

Properties of interest include:
- Density
- Viscosity
- Sound velocity
- Electrical conductivity
- Phase transitions
- Complexation, speciation
- Solubility, partitioning
- Kinetics of mineral-fluid and fluid-fluid interaction

Many of these properties need or should be studied \textit{in situ} at high P and T.
Introduction

Bassett et al. (1993): HDAC

- Designed to study fluids in situ at lithospheric $P$-$T$ conditions

- Approximately 180 citations in Scopus

- HDACs used particularly for experiments with hydrous fluids to 23 GPa at 750 °C (Lin et al., 2004) and 1025±10 °C at ~2 GPa (Audétat and Keppler, 2005)
Construction

central portion with sample chamber

- objective lens of microscope
- ceramic support
- tungsten carbide seat
- heater wires (Mo, Pt, PtRh, NiCr)
- sample chamber, fluid
- metal gasket (Ir, Re ± Au coating)
- pressure sensor (e.g., quartz)
- thermocouples (K type)
- diamond anvils
- pressure generation
Construction
upper and lower platen

design minimizes temperature gradient in sample chamber and permits accurate measurement + control of sample temperature
Construction

alignment of culet faces of anvils

- rocker for rotation
- sliding disk for translation

interference color pattern indicates parallelism of culet faces

Smith and Fang (2009)
Construction

assembled HDAC on xyz-stage of Raman spectrometer

Bassett et al. (1993)
temperature measurement

**calibration using melting points**

**melting points at atmospheric pressure, e.g. of**

- NaCl (halite) (800.7 °C)
- CsCl (645 °C)
- K$_2$Cr$_2$O$_7$ (398 °C) heating to >500 °C damages culet
- NaNO$_3$ (306.8 °C) heating to >500 °C damages culet
- S (112.8 °C)
- azobenzene (68 °C)

**triple points of water for calibration at low temperature**

- ice I + liquid + vapor at 0.01 °C, 0.6 kPa
- ice I + ice III + liquid at -21.985 °C, 209.9 MPa
temperature measurement
calibration using $\alpha$$\rightarrow$$\beta$ quartz transition

- displacive, very little hysteresis
- 574 °C upon heating at 0.1 MPa
- optical observation under crossed polars
- should be cut parallel to c axis, section ~75 µm thick
pressure determination
overview

indirectly: optical microscopy, measurement of phase-transition temperatures in
• solid calibrant
• fluid in sample (with application of appropriate EoS)

directly: X-ray diffractometry or optical spectrometry, measurement of \( P \)-dependent property of a standard
• angle or energy positions of Bragg reflections of e.g. Au, Pt, NaCl, MgO. Rarely applied in studies on fluids
• frequency shifts of Raman or fluorescence lines of optical pressure sensors
  - fluorescence sensors: ruby (\( \alpha \)-\( \text{Al}_2\text{O}_3 \cdot \text{Cr}^{3+} \)), Sm:YAG, \( \text{SrB}_4\text{O}_7 \cdot \text{Sm}^{2+} \)
  - Raman spectroscopic sensors (work often better at high \( T \)): \( \alpha \)-quartz, berlinite (\( \text{AlPO}_4 \)), zircon, c-BN, \( ^{13}\text{C} \)-diamond
pressure determination

Raman bands: $\alpha$-quartz

$v_{206} < 2.5$ GPa at RT, but high resolution

$v_{464}$ to $\sim 600$ °C, to $\sim 3$ GPa (10 GPa at RT)

Schmidt and Ziemann (2000)
Pressure determination

Raman bands: $\nu_3(SiO_4)$ band of zircon

$\nu_{1008}$: to $\sim 1000$ °C, to $\sim 10$ GPa

Schmidt et al. (in revision)
pressure determination

Raman bands: $\nu_{1055} (= \nu_{TO})$ of $c$-BN

c-BN Raman spectr. pressure scales
• to 900 K, 80 GPa (Datchi et al. 2007)
• to 3300 K, 70 GPa (Goncharov et al. 2007)

inert

nearly linear dependence of $\nu$ on $P$, but small
($\partial \nu / \partial P \sim 3 \text{ cm}^{-1} \text{ GPa}^{-1}$)

Datchi and Canny (2004)
pressure determination

Raman bands: $\nu_{1111} - \nu_{462}$ of berlinite

- $\nu_{1111}$ and $\nu_{462}$: shift in opposite direction with $P$ and $T$
- $\partial (\nu_{1111} - \nu_{462}) / \partial P \sim 10 \text{ cm}^{-1} \text{GPa}^{-1}$
- reacts with aqueous fluids at elevated $T$

Watenphul and Schmidt (2012)
pressure determination
fluorescence bands: ruby

most common technique to measure pressure in DACs

doublet, at ambient P-T:
• $R_1$ at $\sim 14404$ cm$^{-1}$ ($\sim 694.25$ nm)
• $R_2$ at $\sim 14433$ cm$^{-1}$ ($\sim 693.85$ nm)
• $\partial \nu / \partial P \sim -7.5$ cm$^{-1}$GPa$^{-1}$
  ($=0.365$ nmGPa$^{-1}$ )
• has been used to 0.55 TPa
• recent ruby pressure scales to $\sim 300$ GPa (e.g., Dorogokupets and Oganov 2007)
• original calibration by Piermarini et al. (1975) still valid to $\sim 10$ GPa

Piermarini et al. (1975)

FIG. 1. The pressure dependence at 25°C of the ruby $R_1$ fluorescence line at 6942 Å as a function of wavelength (Å) and also wave number or frequency (cm$^{-1}$). Pressure values are based on the Decker equation of state for NaCl.
pressure determination
fluorescence bands: ruby

with increasing T:
• broadening
• $R_1$ and $R_2$ merge
• intensity decreases
• strong and nonlinear shift in wavenumber

$$\left( \frac{\partial \nu_{R_1}}{\partial T} \sim -0.14 \text{ cm}^{-1}\text{K}^{-1} \right)$$

accurate pressure determination becomes difficult at $T > 300 \, ^\circ\text{C}$, particularly at relatively low $P$ to a few GPa

Datchi et al. (2007)
pressure determination
fluorescence bands: SrB$_4$O$_7$:Sm$^{2+}$

single, very intense, fluorescence line at
~685.41 nm at ambient $PT$

- $\partial \nu / \partial P \sim -5.5$ cm$^{-1}$GPa$^{-1}$
  ($=0.26$ nmGPa$^{-1}$)
- $\partial \nu / \partial T \sim 0$
- still detectable at 900 K
- calibrated to 130 GPa (Datchi et al. 1997)
- drawback: quite soluble in aqueous fluids

Datchi et al. (2007)
pressure determination

phase transitions and isochores in fluid

modified from Schmidt and Ziemann (2000)
pressure determination

dilute aqueous fluids: EoS of water

pressure determination
melting curve of pressure medium

Ice I
Ice II
Ice III
Ice IV
Ice V
Ice VI
Ice VII
Ice VIII

Ice melting curves (Wagner et al. 1994)

33 °C

Ice VI

liquid H₂O

-50
0
50
100
150

Temperature, °C

0
1
2

Pressure, GPa

Ice VI
Ice VII
Ice VIII
• α-β quartz transition is sensitive to pressure (~260 K GPa$^{-1}$),
• drawbacks: $T$ too high for many HDAC experiments, high solubility in H$_2$O

other transitions applicable at lower $T$:
• BaTiO$_3$ (tetrag./cubic)
• Pb$_3$(PO$_4$)$_2$ (monoclinic/trigonal)
• PbTiO$_3$ (tetrag./cubic)
techniques that have been applied to study aqueous fluids/melts *in situ* using HDACs

- optical microscopy, microthermometry, falling sphere technique
- Raman spectroscopy
- synchrotron-radiation X-ray fluorescence and absorption spectroscopy
- inelastic X-ray scattering
- infrared absorption
- Brillouin spectroscopy
- laser-induced phonon spectroscopy
- electrical conductance measurements
Application

optical microscopy, microthermometry

Example: experiment on H$_2$O + 4.5 molal NaHCO$_3$ + SiO$_2$

**fluid-1** = aqueous fluid
**fluid-2** = 2nd fluid (H$_2$O+ carbonate+silicate)

Qtz = quartz
NaHCO$_3$ = nahcolite
Na$_2$CO$_3$(s) = natrite

Thomas et al. (2011)
Raman spectroscopy and HDAC

*In situ* studies on geologic fluids

permits study of molecules and molecular ions of light elements in fluids at high $P$ and $T$

- complexation, speciation, phase transitions, solubility, kinetics, e.g.,
  - complexation in $\text{H}_2\text{O} + \text{KAISi}_3\text{O}_8$ fluids to 900 °C, 2.3 GPa, phase diagram of $\text{H}_2\text{O} + 40$ mass% $\text{KAISi}_3\text{O}_8$ (Mibe et al., 2008)
  - silica speciation and solubility of quartz in $\text{H}_2\text{O}$ to 900 °C, 1.4 GPa (Zotov and Keppler 2002)
  - ammonium in aqueous fluids to 600 °C, 1.3 GPa: silica and N speciation, silica solubility of Qz + Ky + Kfs/Ms in $\text{H}_2\text{O} \pm \text{NH}_4\text{Cl}$, kinetics of Kfs to Ms reaction (Schmidt and Watenphul 2010)
  - ice VII melting curve to 630 °C, 22 GPa (Lin et al. 2004)
Raman spectroscopy and HDAC

*In situ* studies on geologic fluids

Quantification (e.g. solubility measurement) possible in in some cases

**Difficulties:**

- rather high detection limits for most species
- not all relevant species are Raman active or Raman distinguishable
- changes in the Raman scattering cross sections with P,T,X are unknown for most species
Raman spectroscopy and HDAC measurement of species concentration
Raman spectroscopy and HDAC vertical scan of $\nu_1$-SO$_4^{2-}$ intensity in fluid

Schmidt (2009)
Raman spectroscopy and HDAC
change in $\nu_1$-$\text{SO}_4^{2-}$ cross section with $P$ and $T$

probably effect of bond expansion with temperature on polarizability

Schmidt (2009)
Raman spectroscopy and HDAC

$m \text{SiO}_2(aq)$ in Qz+Ky+Kfs/Ms+H$_2$O±NH$_4$Cl

Schmidt and Watenphul (2010)

for calibration:

$m \text{SiO}_2(aq)$

= 0.375

at 600 °C, 970 MPa

(Manning 1994)

Schmidt and Watenphul (2010)
Raman spectroscopy and HDAC

$m \text{SiO}_2(aq)$ in Qz+Ky+Kfs/Ms+$\text{H}_2\text{O} \pm \text{NH}_4\text{Cl}$

Schmidt and Watenphul (2010)

[Graph showing quartz solubility in H$_2$O (mol SiO$_2$ / kg H$_2$O) vs. SiO$_2$ concentration in fluid (mol / kg H$_2$O) for different temperatures and pressures.]

- 9.6 $m\text{NH}_4\text{Cl} + \text{Qz} + \text{Ky} + \text{Kfs}$, this study
- 9.6 $m\text{NaCl} + \text{Qz}$, NM2000
- 6.6 $m\text{NH}_4\text{Cl} + \text{Qz}$, this study
- 6.6 $m\text{NaCl} + \text{Qz}$, NM2000
- $\text{H}_2\text{O} + \text{Qz} + \text{Ky} + \text{Kfs}$, this study

Temperatures and pressures:
- 600 °C, 920 MPa (+Ms)
- 600 °C, 750 MPa
- 600 °C, 1290 MPa
- 500 °C, 1100 MPa (+Ms/Tob)
- 500 °C, 780 MPa
- 500 °C, 355 MPa
- 500 °C, 555 MPa (+Ms/Tob)
Thank you for your attention!