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

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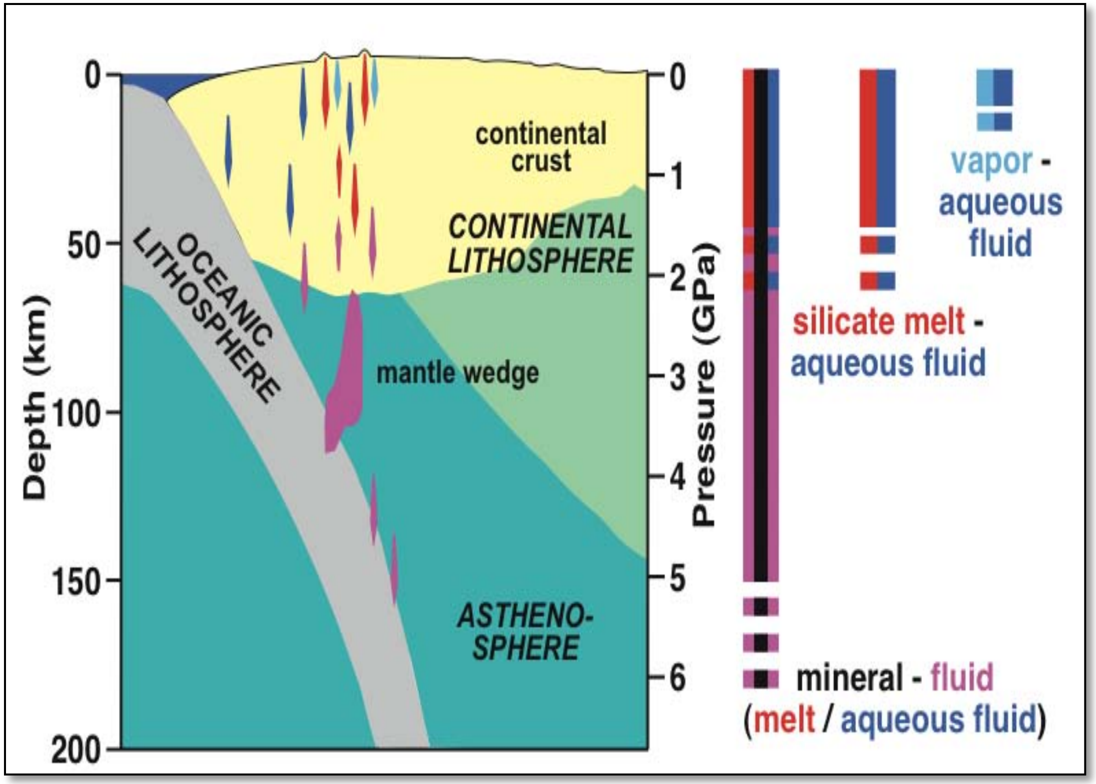
Introduction

hydrous fluids/melts in crust and mantle

crucial for element cycling

properties of interest

- 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 *in situ* at high P and T

Introduction

Bassett et al. (1993): HDAC

- designed to study fluids in situ at lithospheric *P*-*T* conditions

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A new diamond anvil cell for hydrothermal studies to 2.5 GPa and from −190 to 1200 °C

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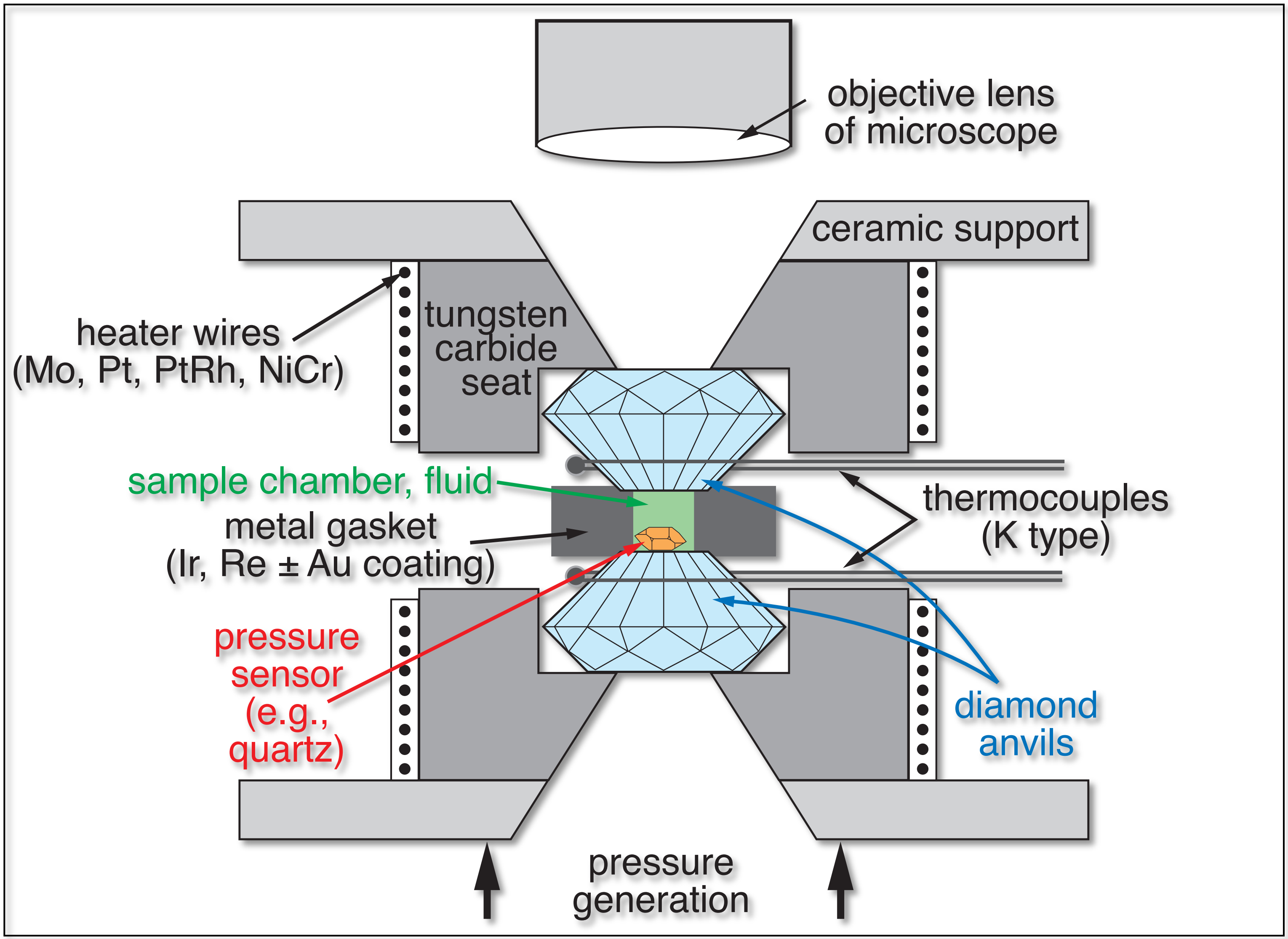
A new style of diamond anvil cell (DAC) has been designed and built for conducting research in fluids at pressures to 2.5 GPa and temperatures from −190 to 1200 °C. The new DAC has

- ~ 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)

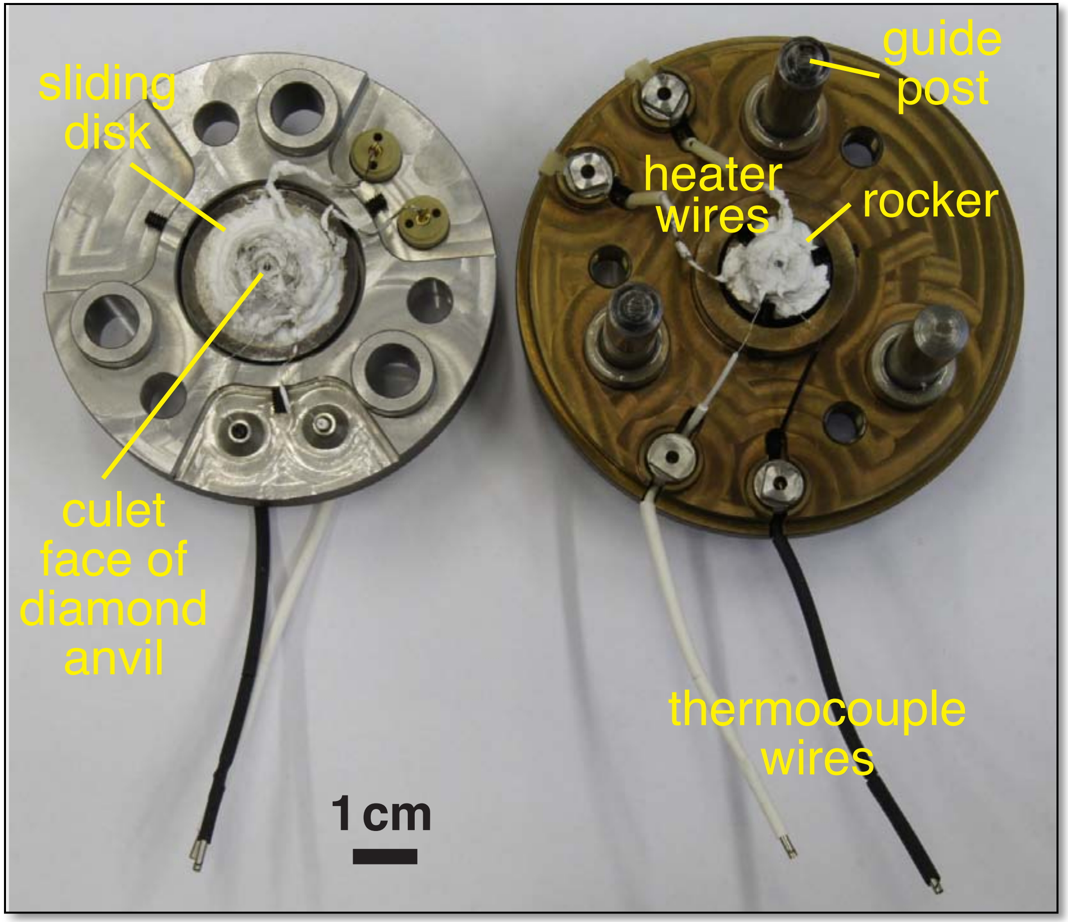
Construction

central portion with sample chamber



Construction

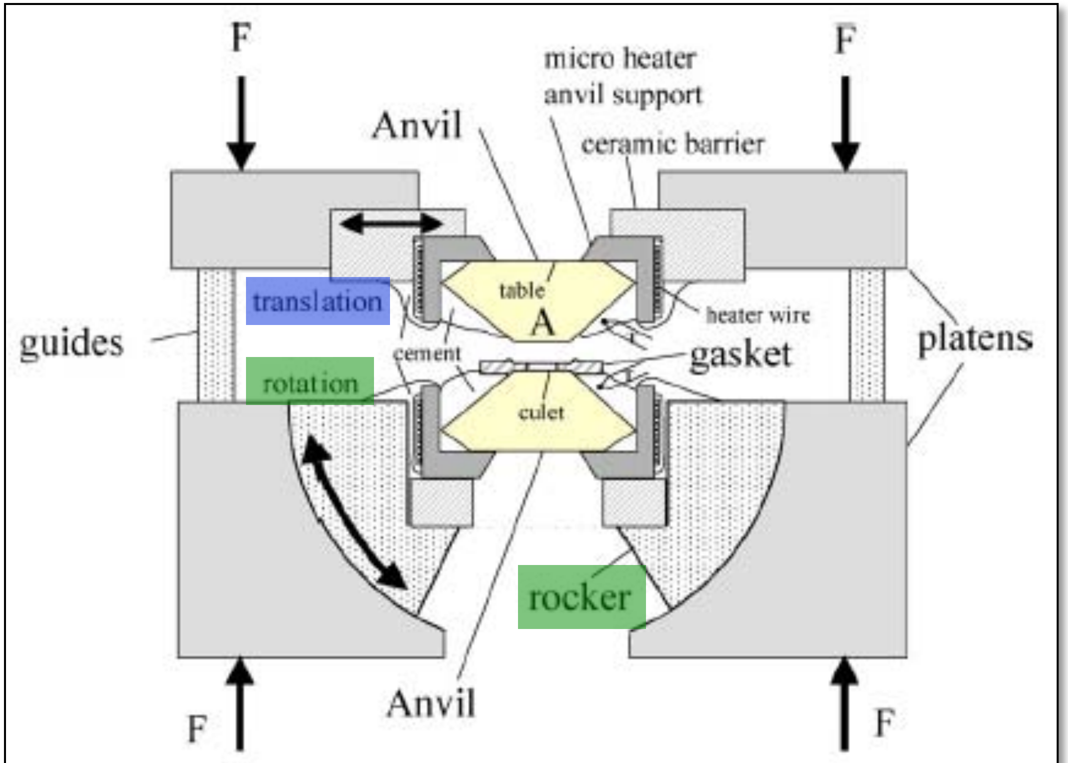
upper and lower platen



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

Construction

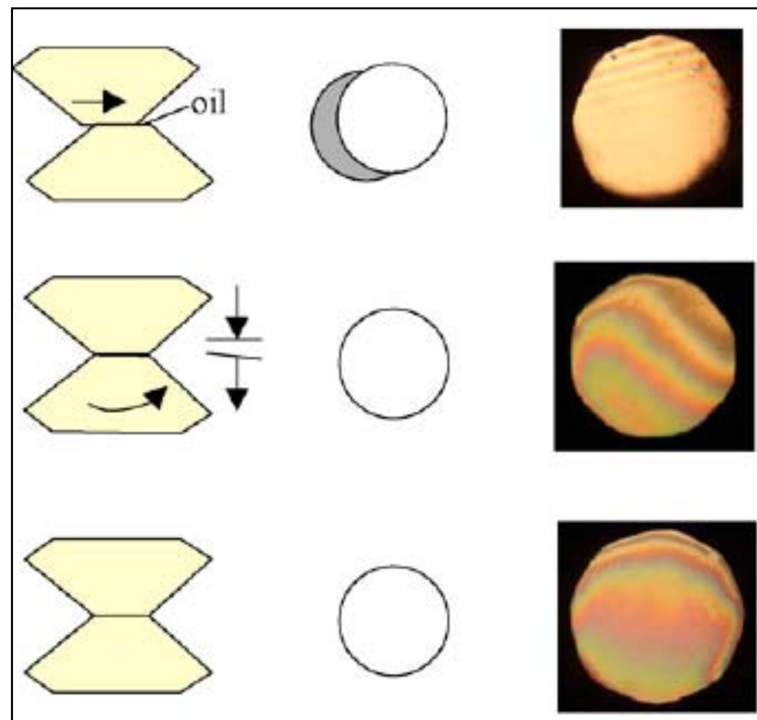
alignment of culet faces of anvils



- rocker for rotation
- sliding disk for translation

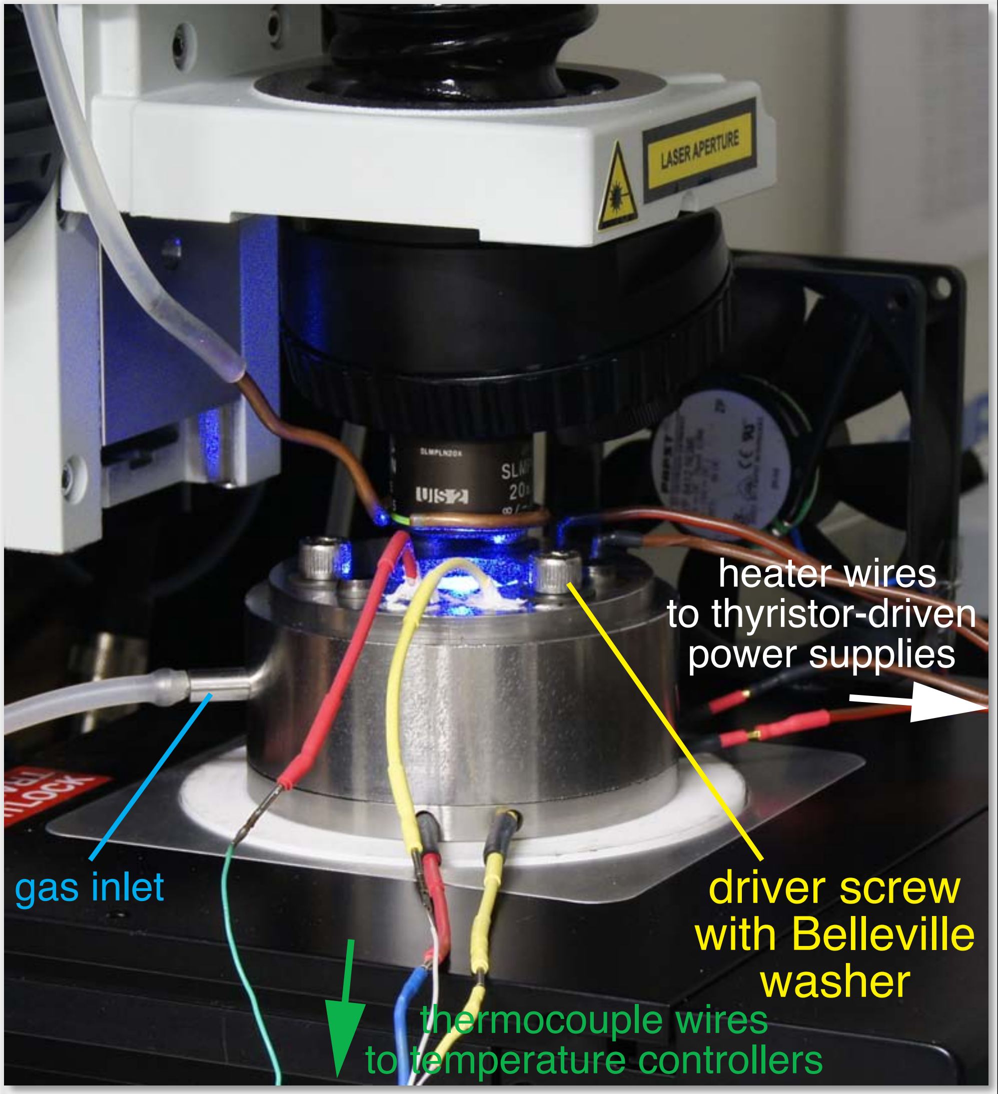
Smith and Fang (2009)

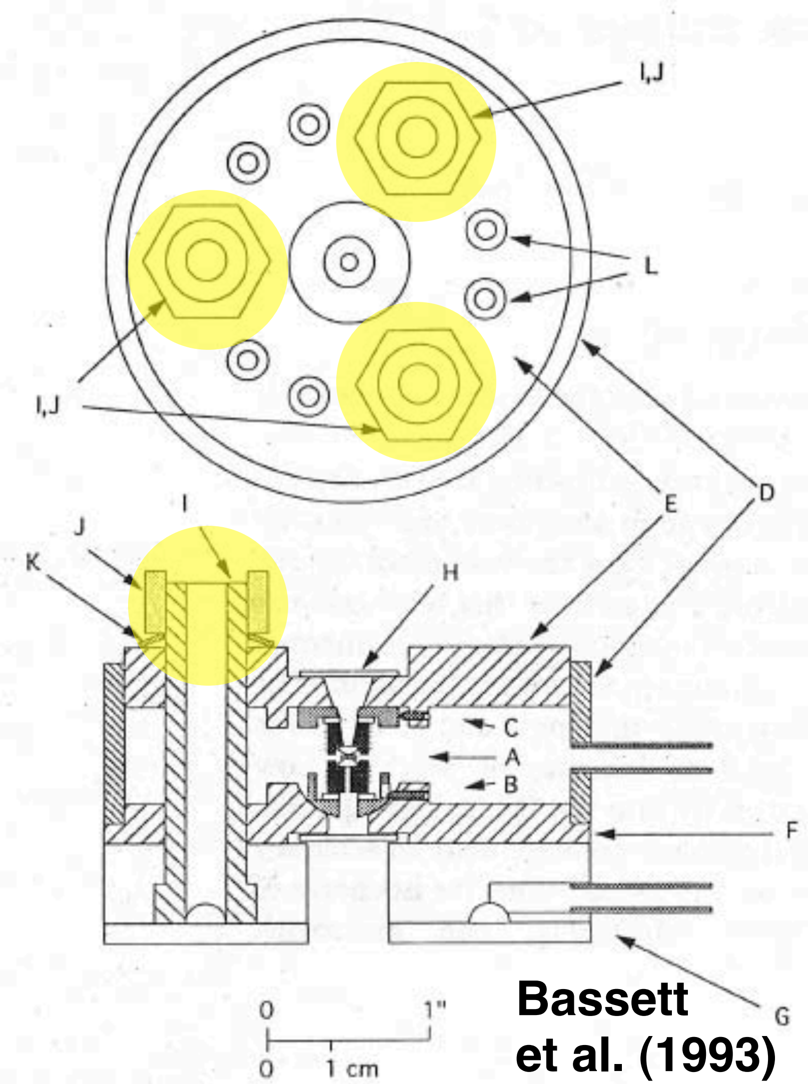
interference color pattern indicates parallelism of culet faces



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

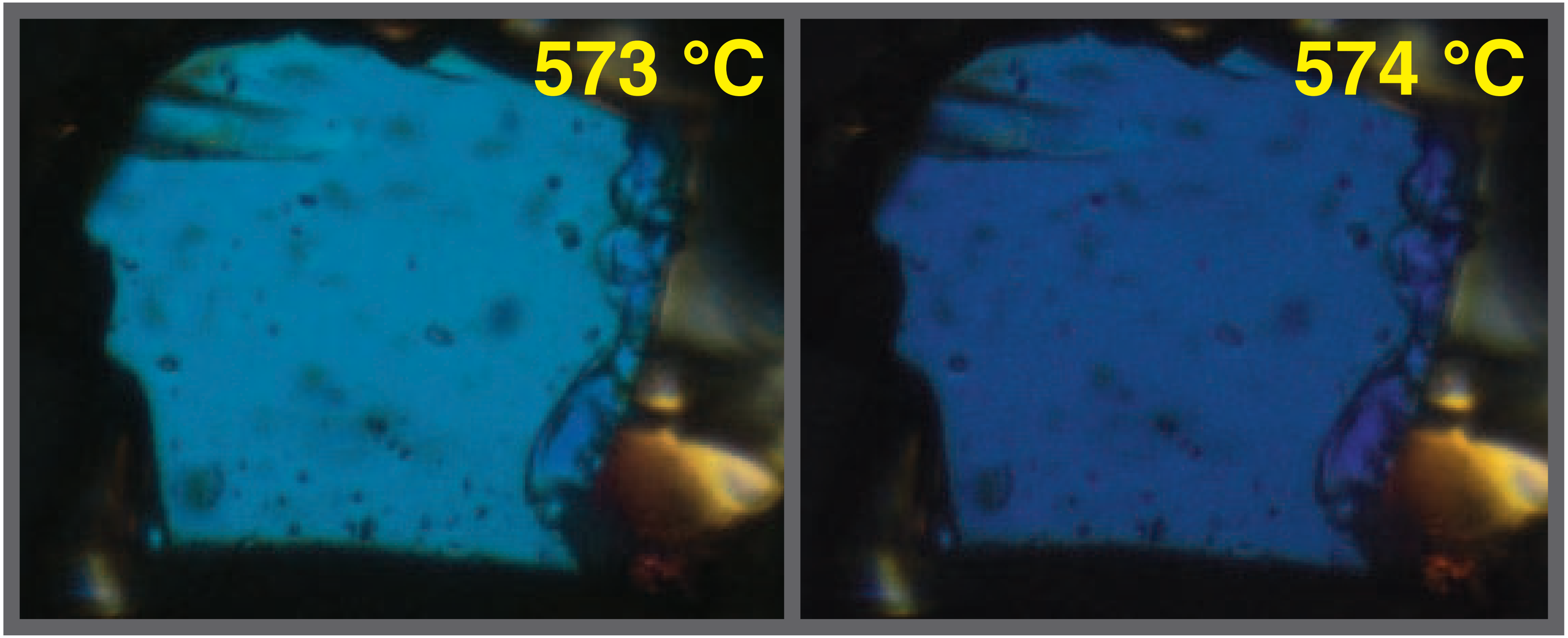
- NaCl (halite) (800.7 °C)
- CsCl (645 °C)
- $K_2Cr_2O_7$ (398 °C) heating to >500 °C damages culet
- $NaNO_3$ (306.8 °C) heating to >500 °C damages culet
- S (112.8 °C)
- azobenzene (68 °C)

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 α-β 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

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indirectly: optical microscopy, measurement of phase-transition temperatures in

- solid calibrant
- fluid in sample (with application of appropriate EoS)

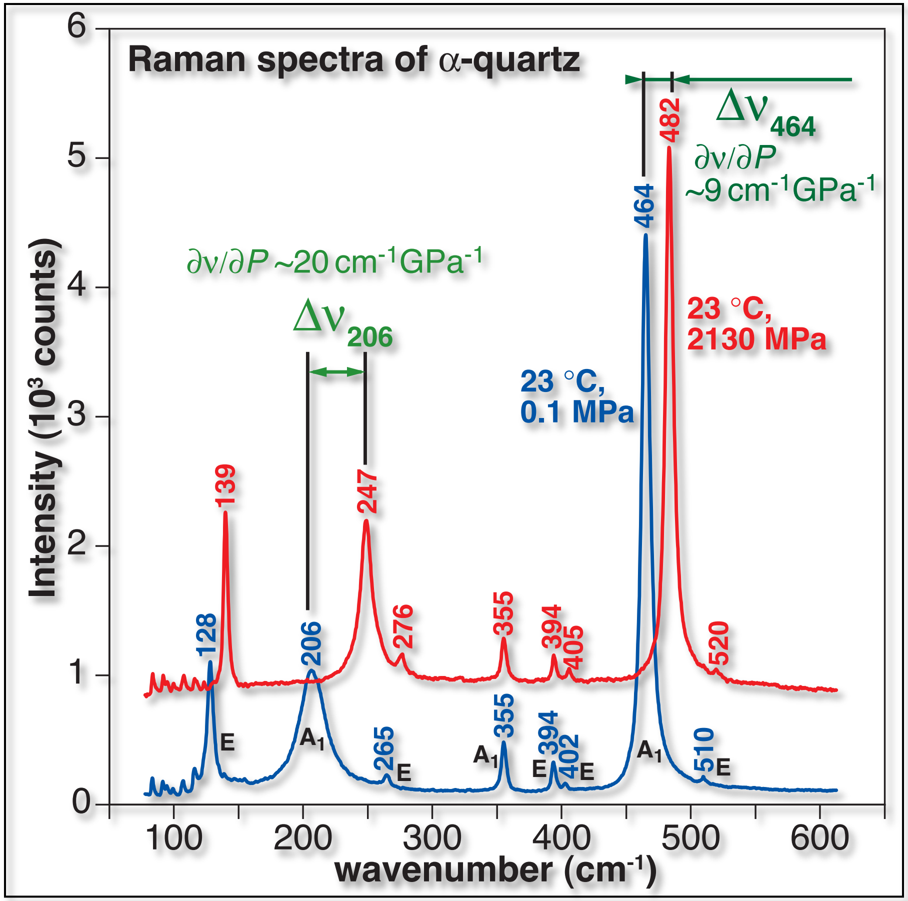
directly: X-ray diffractometry or optical spectrometry, measurement of *P*-dependent property of a standard

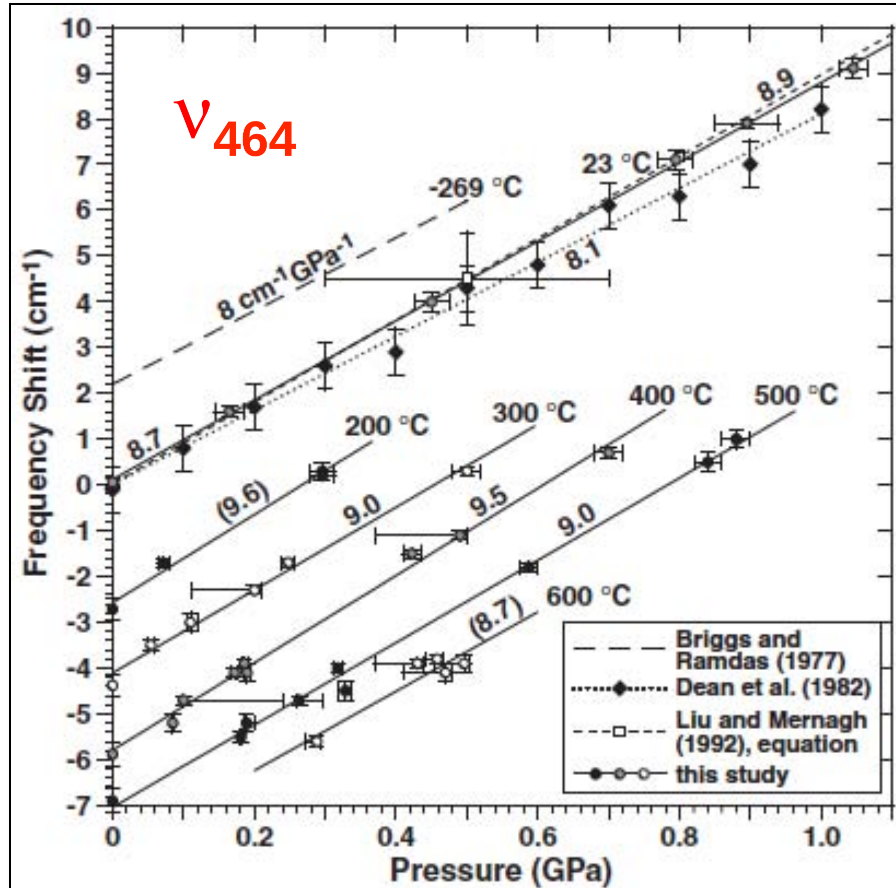
- angle or energy positions of Bragg reflections of e.g. Au, Pt, NaCl, MgO. Rarely applied in studies on fluids
- frequency shifts of Raman or fluorescence lines of optical pressure sensors

- fluorescence sensors: ruby (α-Al_2O_3:Cr^{3+}), Sm:YAG, SrB_4O_7:Sm^{2+}
- Raman spectroscopic sensors (work often better at high *T*): α-quartz, berlinite ($AlPO_4$), zircon, *c*-BN, ^{13}C-diamond

pressure determination

Raman bands: α-quartz





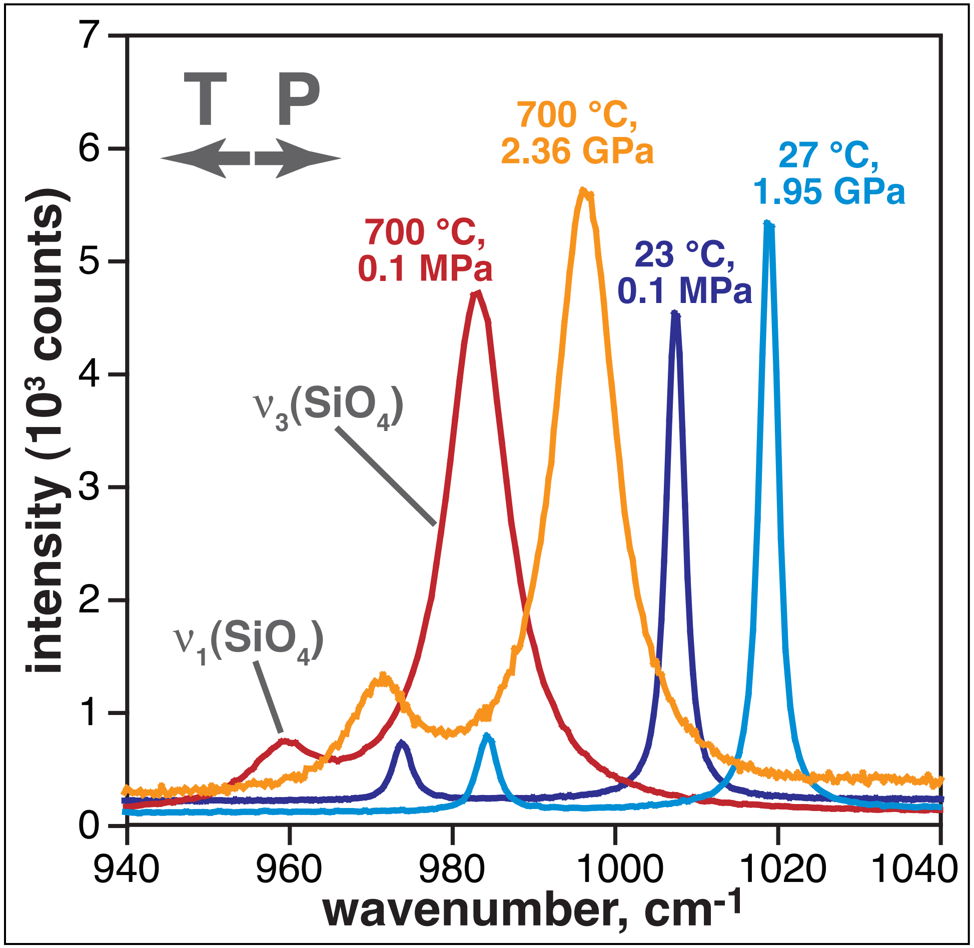
ν_{206}: <2.5 GPa at RT, but high resolution

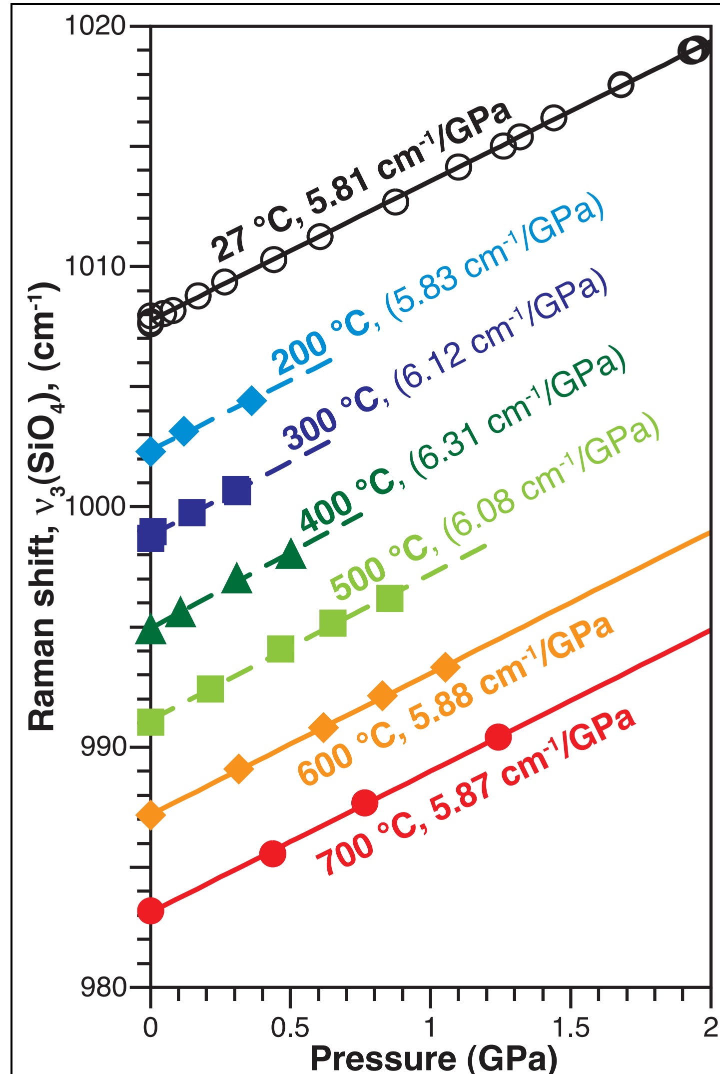
ν_{464}: to ~600 °C, to ~3 GPa (10 GPa at RT)

Schmidt and Ziemann (2000)

Pressure determination

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





ν_{1008}: to ~1000 °C, to ~10 GPa

Schmidt et al. (in revision)

pressure determination

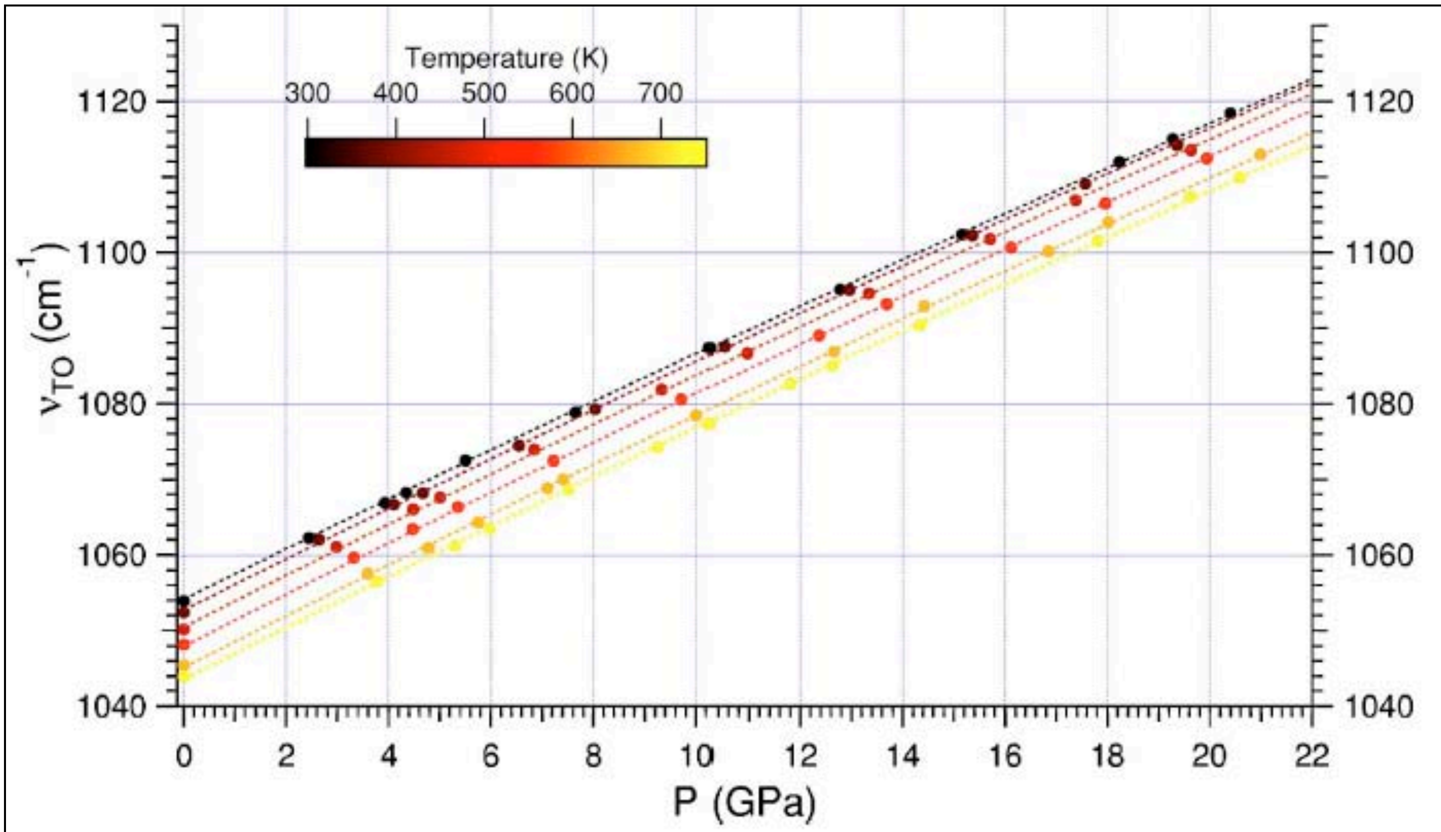
Raman bands: ν_{1055} (= ν_{TO}) of *c*-BN

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 ν on *P*, but small
($\partial\nu/\partial P$ ~3 $cm^{-1}GPa^{-1}$)

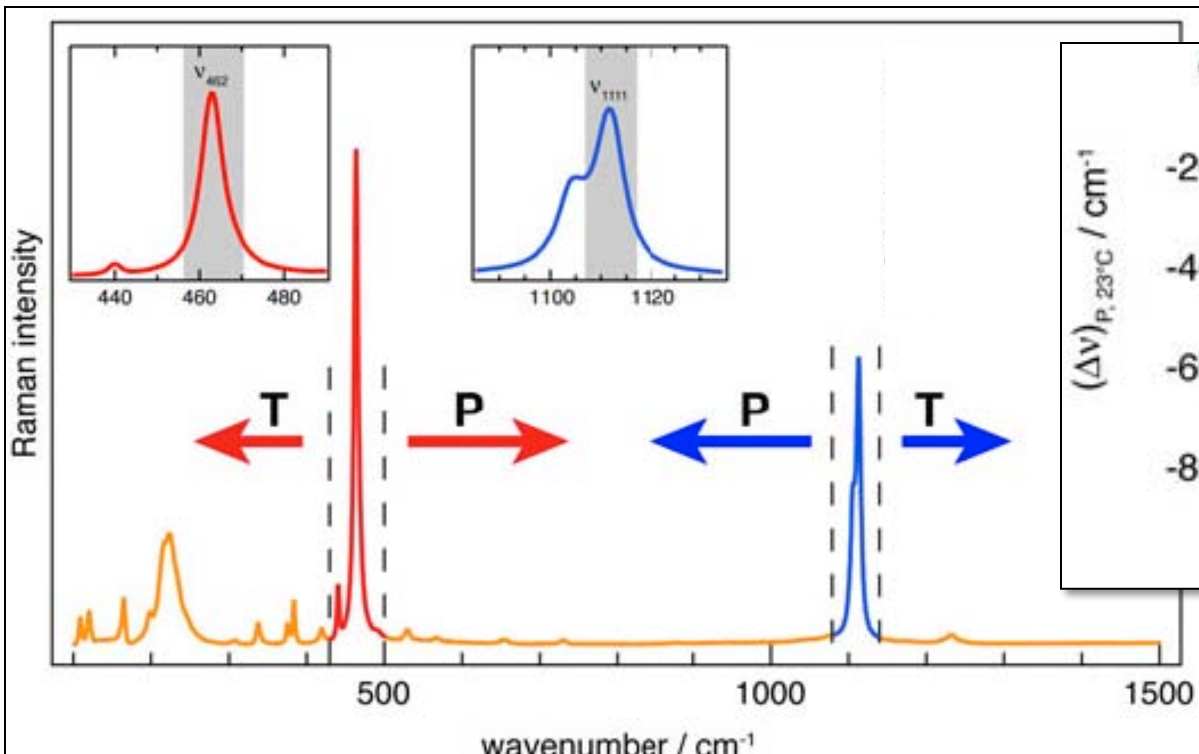


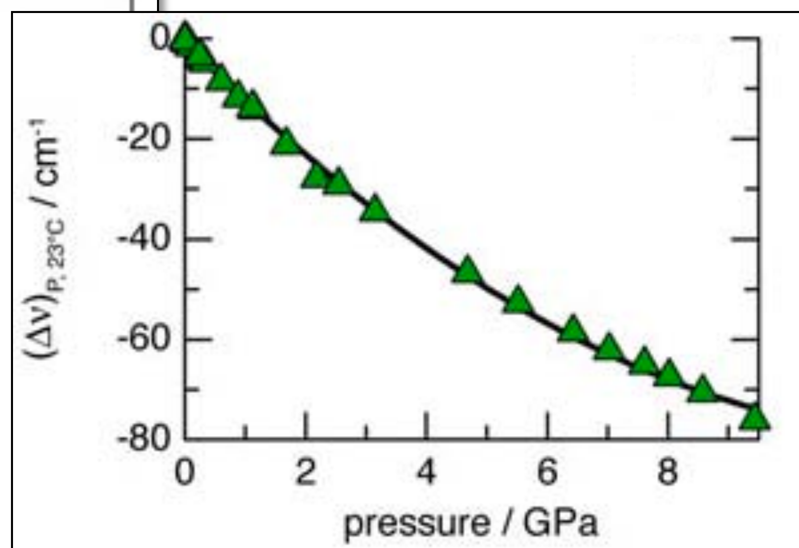
Datchi and Canny (2004)

pressure determination

Raman bands: ν_{1111}-ν_{462} of berlinite

- ν_{1111} **and** ν_{462}**: shift in opposite direction with P and T**
- $\partial(\nu_{1111}-\nu_{462})/\partial P \sim 10\ cm^{-1}GPa^{-1}$
- 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 ~14404 cm^{-1} (~694.25 nm)**
- ***R*2 at ~14433 cm^{-1} (~693.85 nm)**

- $\partial\nu/\partial P$ ~-7.5 cm^{-1}GPa^{-1} (=0.365 nmGPa^{-1})
- has been used to 0.55 TPa
- recent ruby pressure scales to ~300 GPa (e.g., Dorogokupets and Oganov 2007)
- original calibration by Piermarini et al. (1975) still valid to ~10 GPa

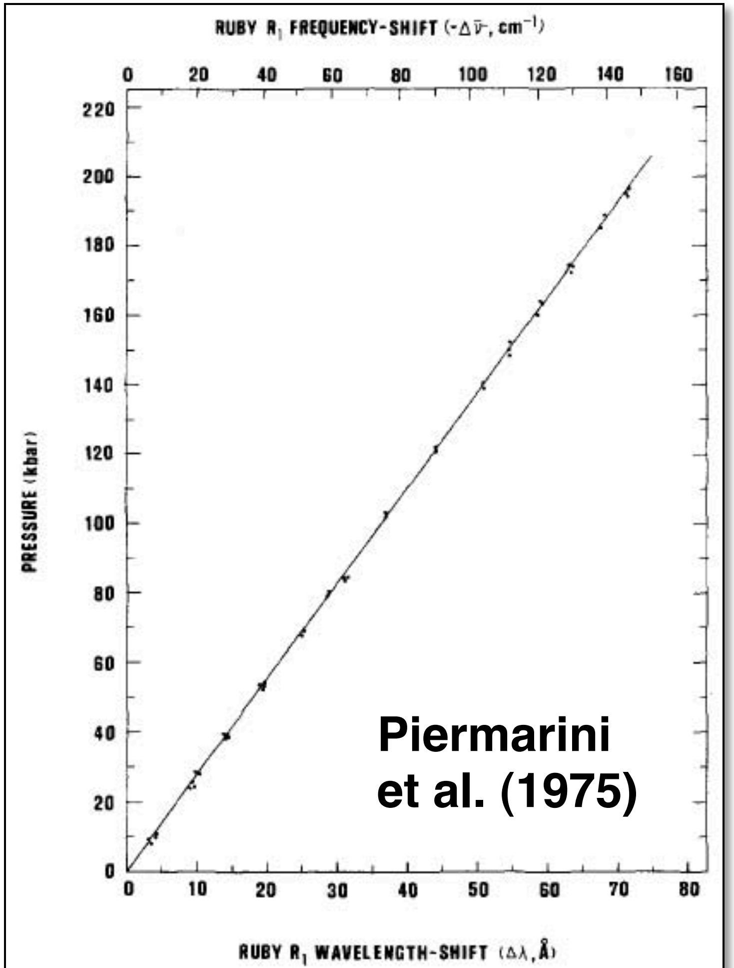


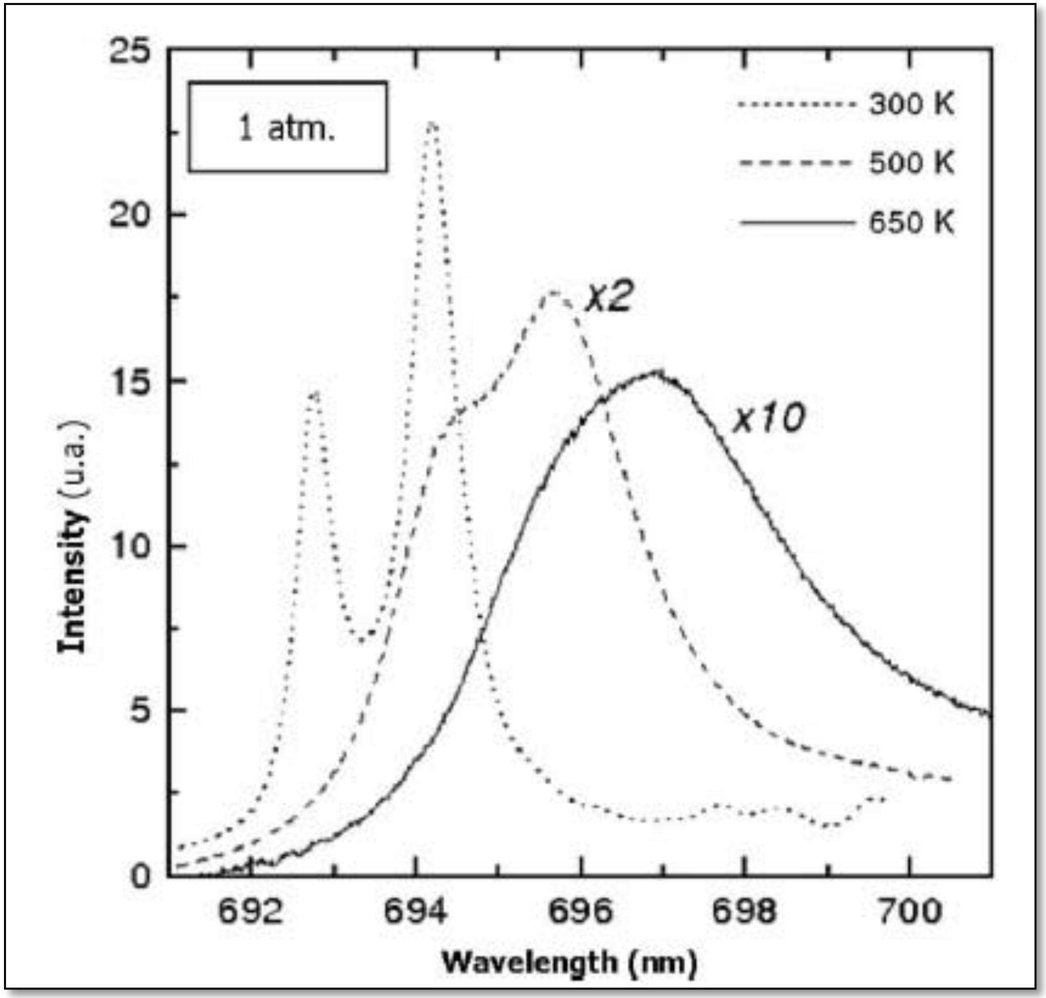
FIG. 1. The pressure dependence at 25 °C of the ruby R_1 fluorescence line at 6942 Å as a function of wavelength (Å) and also wave number or frequency (cm^{-1}). Pressure values are based on the Decker equation of state for NaCl.

pressure determination
fluorescence bands: ruby

with increasing T:

- **broadening**
- ***R*1 and *R*2 merge**
- **intensity decreases**
- **strong and nonlinear shift in wavenumber** ($\partial \nu_{R1}/\partial T \sim -0.14\ cm^{-1}K^{-1}$)

accurate pressure determination becomes difficult at *T* >300 °C, particularly at relatively low *P* to a few GPa



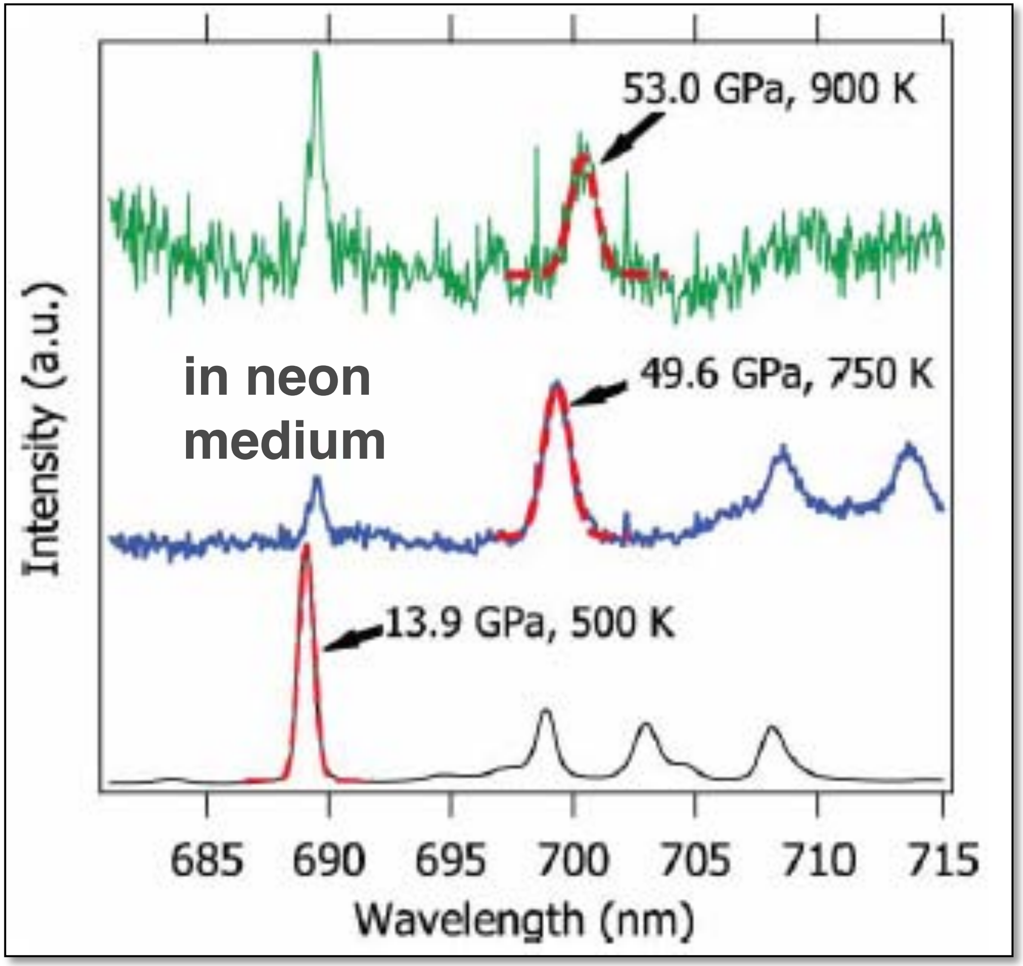
Datchi et al. (2007)

pressure determination

fluorescence bands: $SrB_4O_7:Sm^{2+}$

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

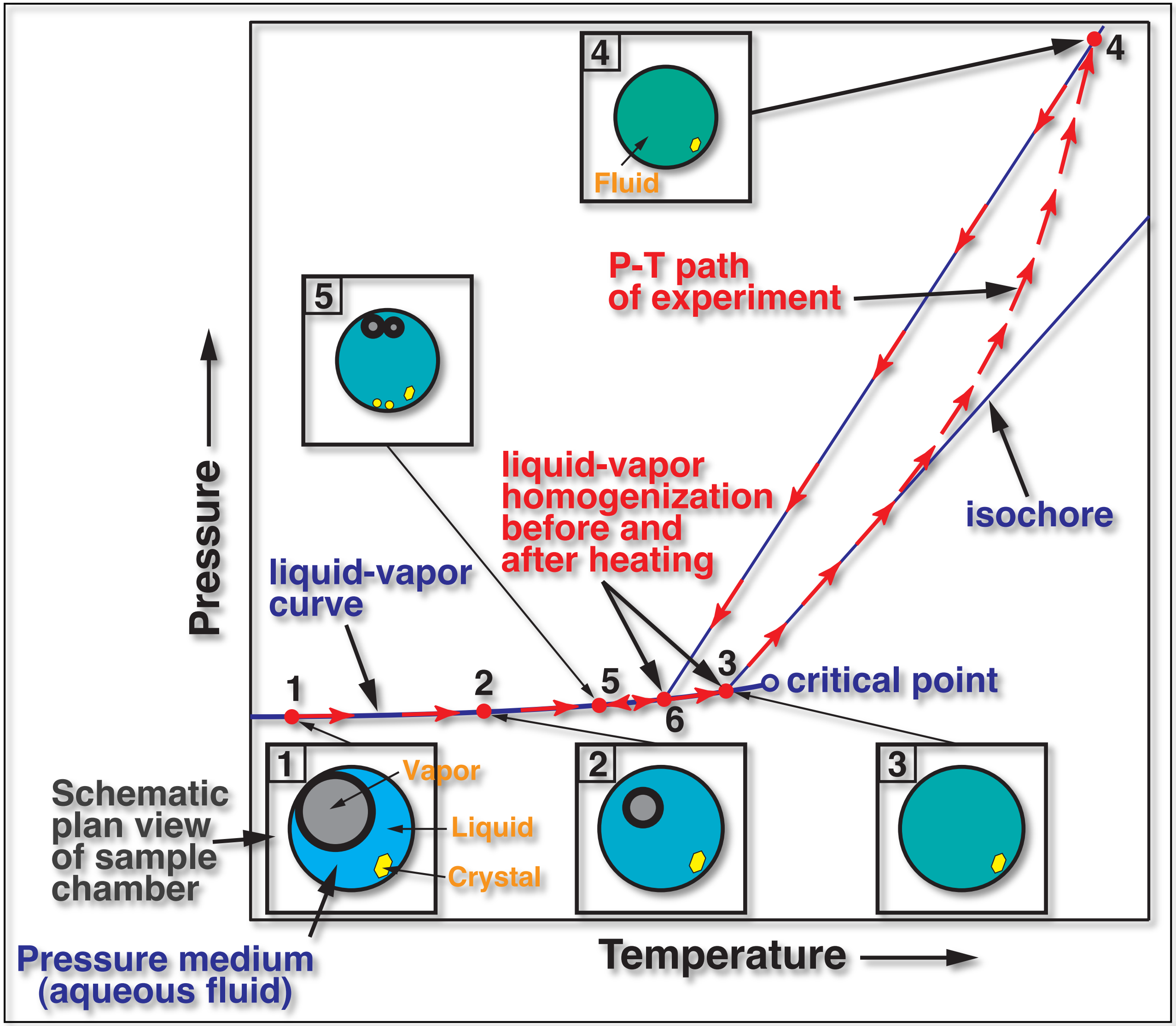
- $\partial\nu/\partial P$ ~-5.5 $cm^{-1}GPa^{-1}$ (=0.26 $nmGPa^{-1}$)
- $\partial\nu/\partial T \sim 0$
- still detectable at 900 K
- calibrated to 130 GPa (Datchi et al. 1997)
- drawback: quite soluble in aqueous fluids



Datchi et al. (2007)

pressure determination

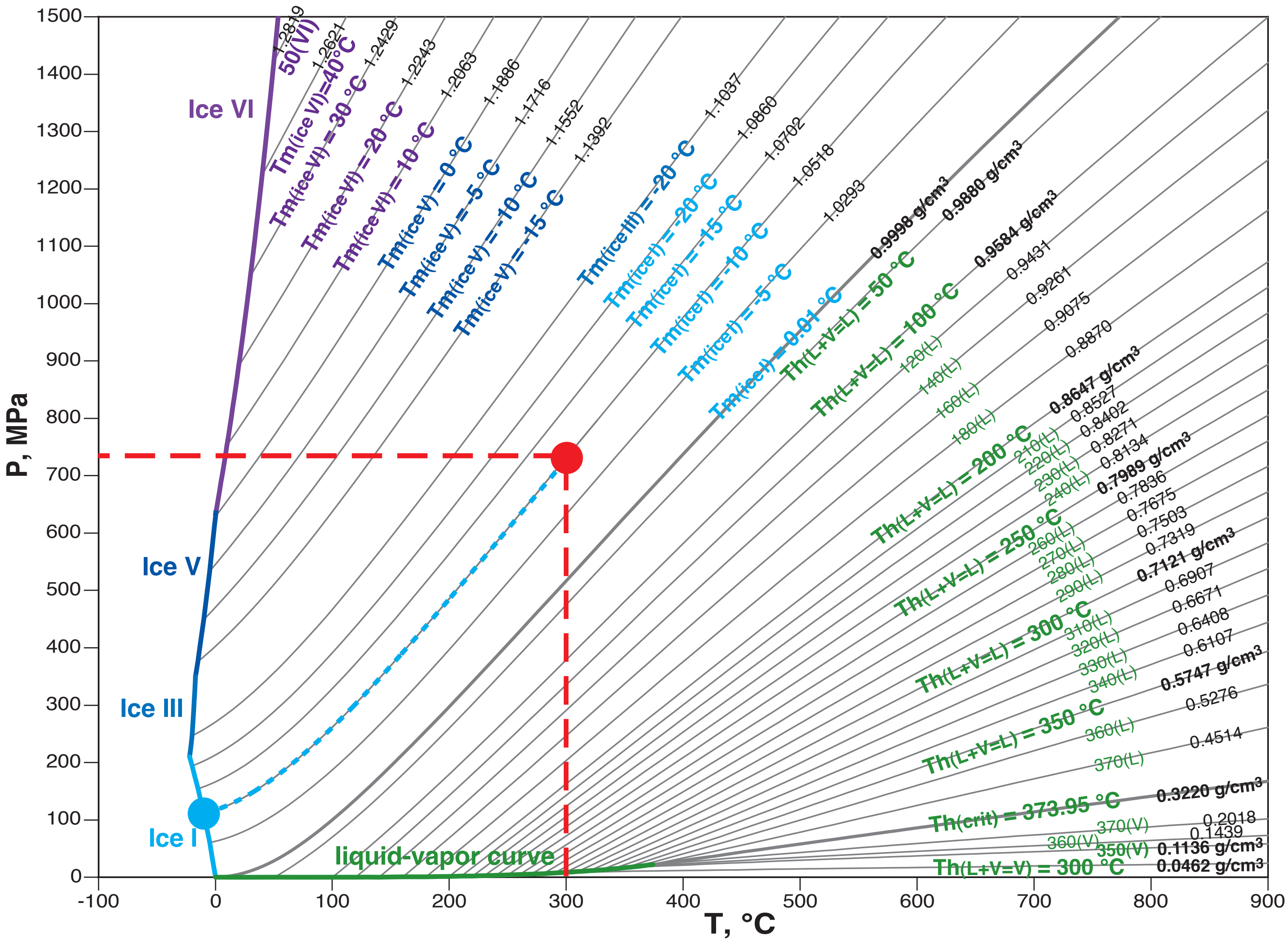
phase transitions and isochores in fluid



modified from Schmidt and Ziemann (2000)

pressure determination

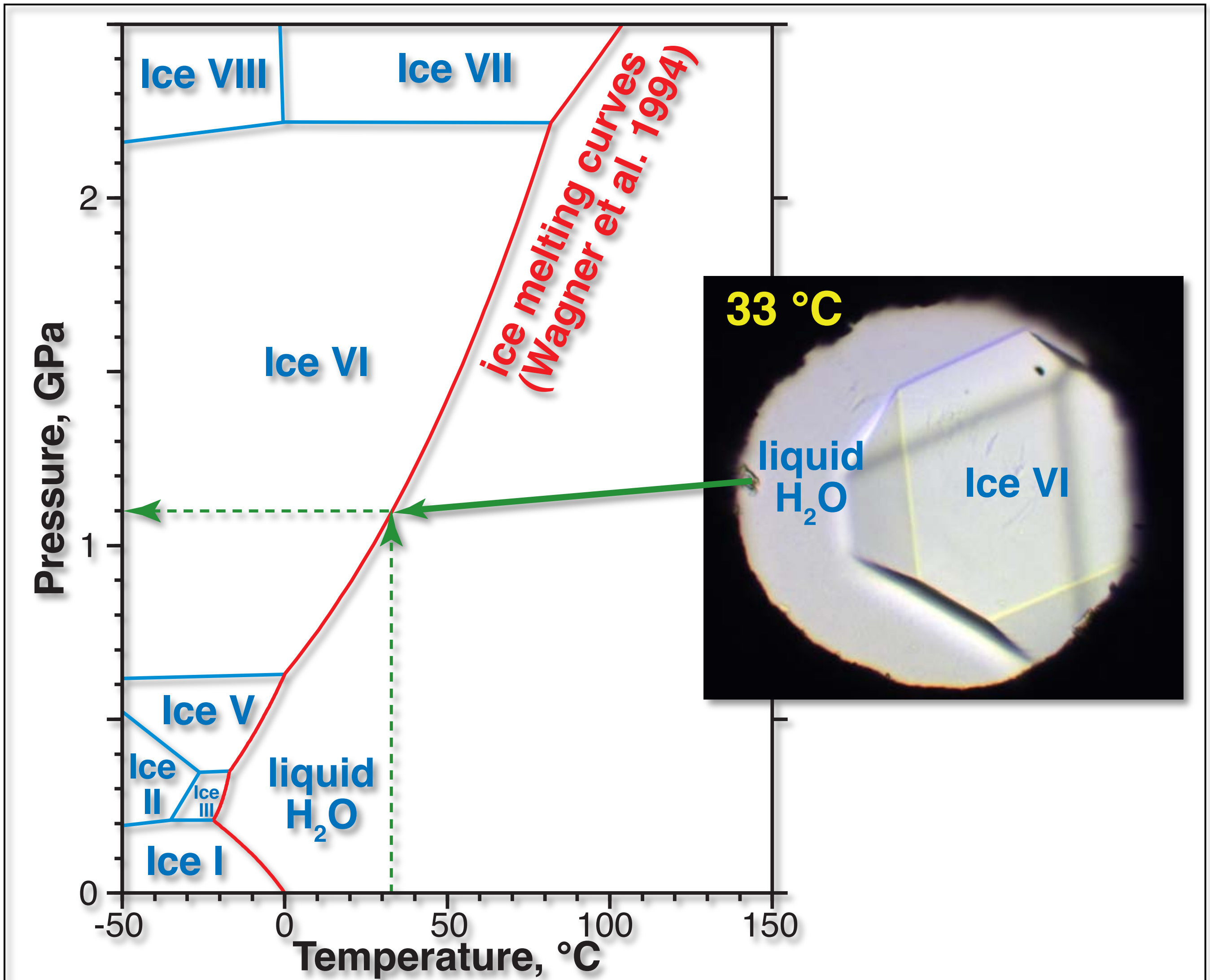
dilute aqueous fluids: EoS of water



equation of state: Wagner and Pruß (2002)

pressure determination

melting curve of pressure medium

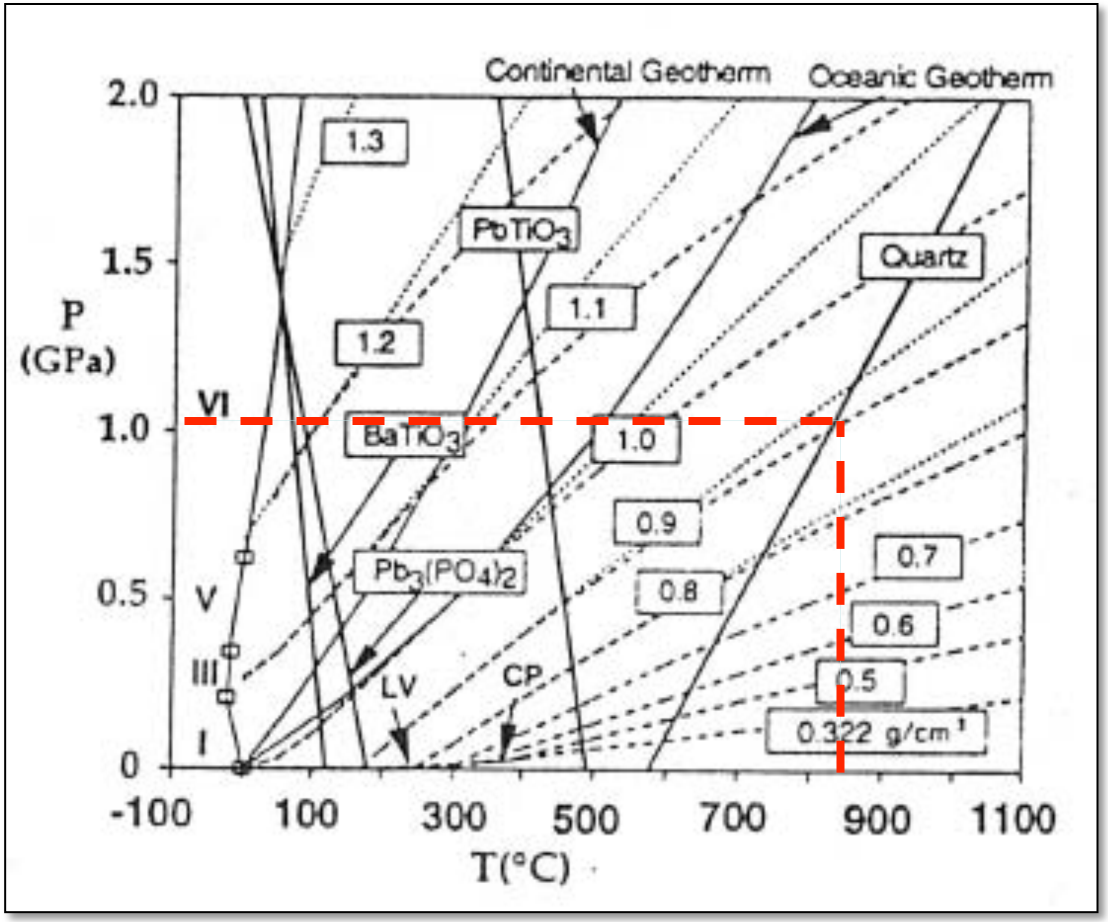


pressure determination
α-β quartz transition temperature

- α-β quartz transition is sensitive to pressure (~260 K GPa^{-1}),
- drawbacks: *T* too high for many HDAC experiments, high solubility in H_2O

other transitions applicable at lower *T*:

- $BaTiO_3$ (tetrag./cubic)
- $Pb_3(PO_4)_2$ (monoclinic/trigonal)
- $PbTiO_3$ (tetrag./cubic)



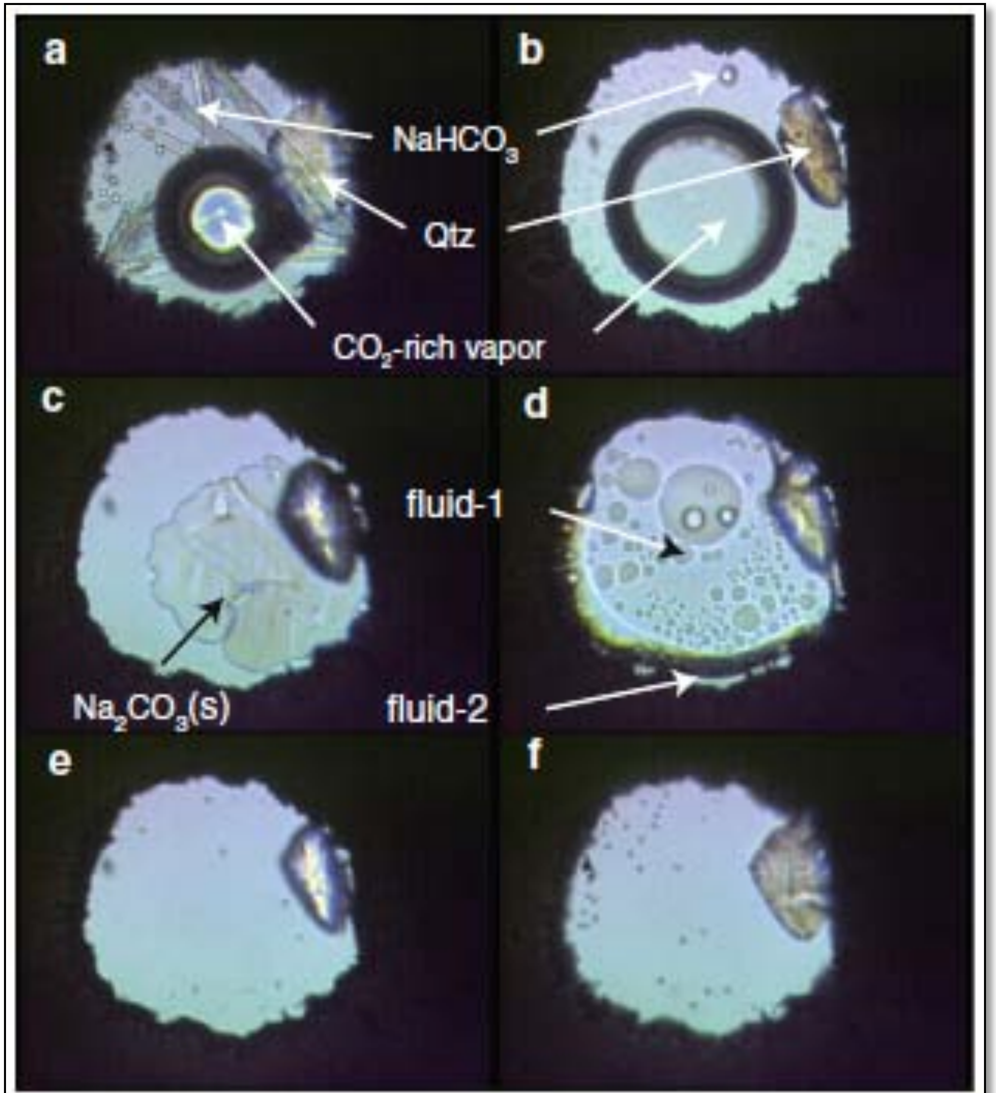
Bassett et al. (1996)

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_2O + 4.5 molal $NaHCO_3$ + SiO_2

fluid-1 = aqueous fluid
fluid-2 = 2nd fluid (H_2O+ carbonate+silicate)
Qtz = quartz
$NaHCO_3$ = nahcolite
Na_2CO_3(s) = natrite

Thomas et al. (2011)

Raman spectroscopy and HDAC
In situ studies on geologic fluids

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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 H_2O + $KAlSi_3O_8$ fluids to 900 °C, 2.3 GPa, phase diagram of H_2O + 40 mass% $KAlSi_3O_8$ (Mibe et al., 2008)
• silica speciation and solubility of quartz in H_2O 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 H_2O ± NH_4Cl, 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

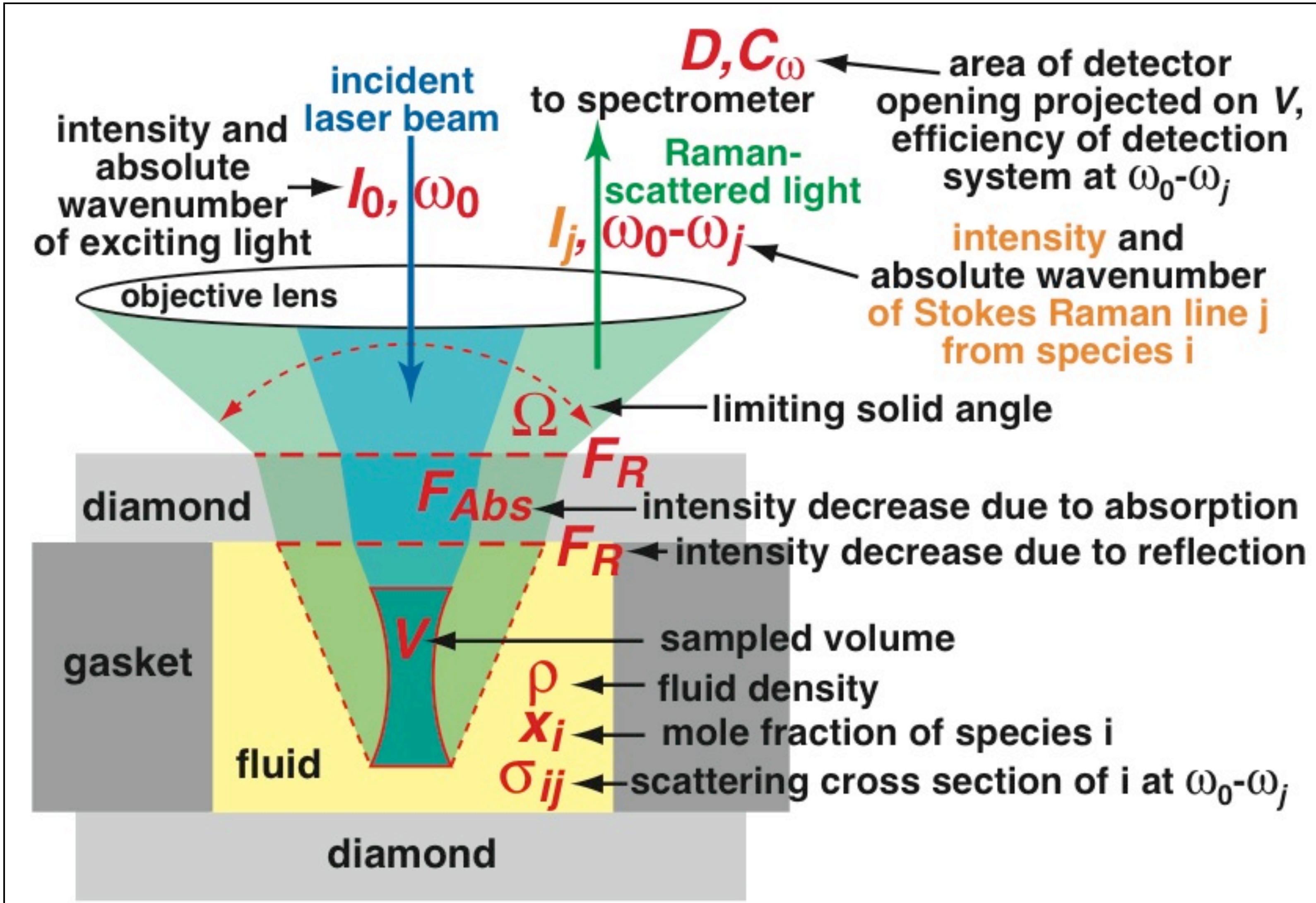
Quantification (e.g. solubility measurement) possible in in some cases

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

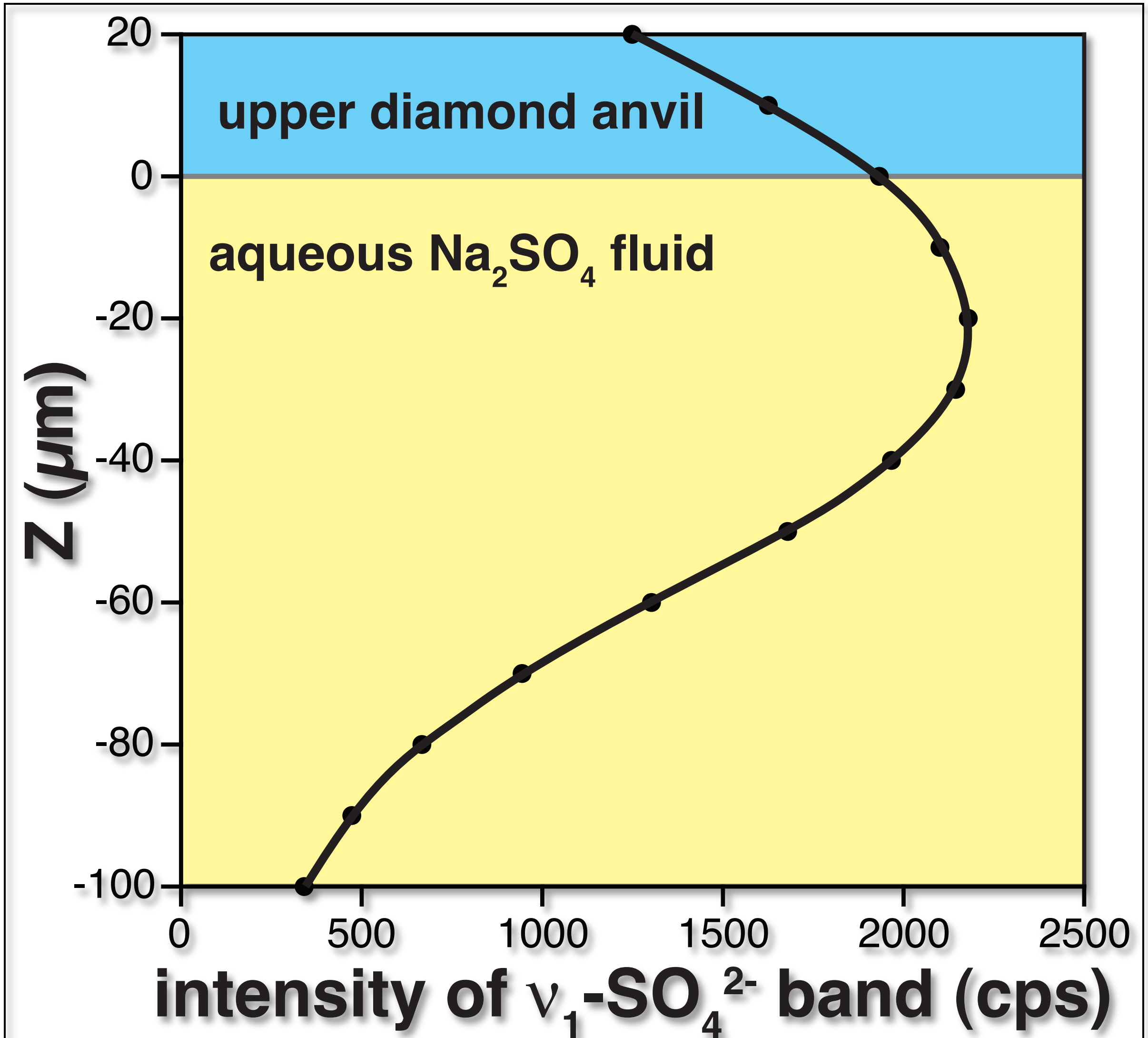
Raman spectroscopy and HDAC

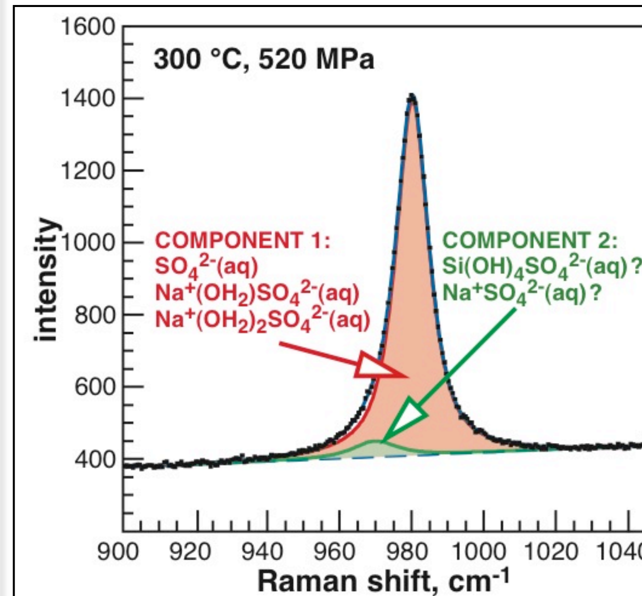
measurement of species concentration



Raman spectroscopy and HDAC

vertical scan of ν_1-SO_4^{2-} intensity in fluid

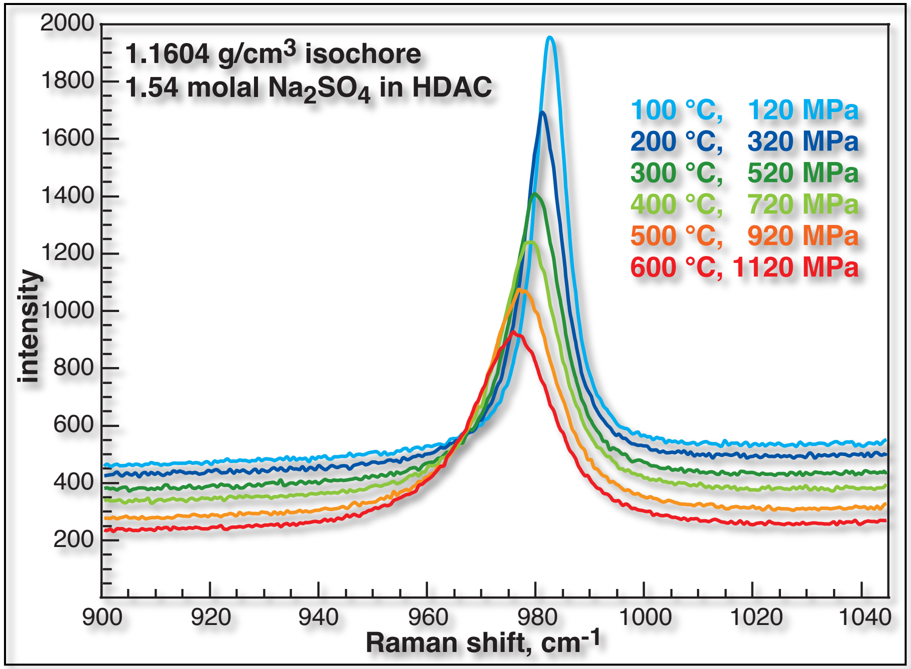


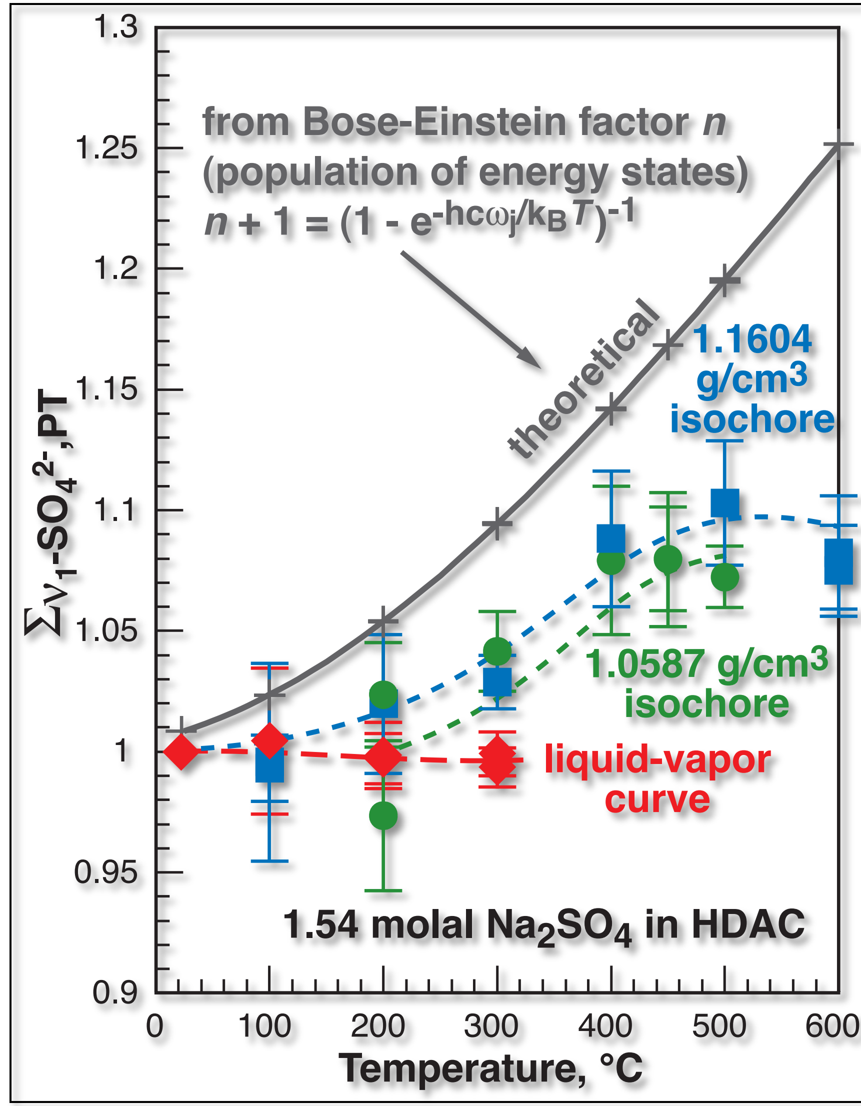


Schmidt (2009)

Raman spectroscopy and HDAC

change in ν_1-SO_4^{2-} cross section with *P* and *T*



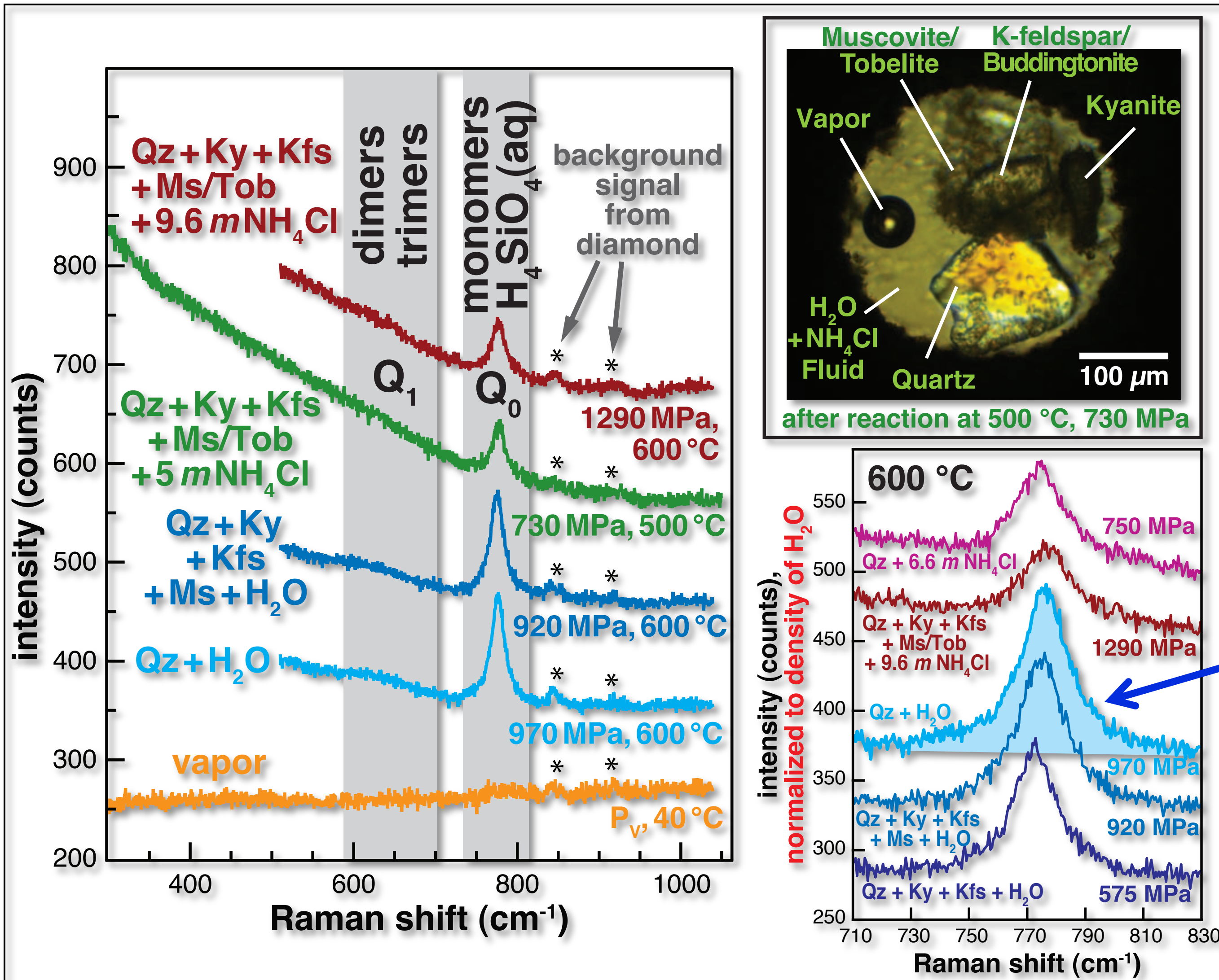


probably effect of bond expansion with temperature on polarizability

Schmidt (2009)

Raman spectroscopy and HDAC

m SiO_2(aq) in Qz+Ky+Kfs/Ms+H_2O±NH_4Cl

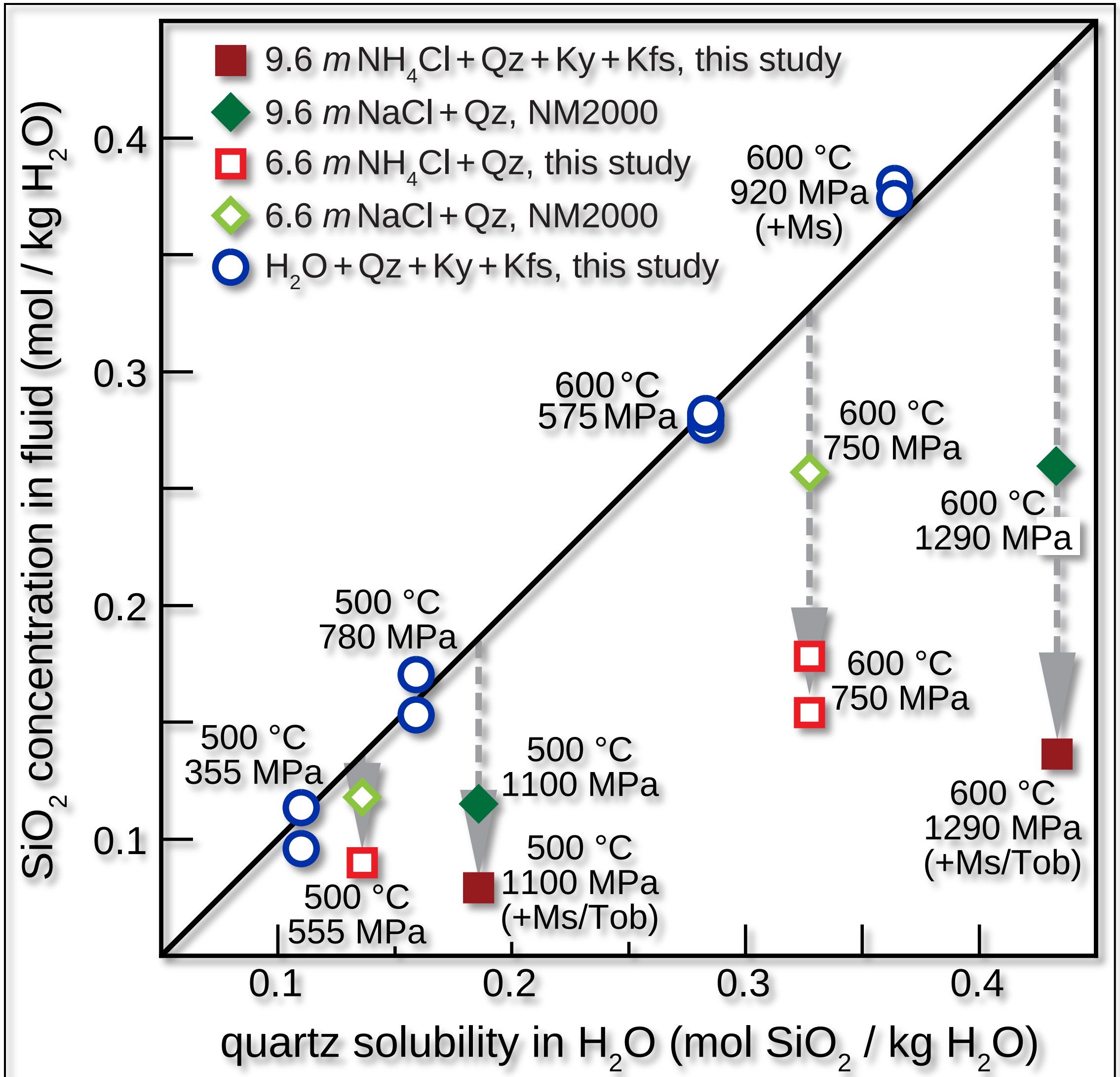


for calibration:
mSiO$_2$(aq)
= 0.375
at 600 °C,
970 MPa
(Manning 1994)

Schmidt and Watenphul (2010)

Raman spectroscopy and HDAC

m SiO_2(aq) in Qz+Ky+Kfs/Ms+H_2O±NH_4Cl



Schmidt and Watenphul (2010)

Thank you for your attention!