Raman spectroscopy at high pressure and temperature for the study of Earth's mantle and planetary minerals

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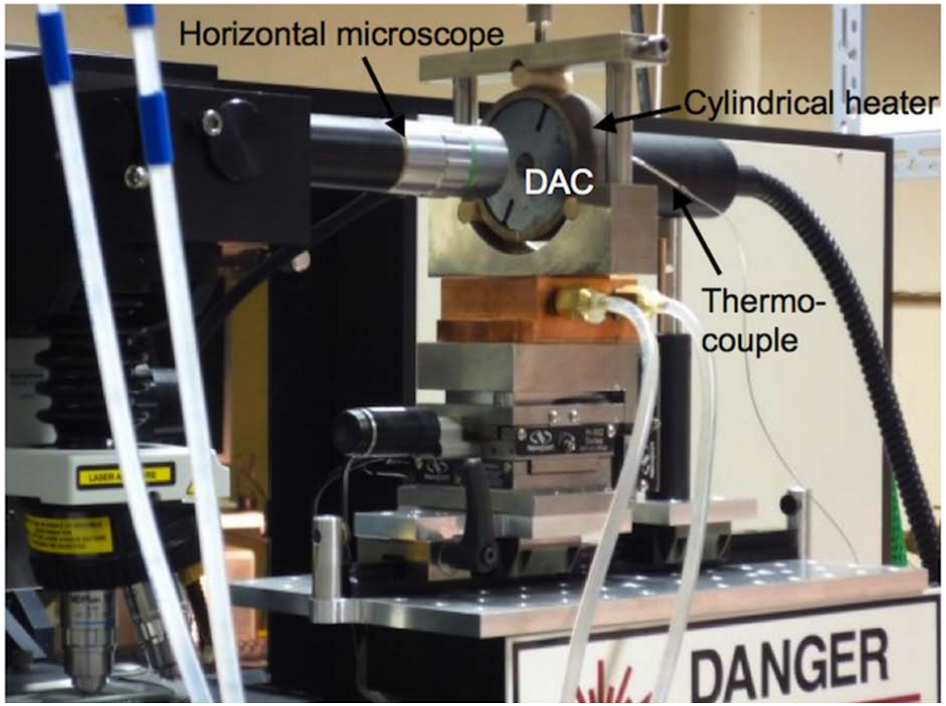
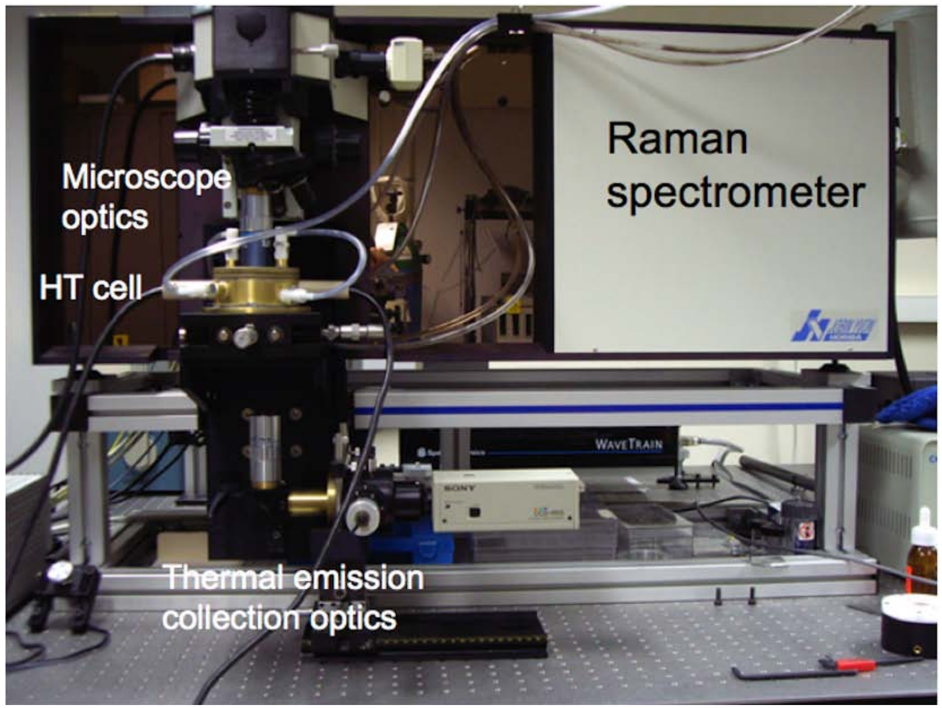
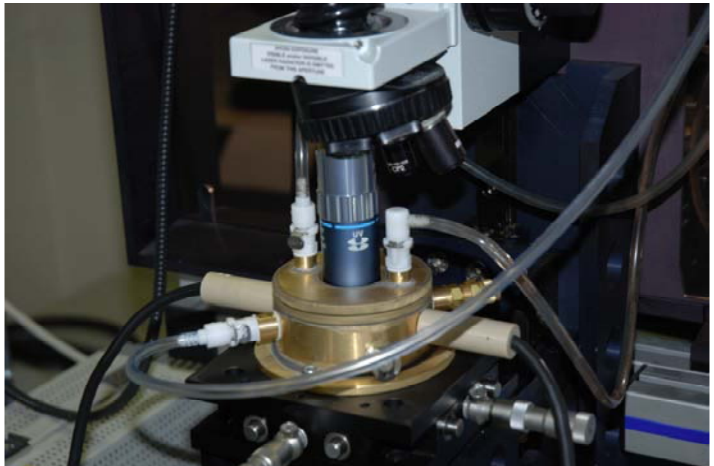
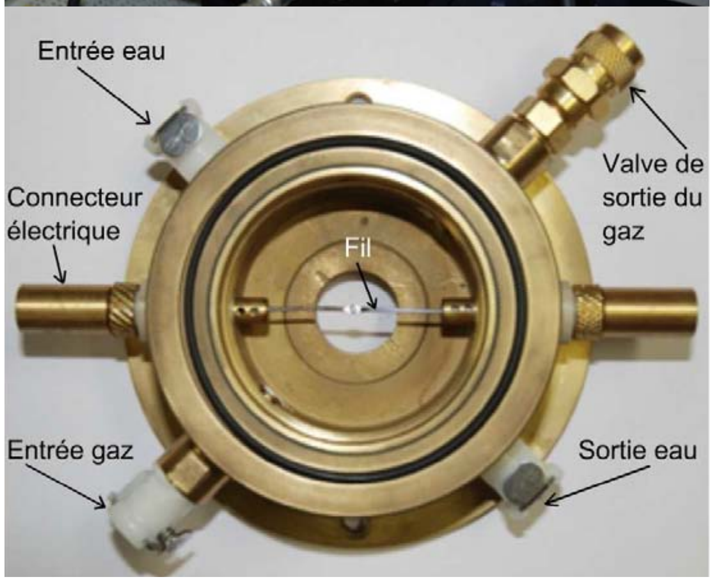
Coupling HP and HT to Raman

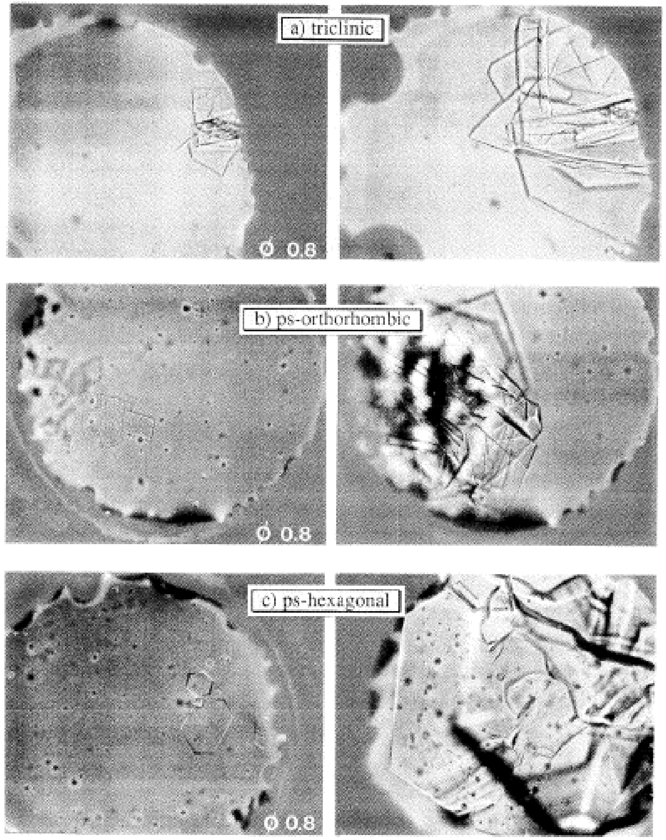




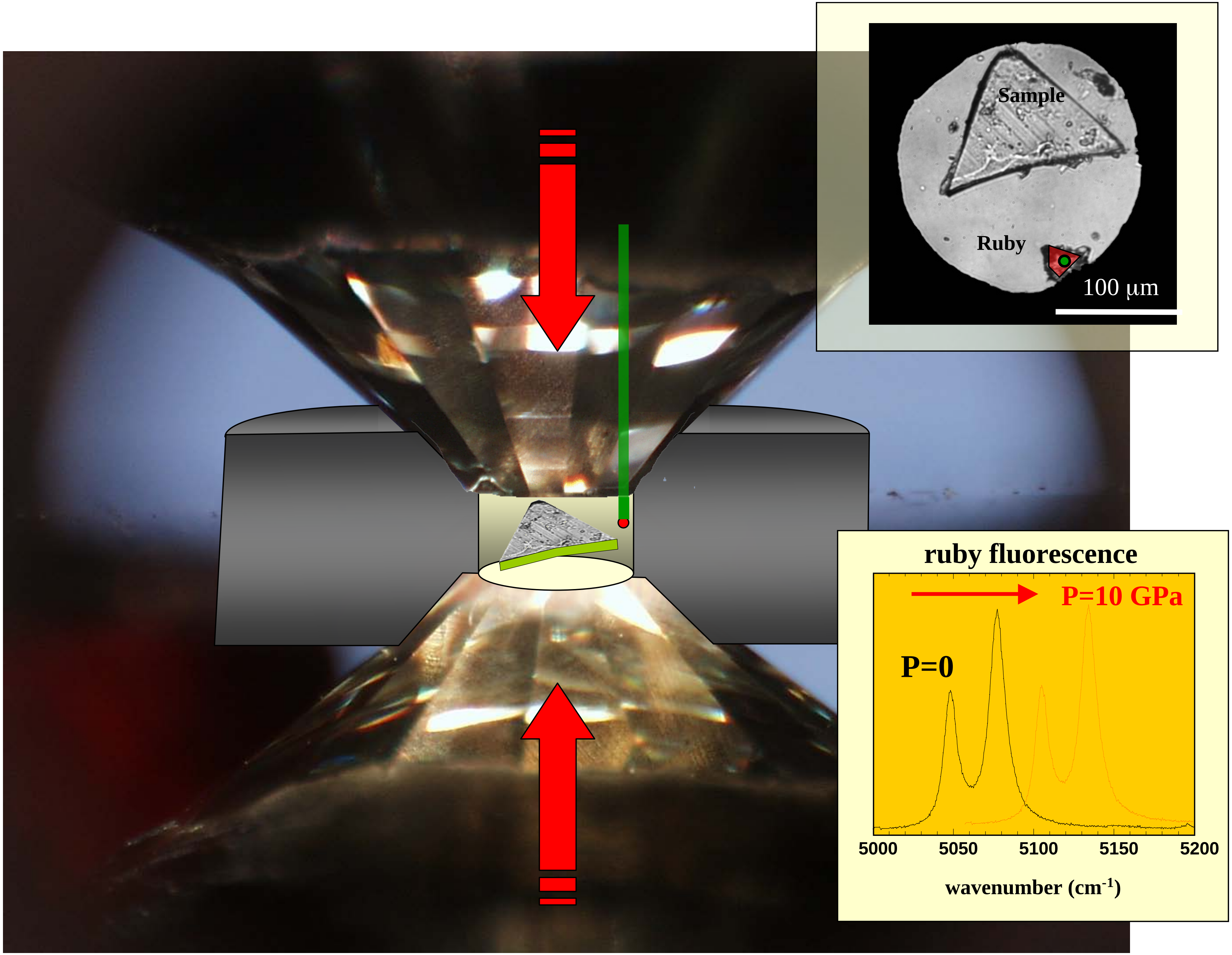
High temperatures

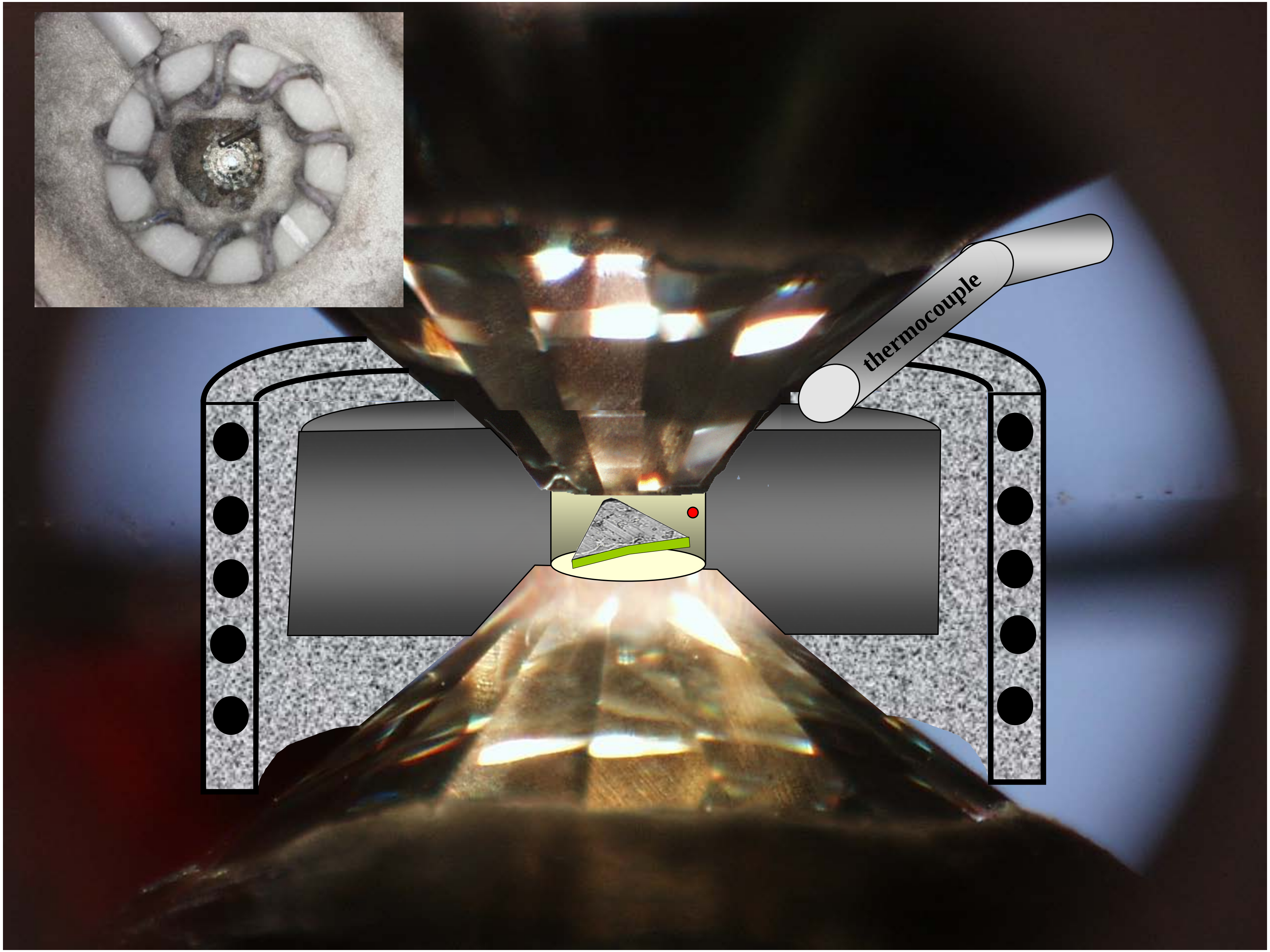


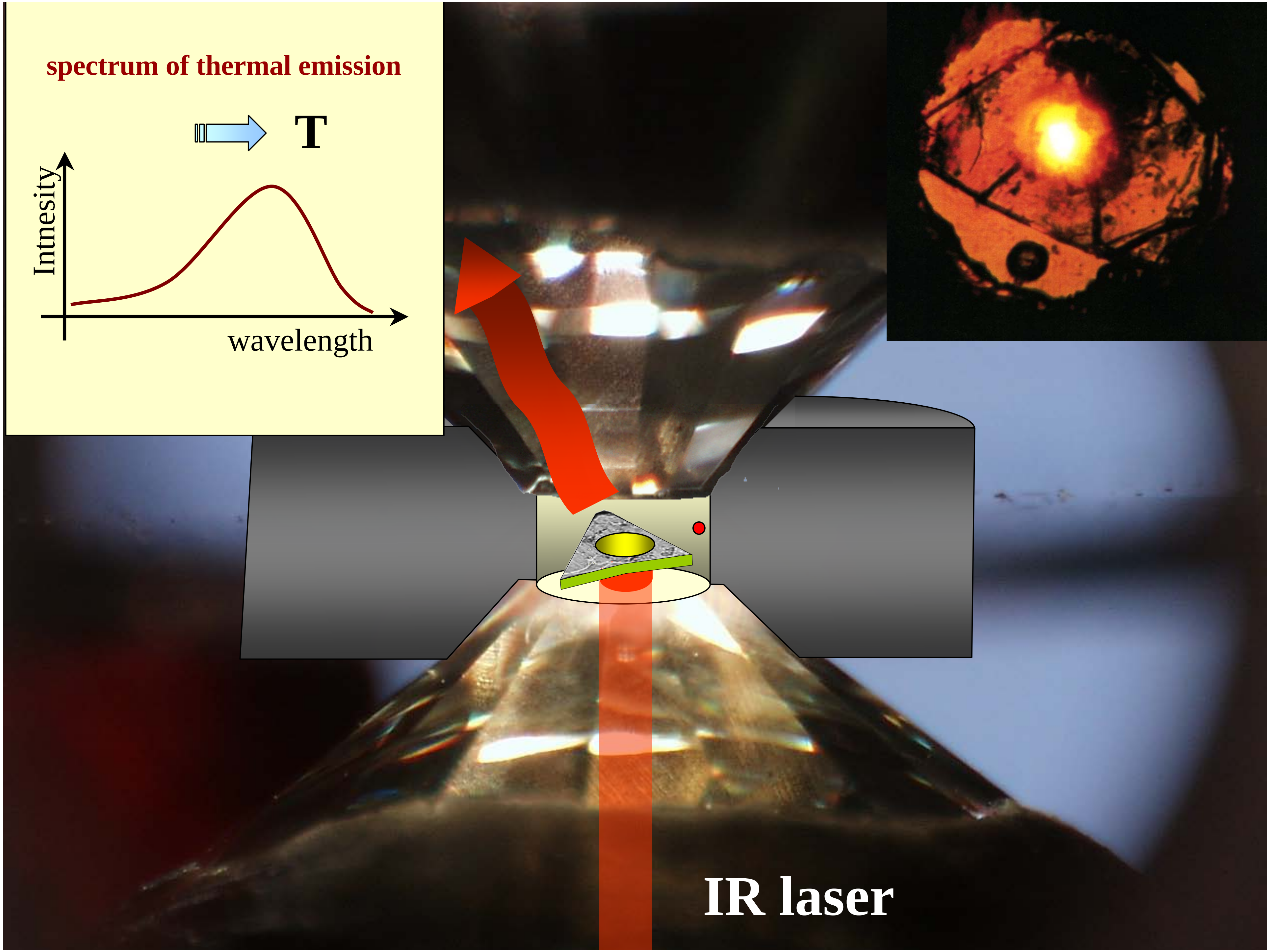


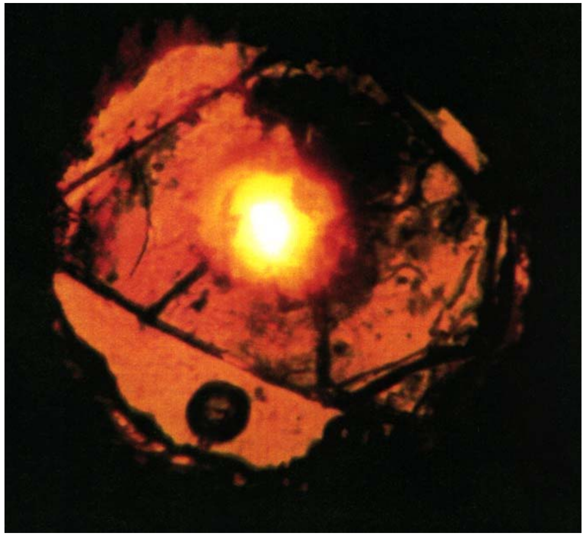


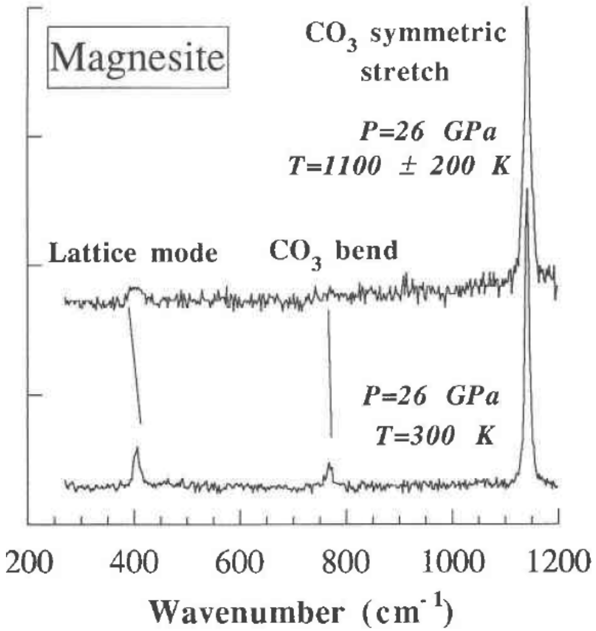
Daniel et al 1995


Sample
Ruby
100 μm
ruby fluorescence
P=10 GPa
P=0
5000
5050
5100
5150
5200
wavenumber (cm-1)

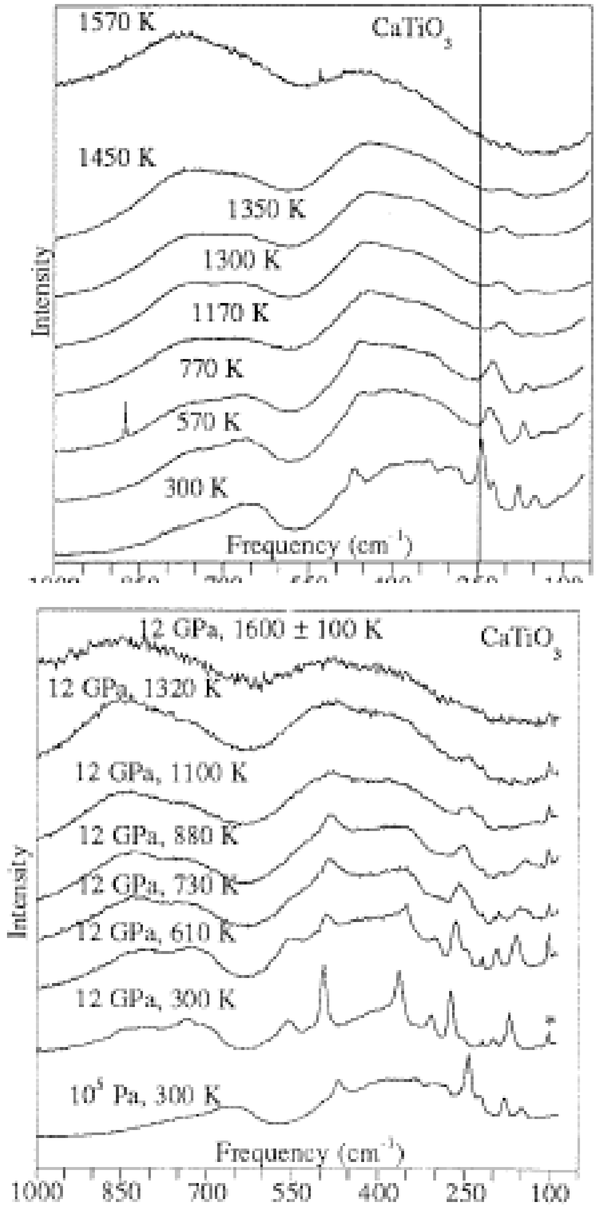

thermocouple


spectrum of thermal emission
T
Intnesity
wavelength
IR laser





Gillet 1993



Gillet et al 1993

Pressure measurements

Ruby fluorescence: up to 150 GPa

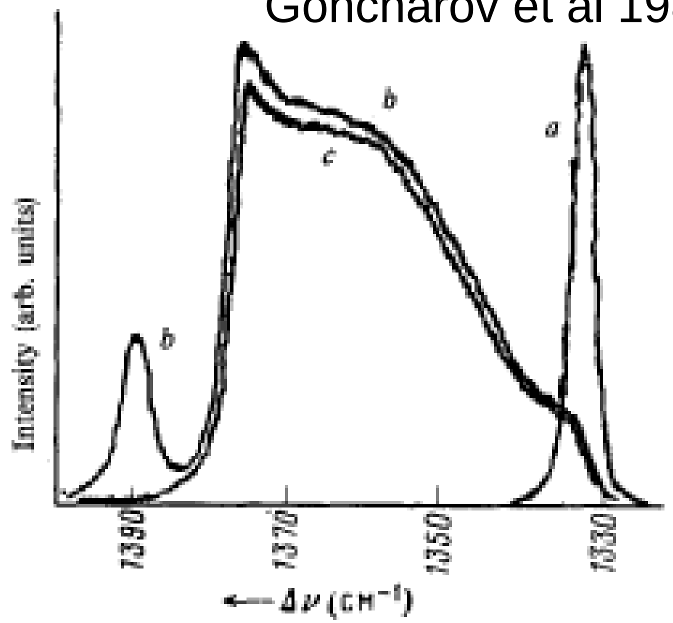
Other fluorescent sensors

Raman sensors

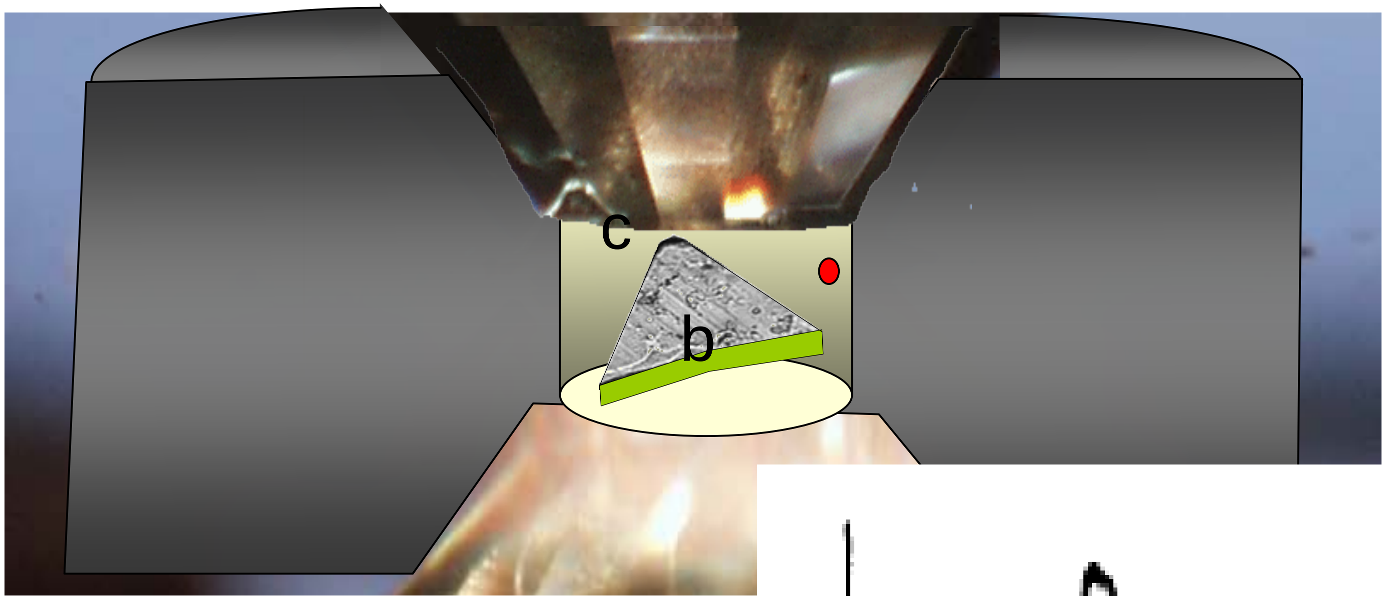
Diamond peak up to 400 GPa

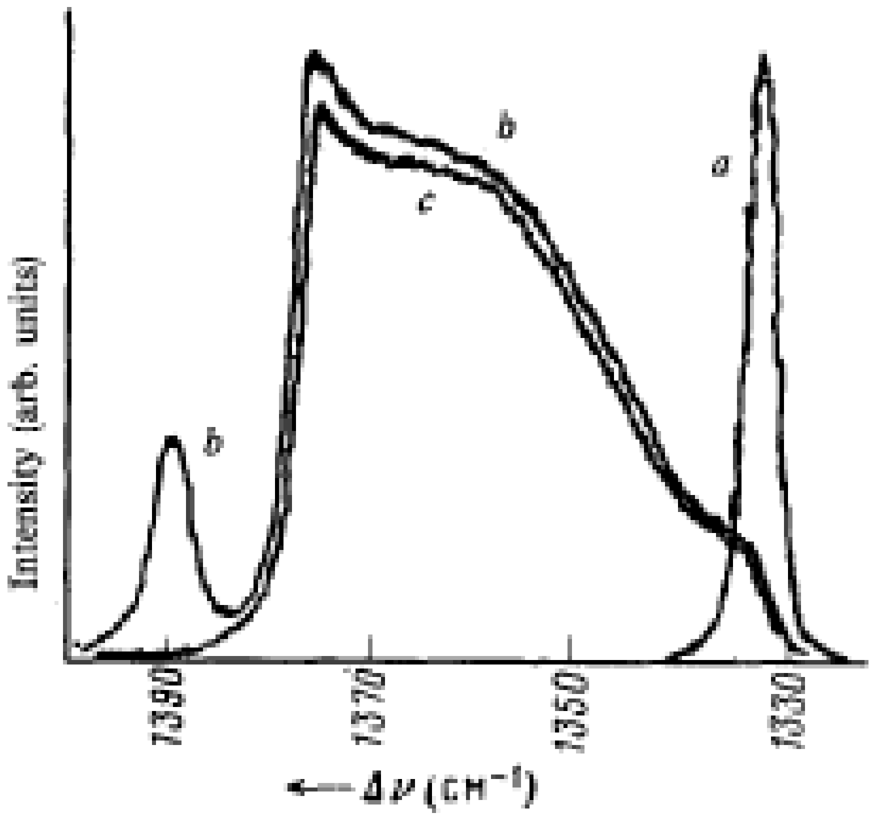
How to choose?

Goncharov et al 1985



Substance that has an incompressibility (or bulk modulus) close to the pressure range you are studying

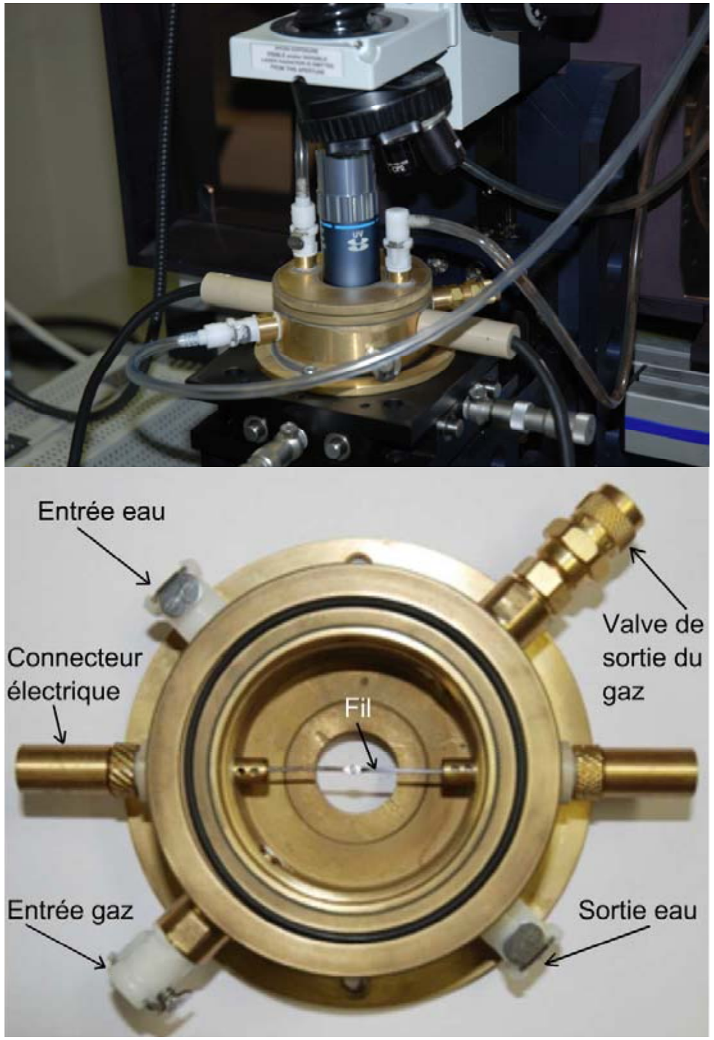


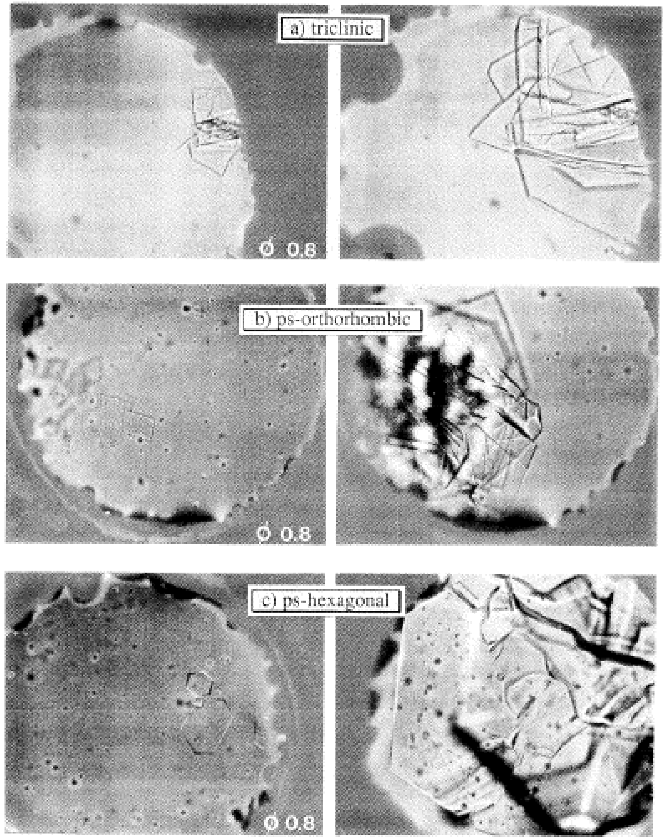


Goncharov et al 1985

Convenient because you do not need to add another material in the experimental chamber

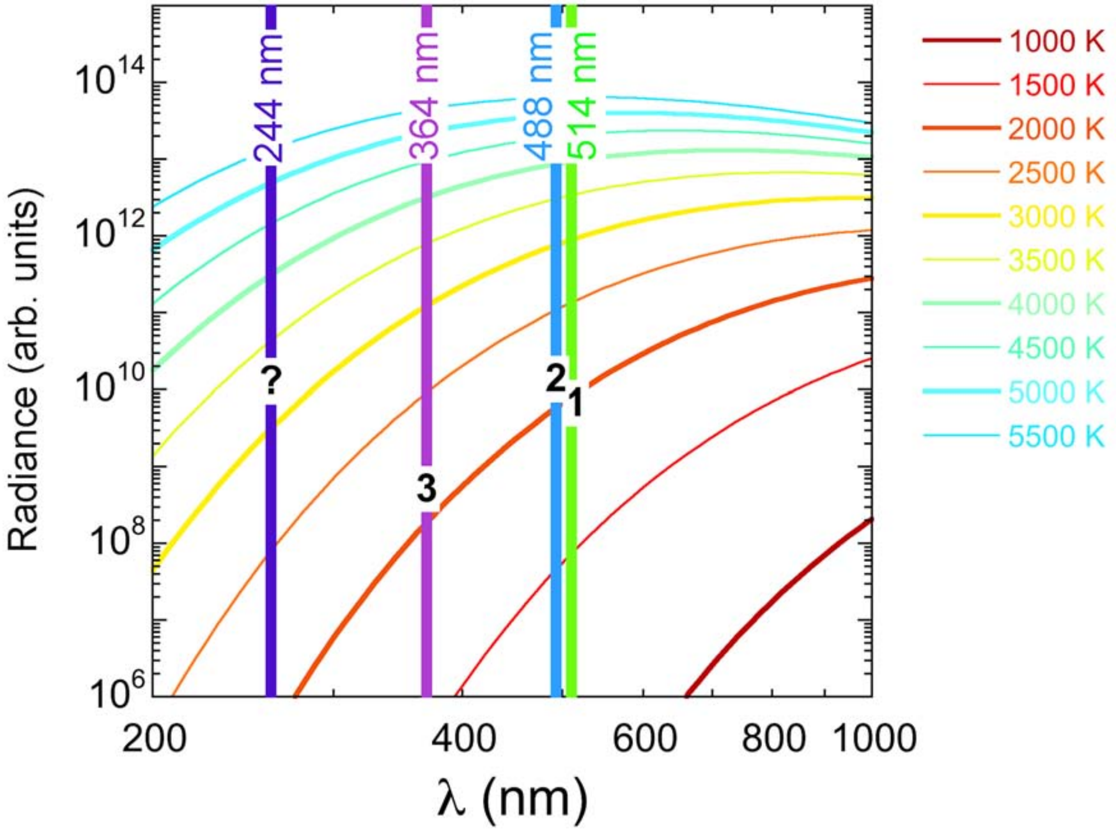
High temperatures



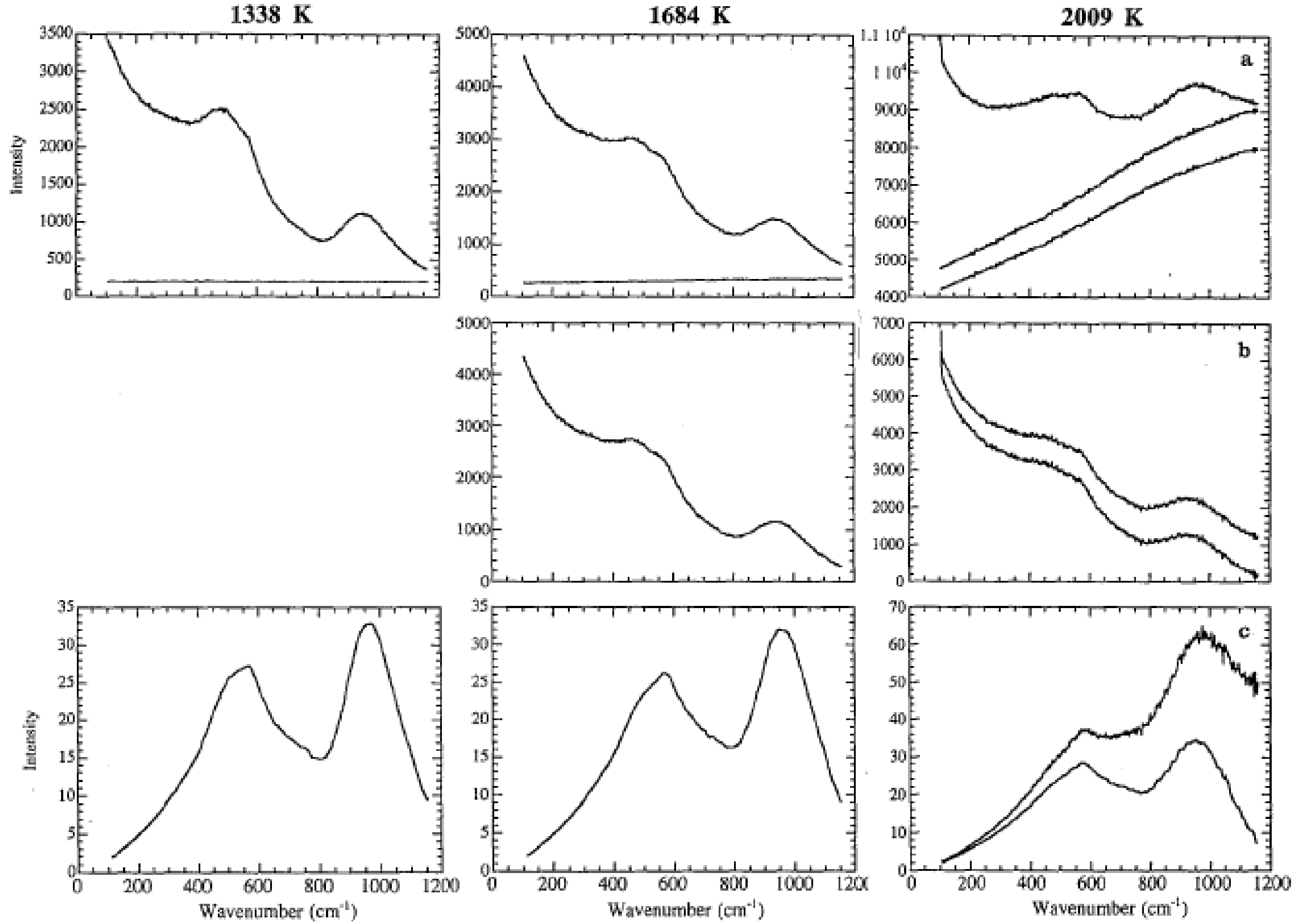


Daniel et al 1995

High temperatures



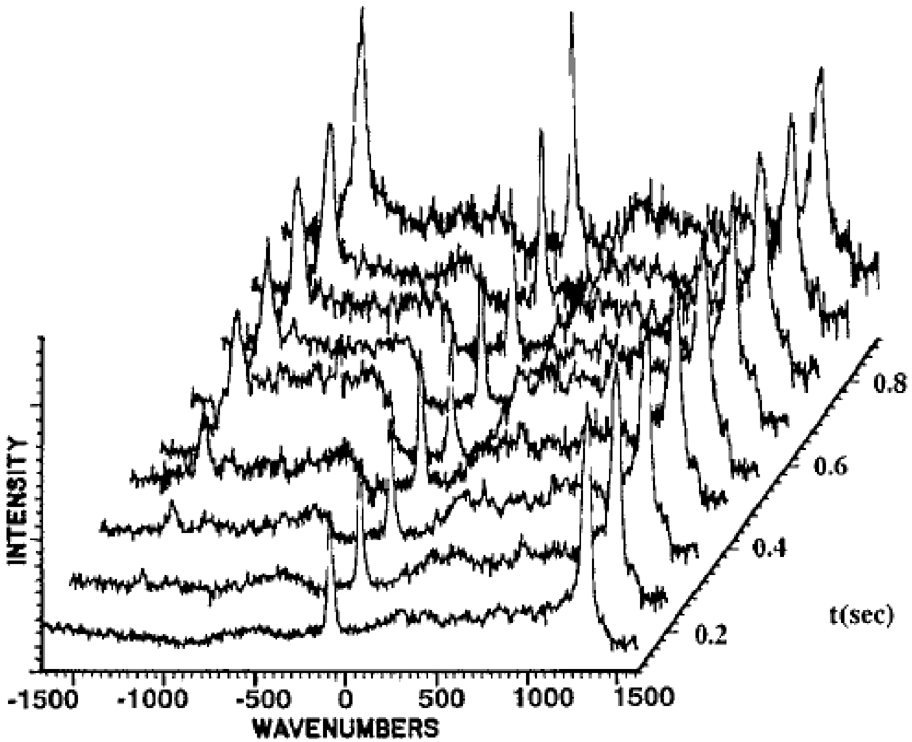
High temperatures

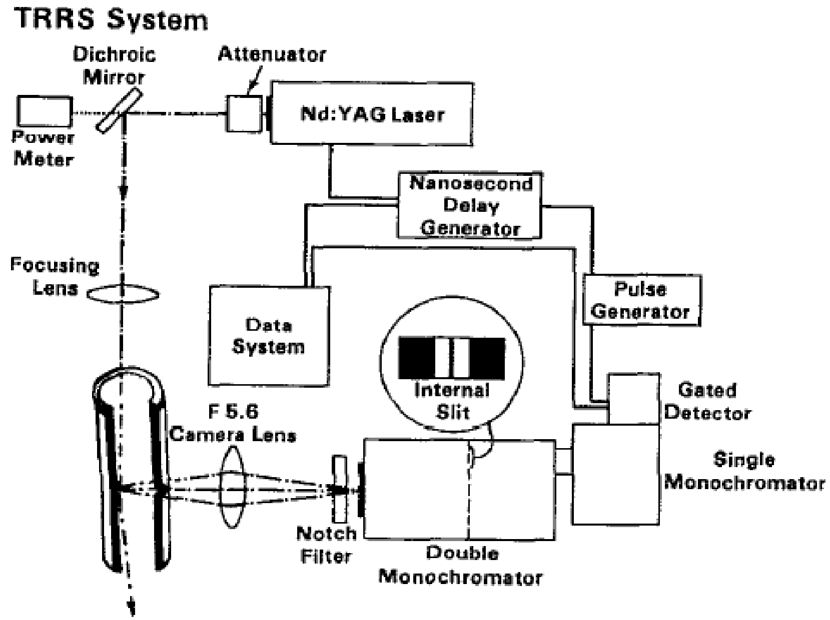


Anorthite liquid

Daniel et al 1995

High temperatures



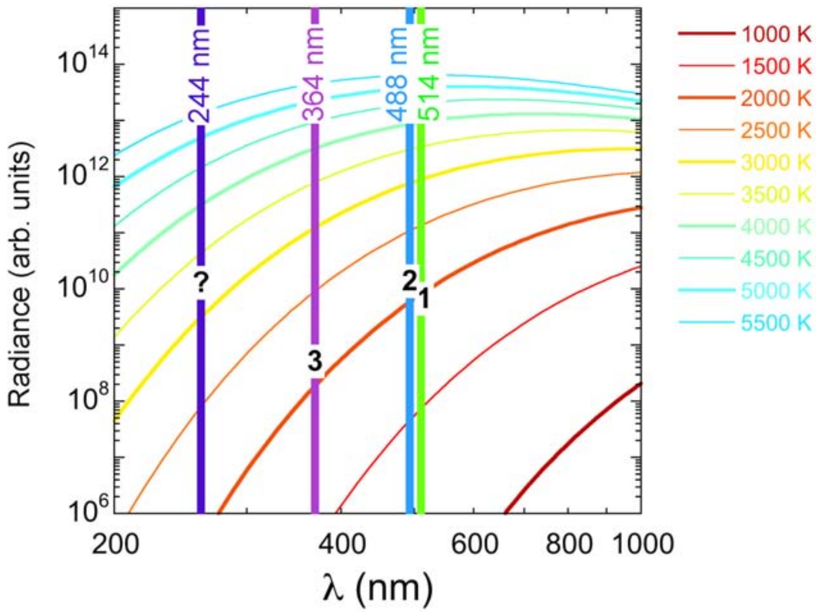


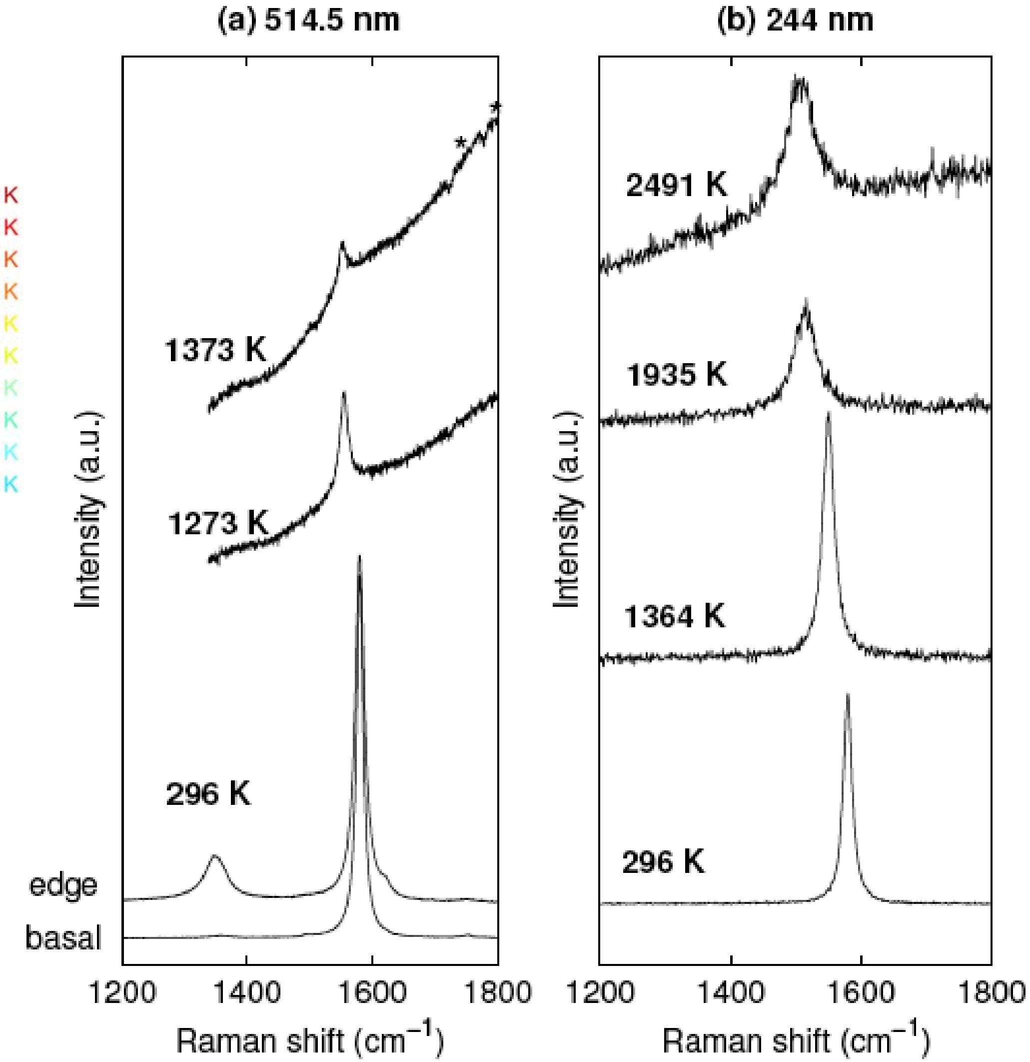
Pulsed-laser gated-detector system

BN up to 2300 K

Exarhos and Schaaf 1991

High temperatures





Why do HP-HT Raman?

Follow structural transformations of materials

Probe the interaction potential of the crystal

Define P-T calibrants for DAC cell

Calculate thermodynamic properties

Relate it to geophysical issues
- high-pressure phases in Earth
- phase transformations in meteorites
- fossil pressure

Upper mantle

Olivine : $(Mg,Fe)_2SiO_4$

Pyroxene : $(Ca,Mg,Fe)SiO_3$

Garnet : $(Ca,Mg,Fe)_3(Al,Fe)_2Si_3O_{12}$

Transition zone

β-$(Mg,Fe)_2SiO_4$

γ-$(Mg,Fe)_2SiO_4$

$(Mg,Fe)SiO_3$-ilmenite

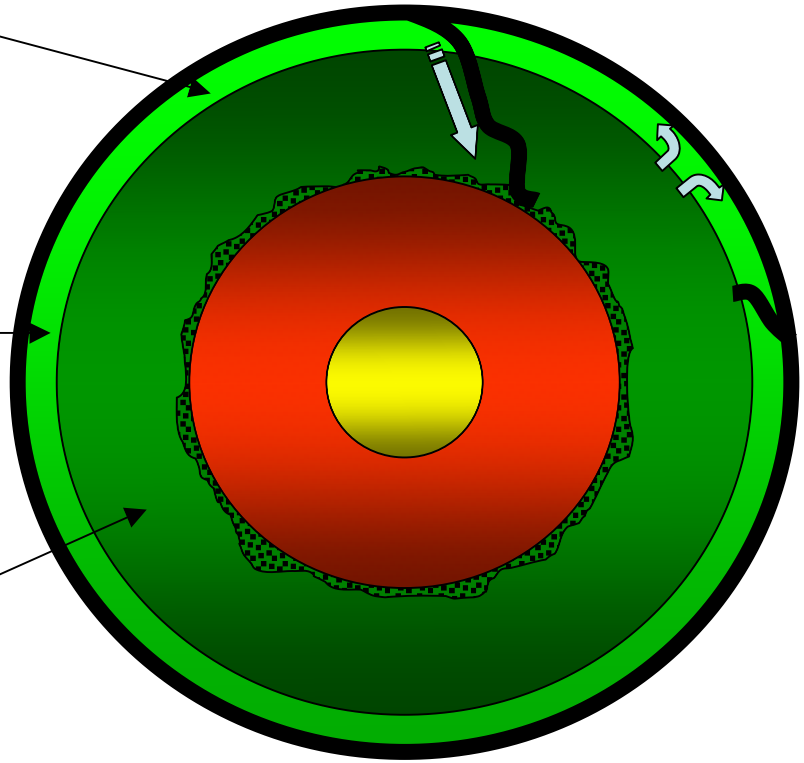
Majoritic garnet

Lower mantle

$(Mg,Fe)SiO_3$-perovskite

$(Mg,Fe)O$ ferropericlase

$CaSiO_3$-perovskite

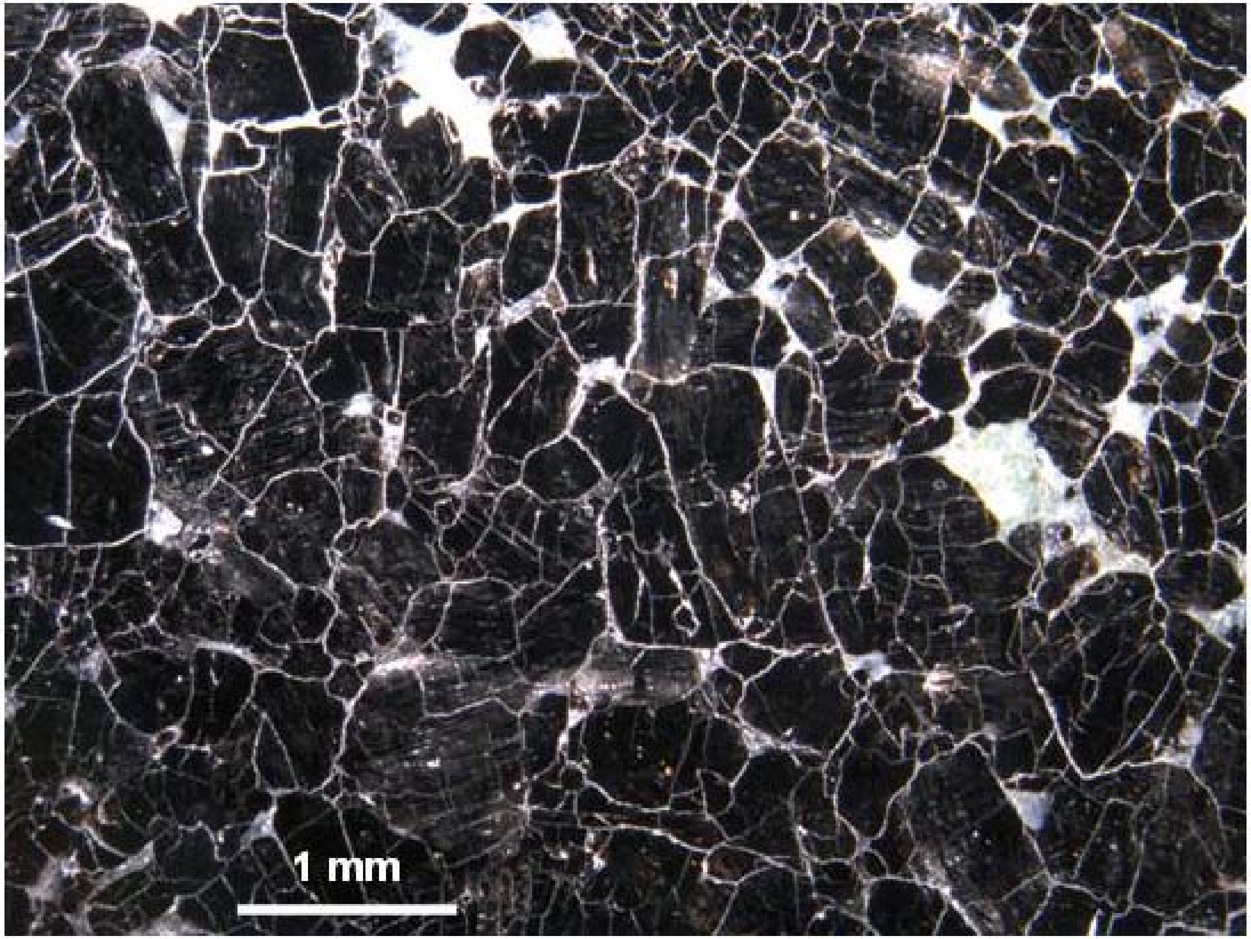


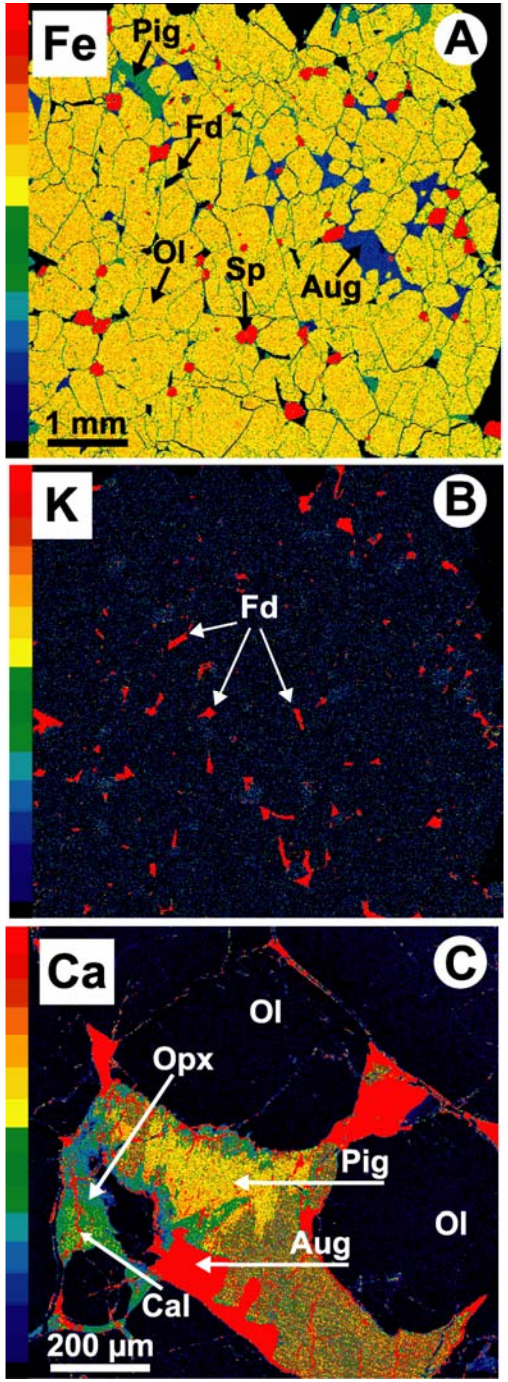
The high-pressure phases of the transition zone and lower mantle are inferred from experiments, minerals observed in shock vein melts of chondritic meteorites and inclusions in diamonds

NWA2737 (Diderot)

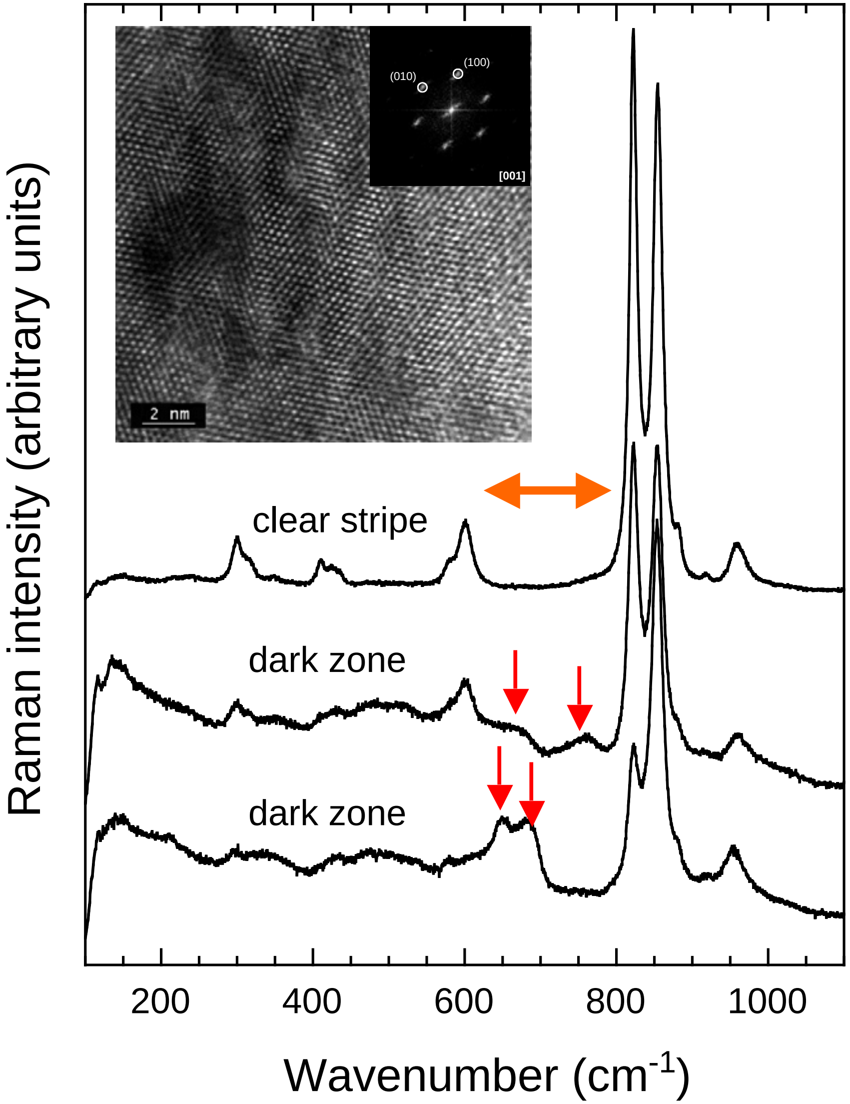
Dunite with homogeneous olivine Fo_{79}

T= 1150-1070°C, fO_2 ≈ FMQ

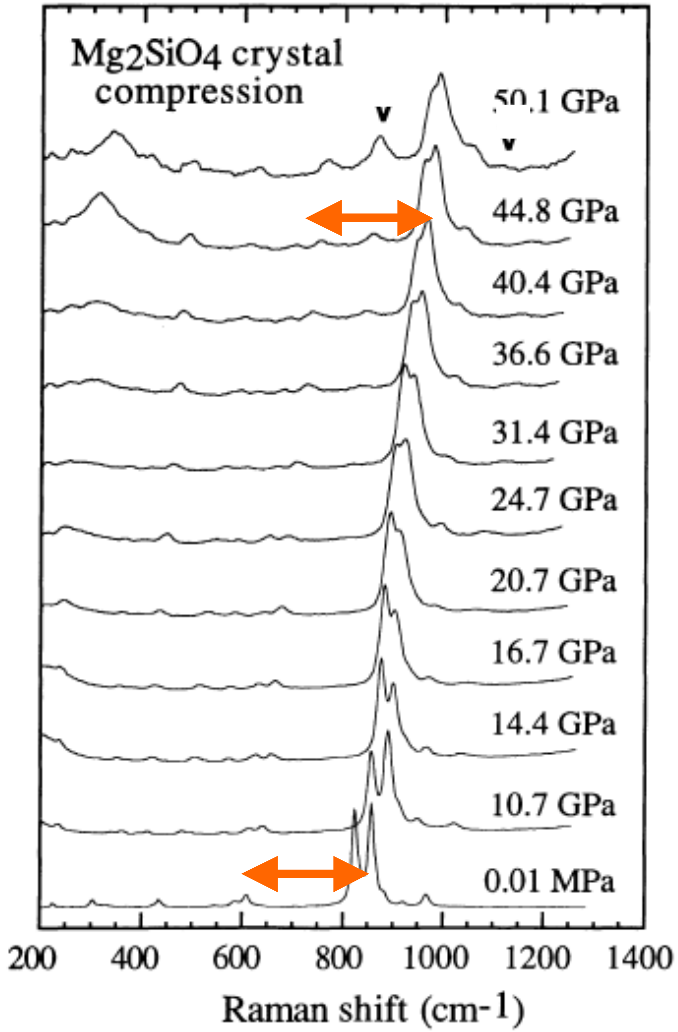




Raman spectroscopy

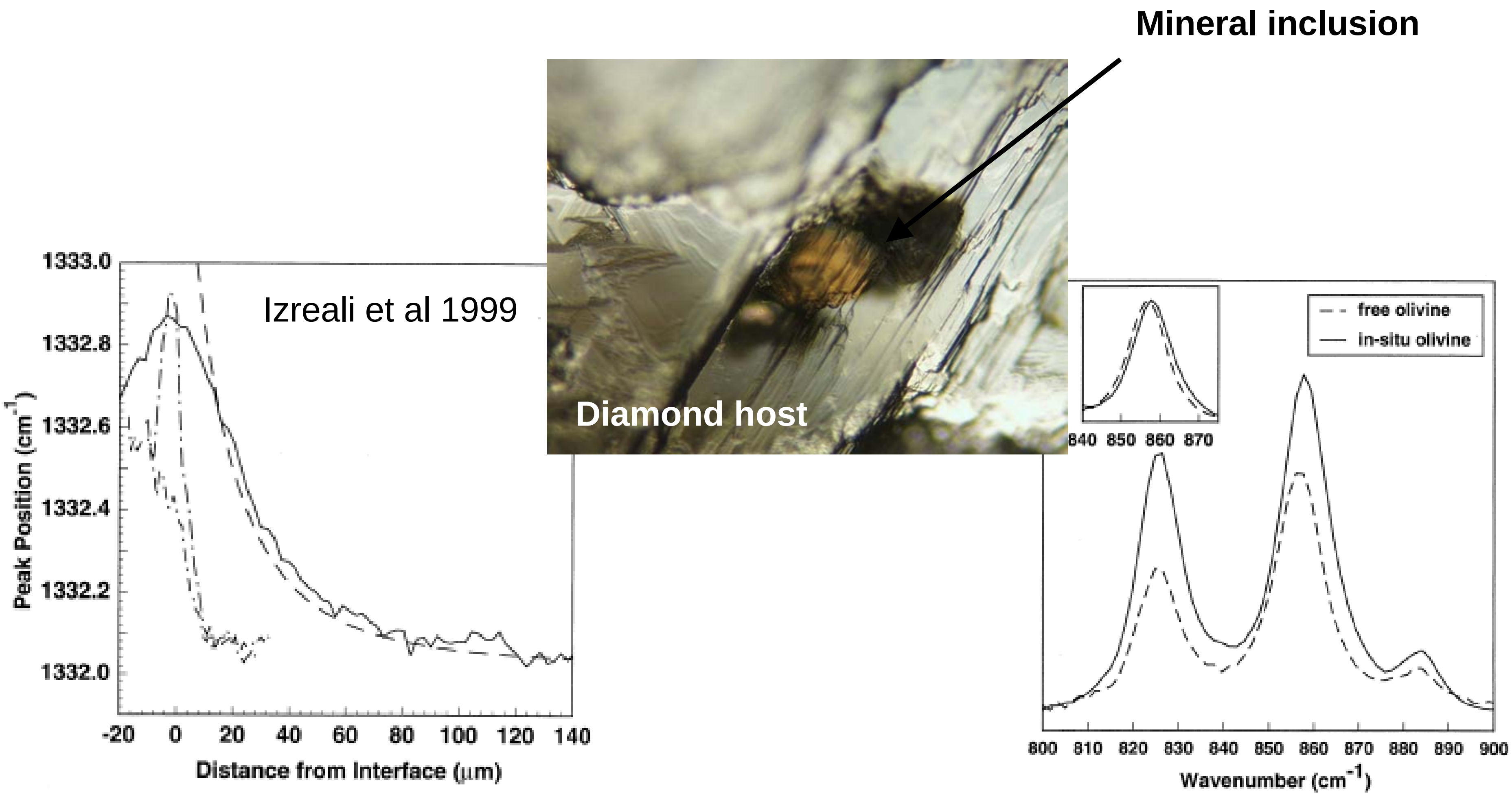


Van de Moortele *et al*. AM 2007ab



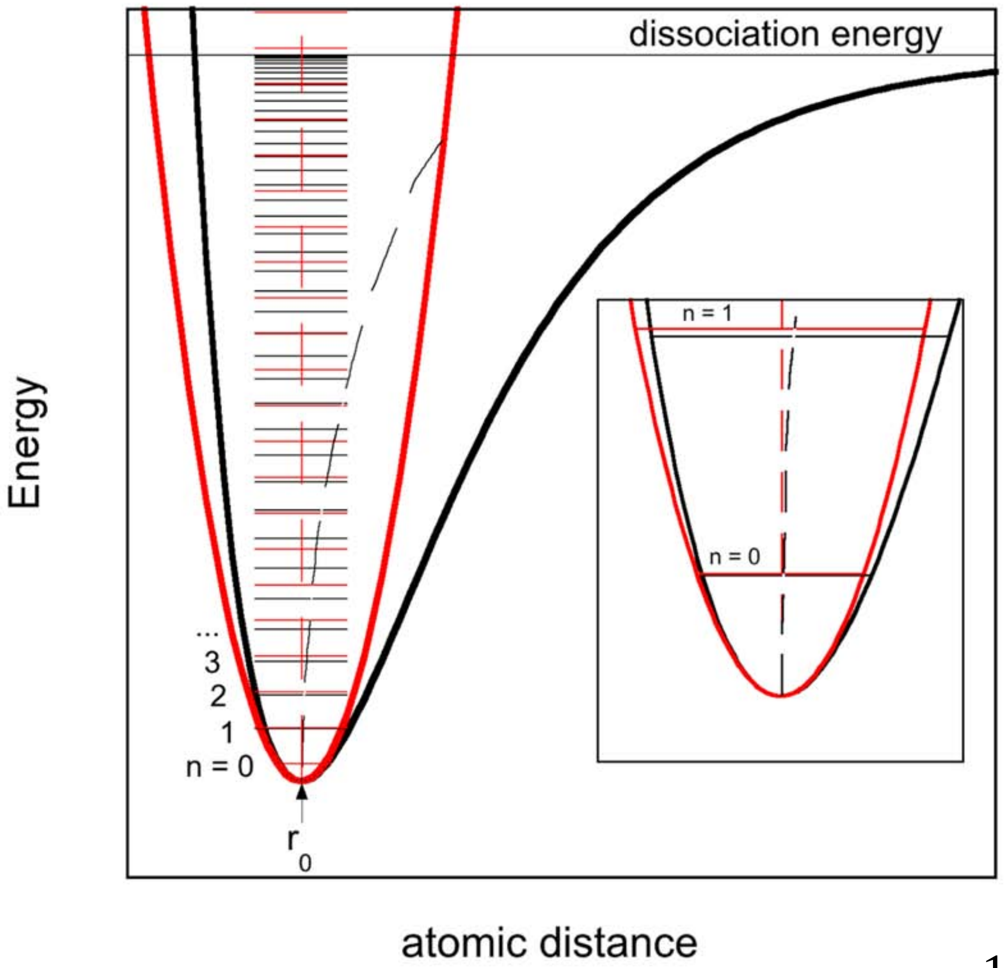
Mg_2SiO_4 Durben *et al*. AM 1993
Mg_2GeO_4 Reynard *et al.* PCM 1994

Paleostress

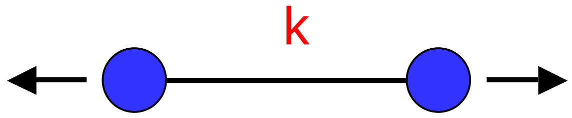


Raman shift of the diamond line because of residual pressure in the inclusions
0.7 cm^{-1} = 1 GPa along <100>, 2.2 cm^{-1} along <111>
Olivine 5-6 cm^{-1} = 1 GPa

Lattice potentials and vibrational levels



crystal = harmonic oscillator



Vibrational energy

$$E_n = (n + \frac{1}{2})\, h\nu$$

$$P_n = \frac{e^{-E_n / k_B T}}{\sum_{i=0}^{N} e^{-E_i / k_B T}}$$

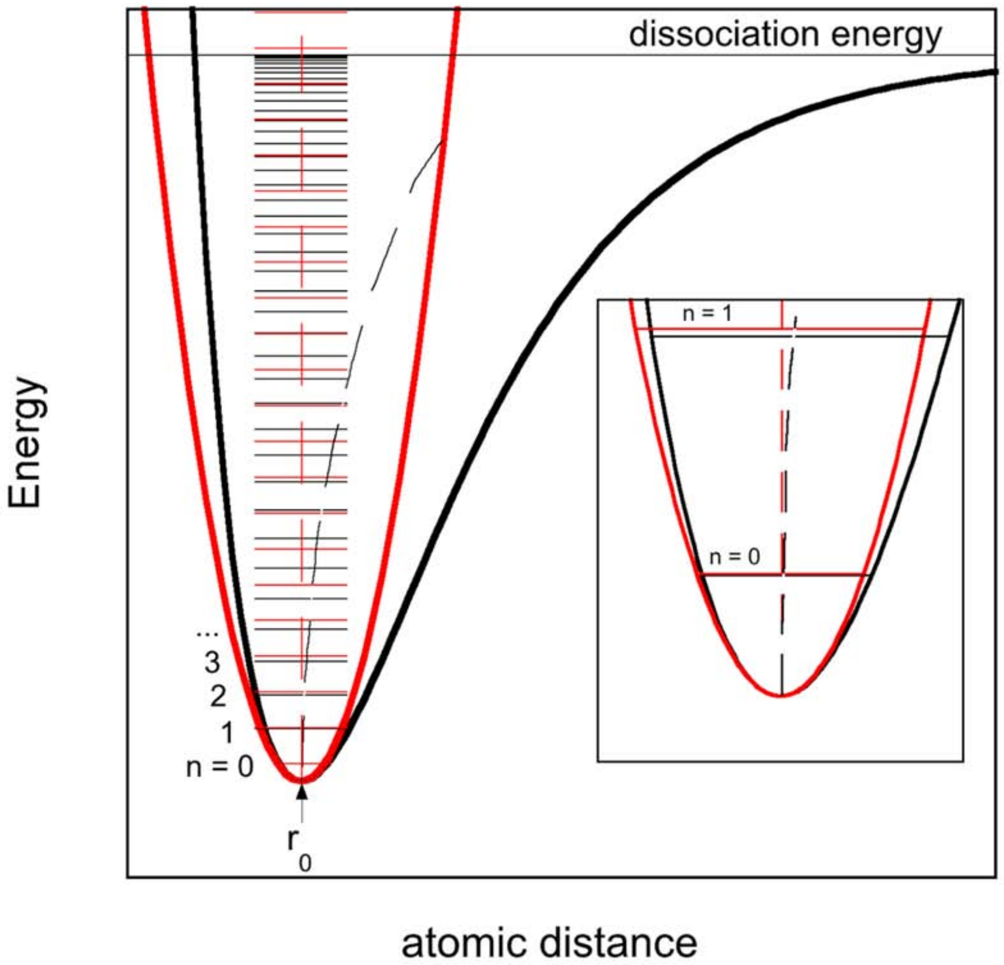
$$U_{vib} = \sum_i P_i \, E_i$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

← Force constant

← Reduced mass; E Δm/mm'

Lattice potentials and vibrational levels



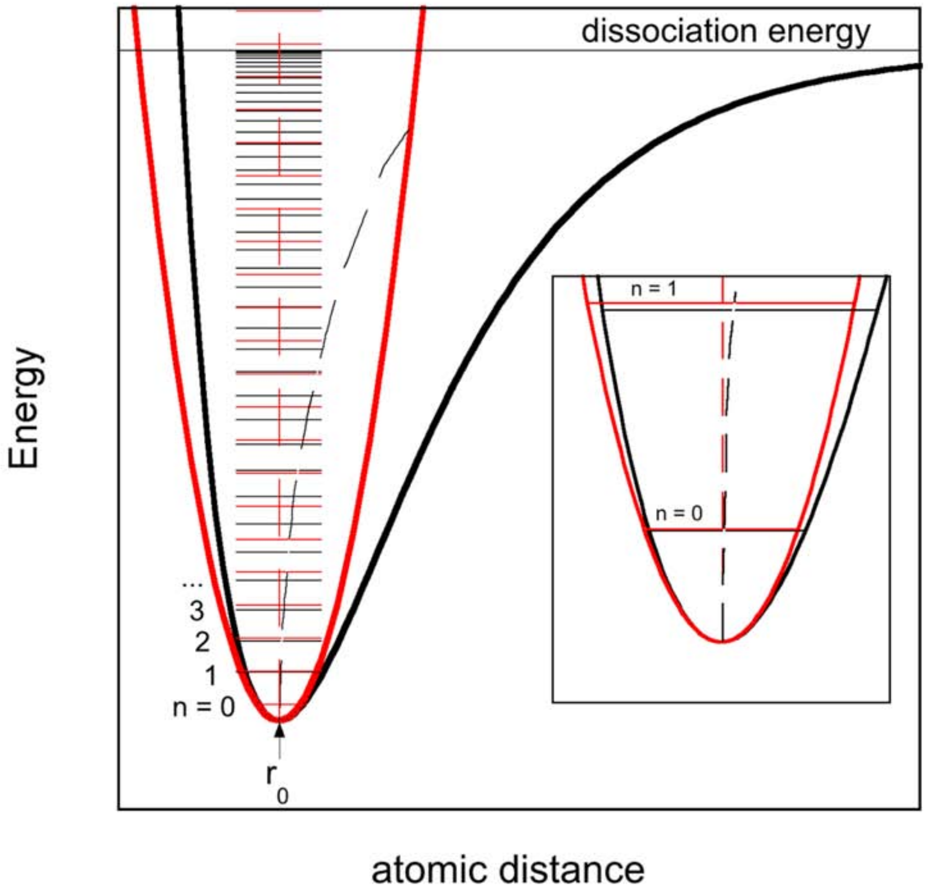
Anharmonicity

e.g. Morse potential

$$\omega_e = \frac{1}{2\pi}\sqrt{\frac{k_e}{\mu}} \qquad a = \sqrt{\frac{k_e}{2D_e}}$$

$$E_n/hc = \omega_e(n+1/2) - \frac{\omega_e^2}{4D_e}(n+1/2)^2$$

Lattice potentials and vibrational levels



$$\omega_e = \frac{1}{2\pi}\sqrt{\frac{k_e}{\mu}}$$

$$a = \sqrt{\frac{k_e}{2D_e}}$$

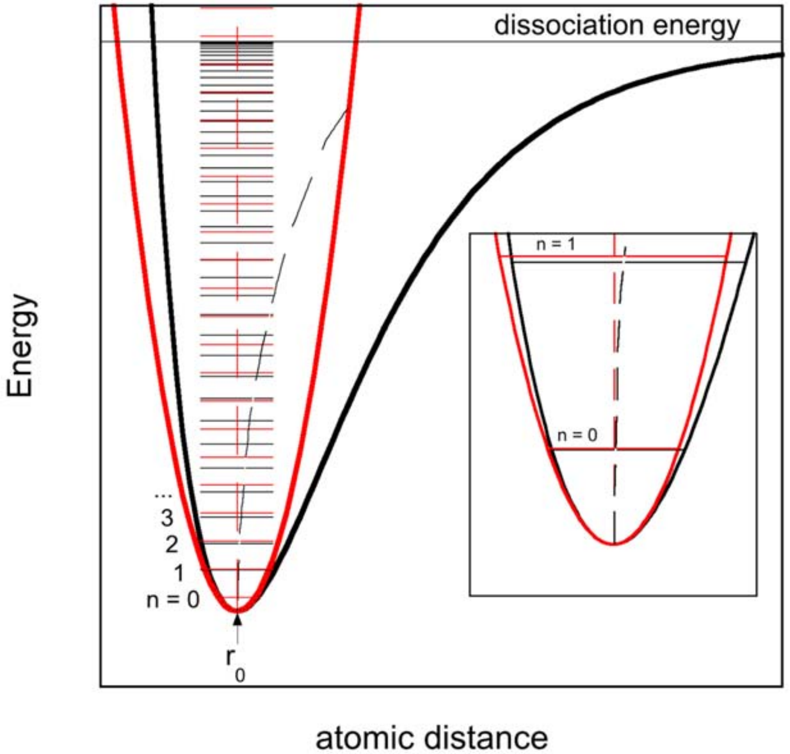
$$E_n / hc = \omega_e\left(n + 1/2\right) - \frac{\omega_e^2}{4D_e}\left(n + 1/2\right)^2$$

$$u_i = \mathrm{hc}\omega_i/\mathrm{k_B}T,\; x_i = \omega_i/4D_e$$

$$(s'/s)\cdot f_{anh} = \prod_i \frac{u_i' \exp\left(-u_i'/2 + x_i' u_i'/4\right)/\left(1-\exp(-u_i')\right)\left[1 - 2x_i' u_i' \exp\left(-u_i'\right)/\left(1-\exp(-u_i')\right)^2\right]}{u_i \exp\left(-u_i/2 + x_i u_i/4\right)/\left(1-\exp(-u_i)\right)\left[1 - 2x_i u_i \exp\left(-u_i\right)/\left(1-\exp(-u_i)\right)^2\right]}$$

Bigeleisen and Mayer 1947; Urey 1947

Lattice potentials and vibrational levels

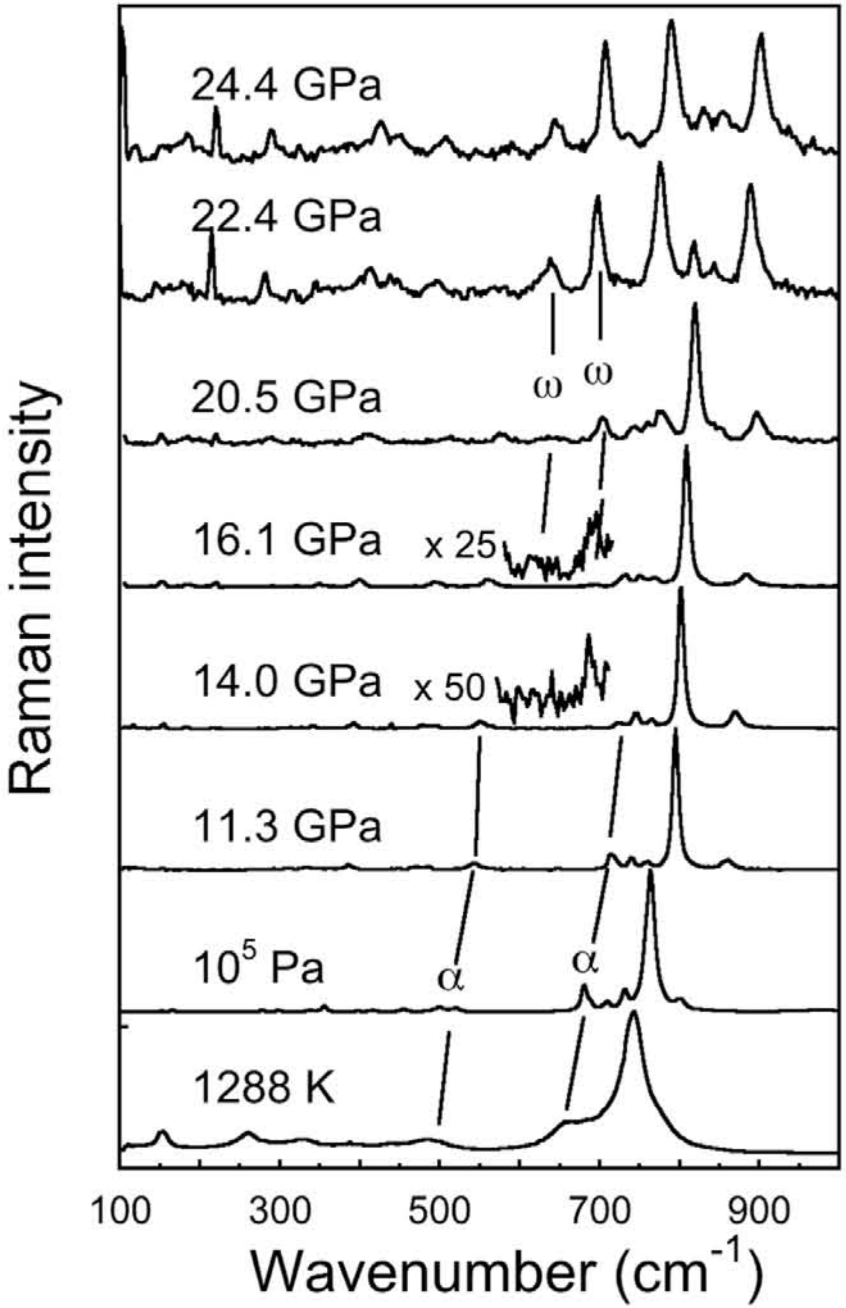


$$V(\langle X_a \rangle) = 1/2 f_0 \langle X_a \rangle^2 + 1/6 g_0 \langle X_a \rangle^3 + 1/24 h_0 \langle X_a \rangle^4 + \cdots,$$

$$a(T) = a_0 - 1/2(g_0/f_0^2)k_B T,$$
$$\omega^2(T) = \omega_0^2[1 - (g_0^2/2f_0^3)k_B T]$$

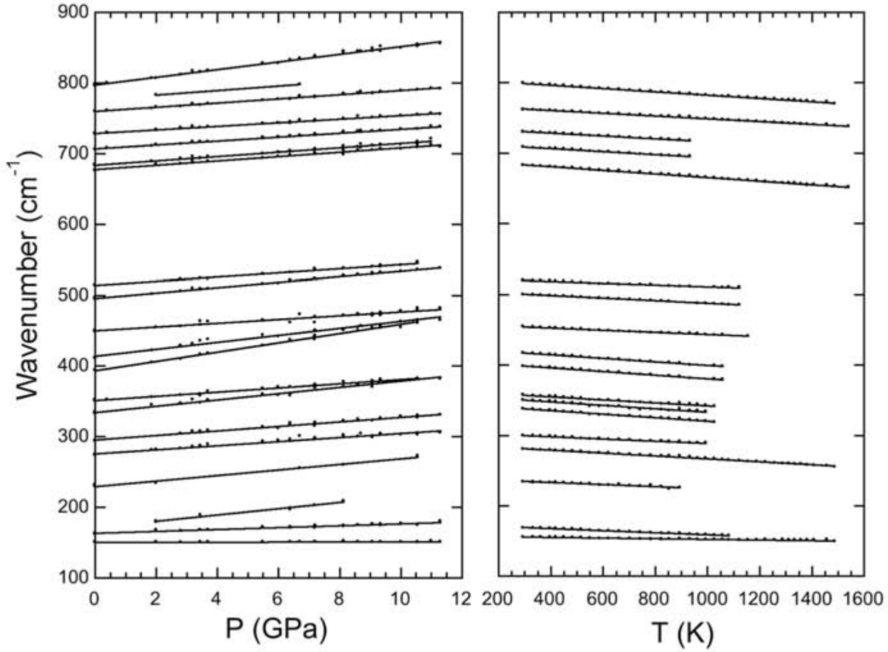
Varying P and T allows exploring the potential parameters and their variations with volume

A case study Mg_2GeO_4



Olivine analogue to forsterite

Modes soften with T and harden with P



Mode anharmonicity

Vibrational frequencies

$\nu_i(P,T_0)$ and $\nu_i(P_0,T)$

Anharmonic parameters

extrinsic (volume dependent)

$\gamma_{iT} = -(\partial \ln\nu_i/\partial \ln V)_{Tamb} = K_T(\partial \ln\nu_i/\partial P)_{Tamb}$

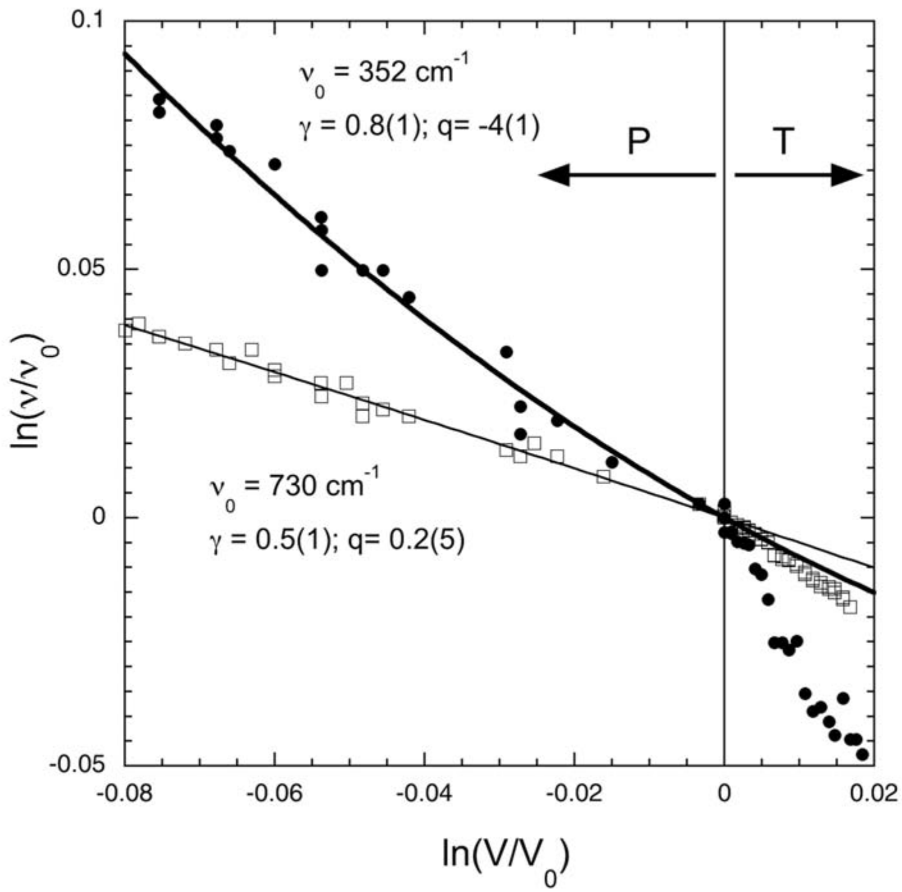
$$\ln(\nu(P_0,T))_{qh} = \ln(\nu(P_0,T_0)) - \left[(\gamma/q)\left(\left(\left(V(P_0,T)/V(P_0,T_0)\right)\right)^q - 1\right)\right]$$

$\gamma_{iP} = -(\partial \ln\nu_i/\partial \ln V)_{Pamb} = -1/\alpha\ (\partial \ln\nu_i/\partial T)_{Pamb}$

intrinsic (volume independent)

$a_i = (\partial \ln\nu_i/\partial T)_V$

$m_i = (\partial \ln a_i/\partial \ln V)_T$



Mode anharmonicity

Vibrational frequencies

$\nu_i(P,T)$

Anharmonic parameters

extrinsic (volume dependent)

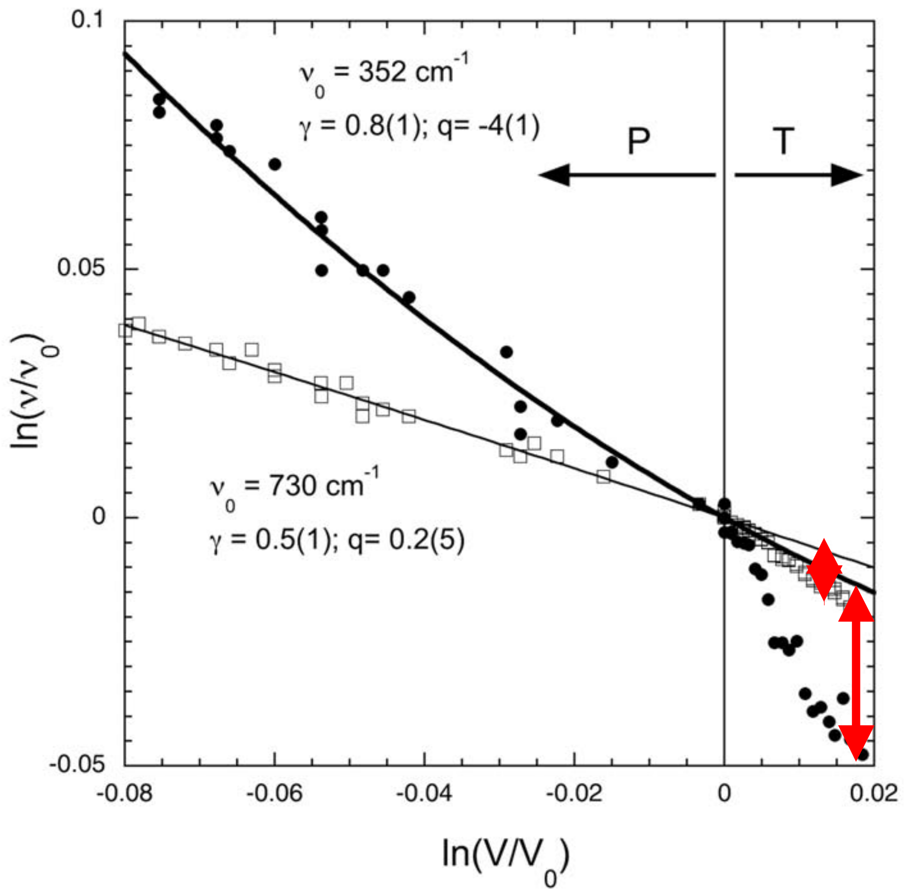
$\gamma_{iT} = -(\partial \ln\nu_i/\partial \ln V)_{Tamb} = K_T(\partial \ln\nu_i/\partial P)_{Tamb}$

$\gamma_{iP} = -(\partial \ln\nu_i/\partial \ln V)_{Pamb} = -1/\alpha\ (\partial \ln\nu_i/\partial T)_{Pamb}$

intrinsic (volume independent)

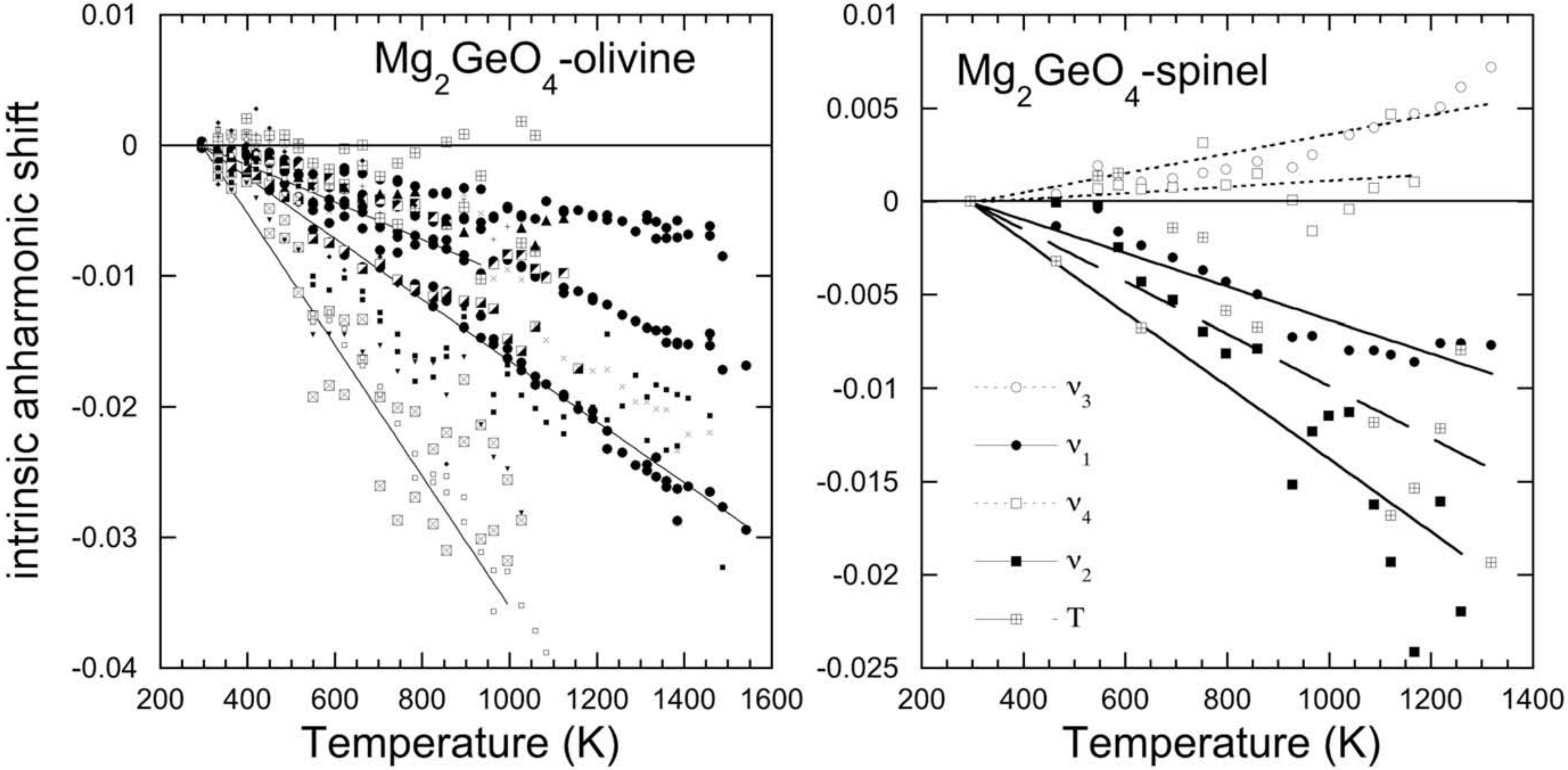
$a_i = (\partial \ln\nu_i/\partial T)_V$

$m_i = (\partial \ln a_i/\partial \ln V)_T$



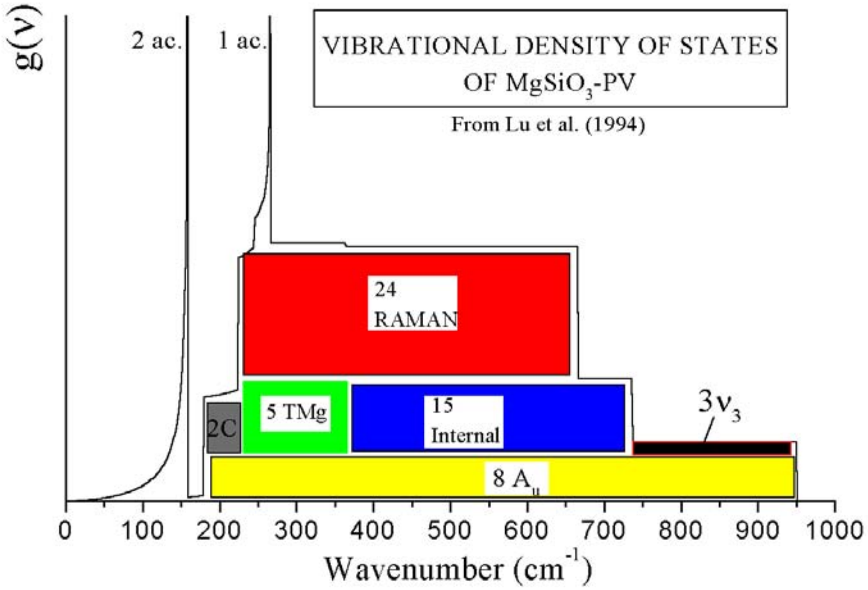
Small quantities difficult to measure

Intrinsic anharmonic parameters



$$\ln(\nu(P_0,T))_{\mathrm{measured}} - \ln(\nu(P_0,T))_{qh} = \int_{T_0}^{T_m} a_i \, dT = \Delta\nu_{th}$$

THERMODYNAMIC MODELLING



Vibrational frequencies

$\nu_i(P,T)$

Anharmonic parameters

$\gamma_{iT} = -(\partial \ln\nu_i/\partial \ln V)_{Tamb} = K_T(\partial \ln\nu_i/\partial P)_{Tamb}$

$\gamma_{iP} = -(\partial \ln\nu_i/\partial \ln V)_{Pamb} = -1/\alpha\ (\partial \ln\nu_i/\partial T)_{Pamb}$

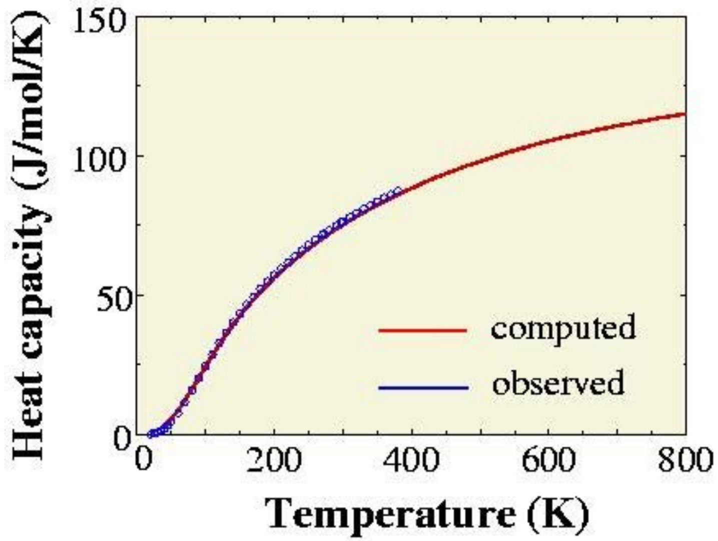
$a_i = (\partial \ln\nu_i/\partial T)_V$

$m_i = (\partial \ln a_i/\partial \ln V)_T$

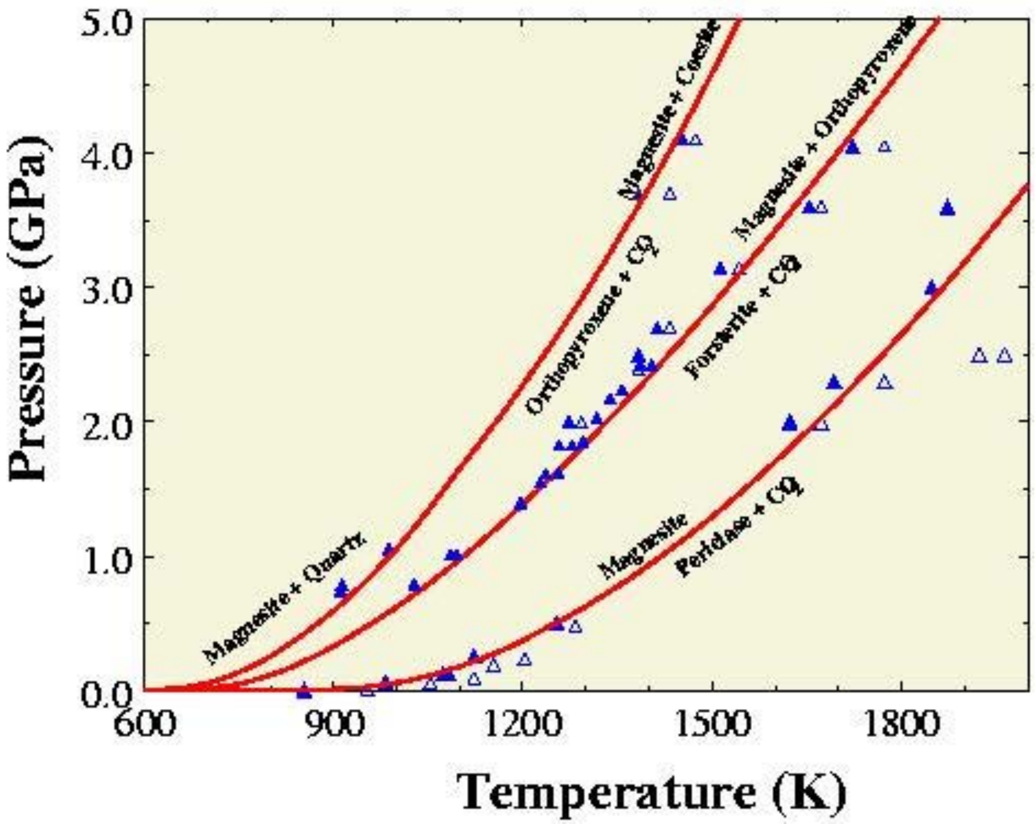
$$F_{vib} = \int \left[\frac{h\nu}{2} + k_B T ln\left(1 - exp\left(\frac{-h\nu}{k_B T}\right)\right) + a k_B T^2 \right] g(\nu) d\nu$$

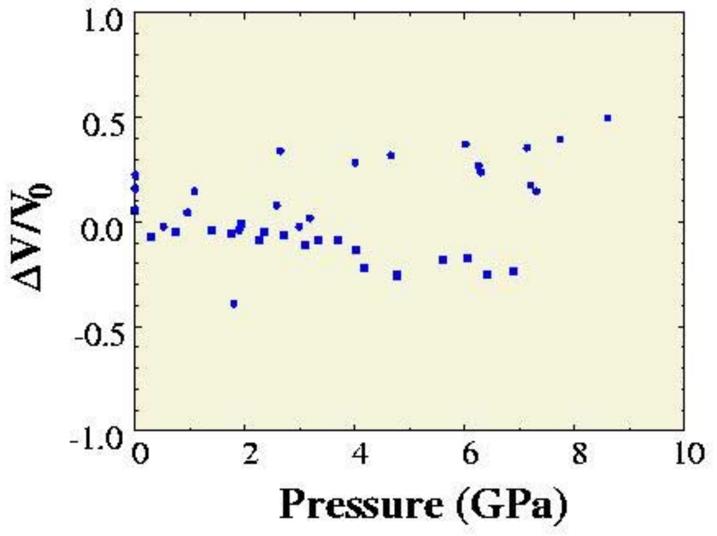
$$P_{th} = \int \left[\frac{\gamma_T}{V} \left(\frac{h\nu}{2} + \frac{h\nu}{\left(exp\left(\frac{h\nu}{k_B T}\right) - 1\right)} \right) - \frac{m a k_B T^2}{V} \right] g(\nu) d\nu$$

Carbonates stability at high P and T

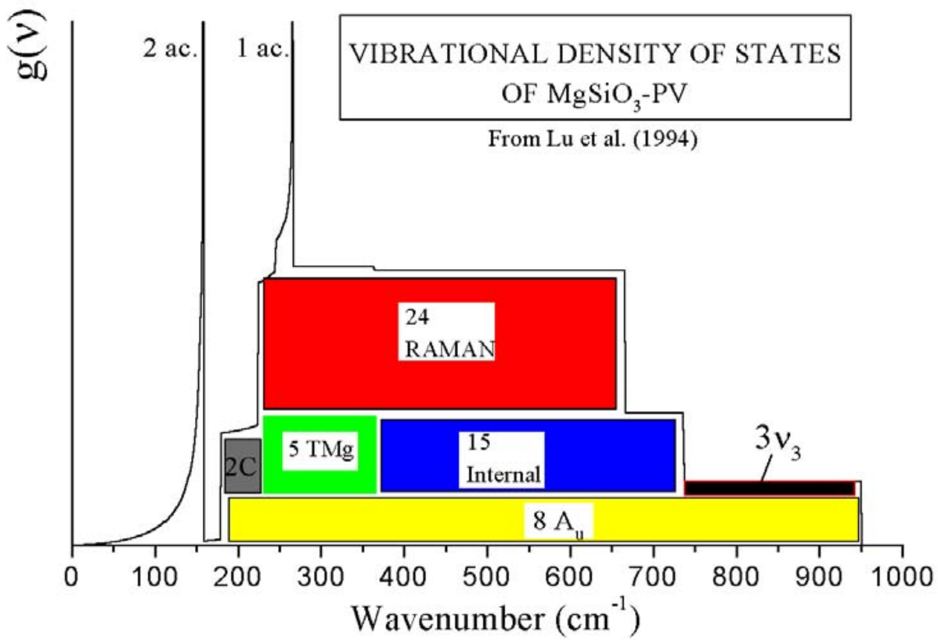


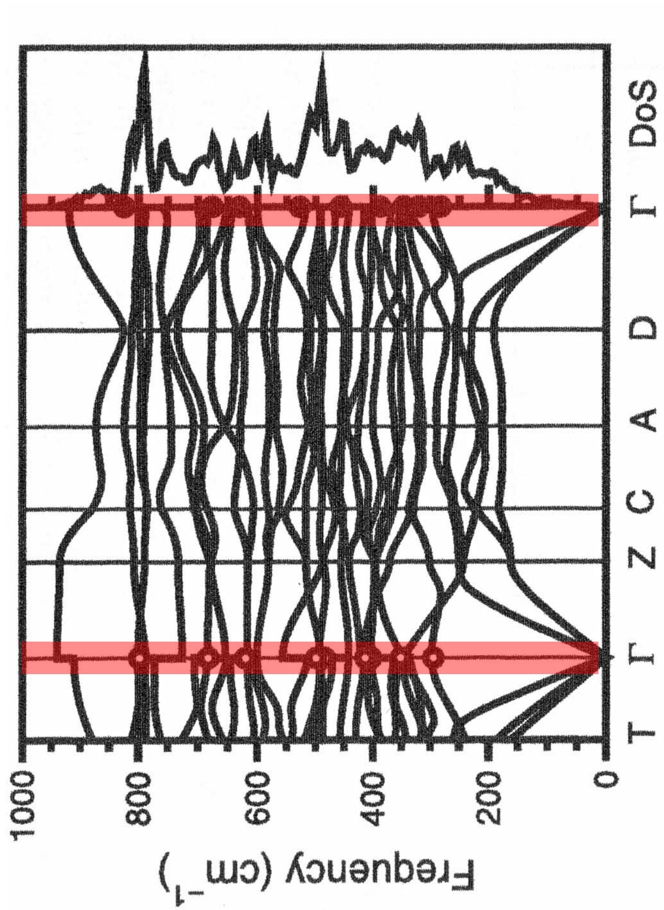
Computed thermodynamic properties of magnesite $MgCO_3$ at low pressures





THERMODYNAMIC MODELLING





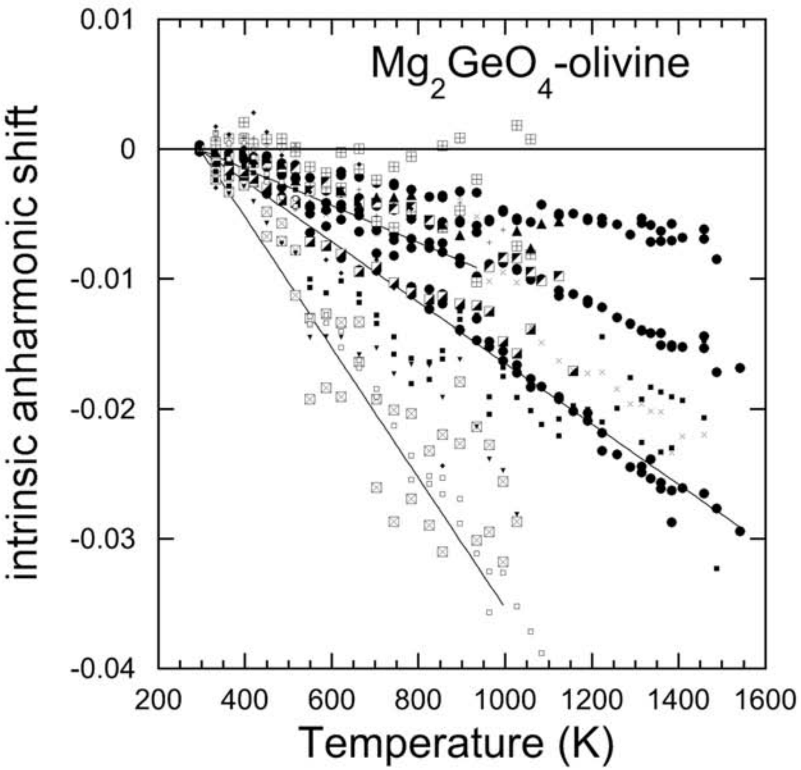
Raman spectroscopy gives a very partial sample of the vibrational density of states, no account of the dispersion in the Brillouin zone

It is necessary to couple Raman and first-principles calculations for prediction of thermodynamics, phase diagrams, isotopic fractionation, …

Intrinsic anharmonic parameters

$$\ln(\nu(P_0,T))_{measured} - \ln(\nu(P_0,T))_{qh} = \int_{T_0}^{T_m} a_i \, dT = \Delta\nu_{th}$$

a_i = constant
m_i = 0



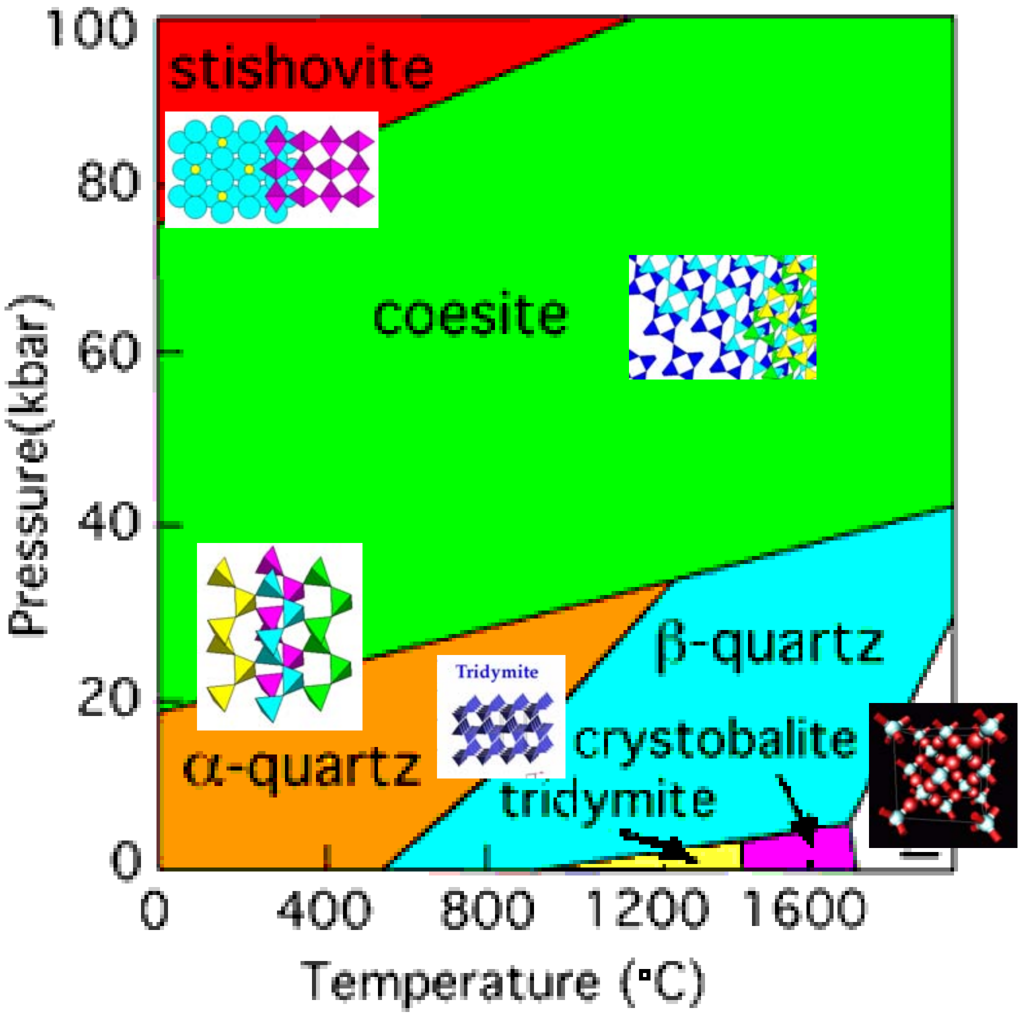
$$F_{vib} = \int \left[\frac{h\nu}{2} + k_B T \ln\left(1 - \exp\left(\frac{-h\nu}{k_B T}\right)\right) + a k_B T^2 \right] g(\nu) d\nu$$

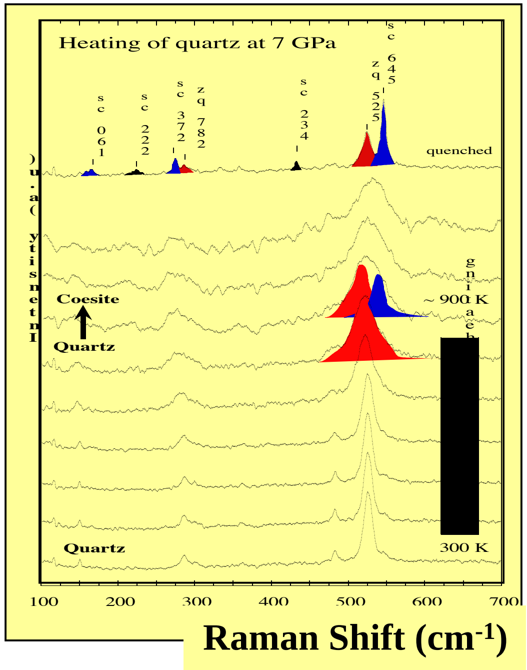
$$P_{th} = \int \left[\frac{\gamma_T}{V} \left(\frac{h\nu}{2} + \frac{h\nu}{\left(\exp\left(\frac{h\nu}{k_B T}\right) - 1\right)} \right) - \frac{m a k_B T^2}{V} \right] g(\nu) d\nu$$

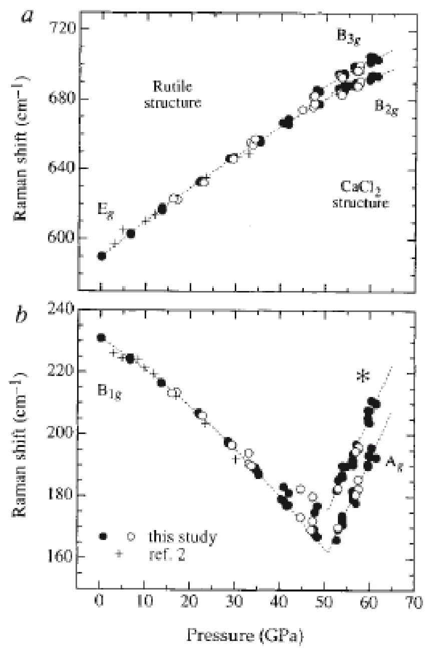
Intrinsic anharmonicity
No contribution to V(P,T)
Contribution to free energy

Phase transitions

SiO_2

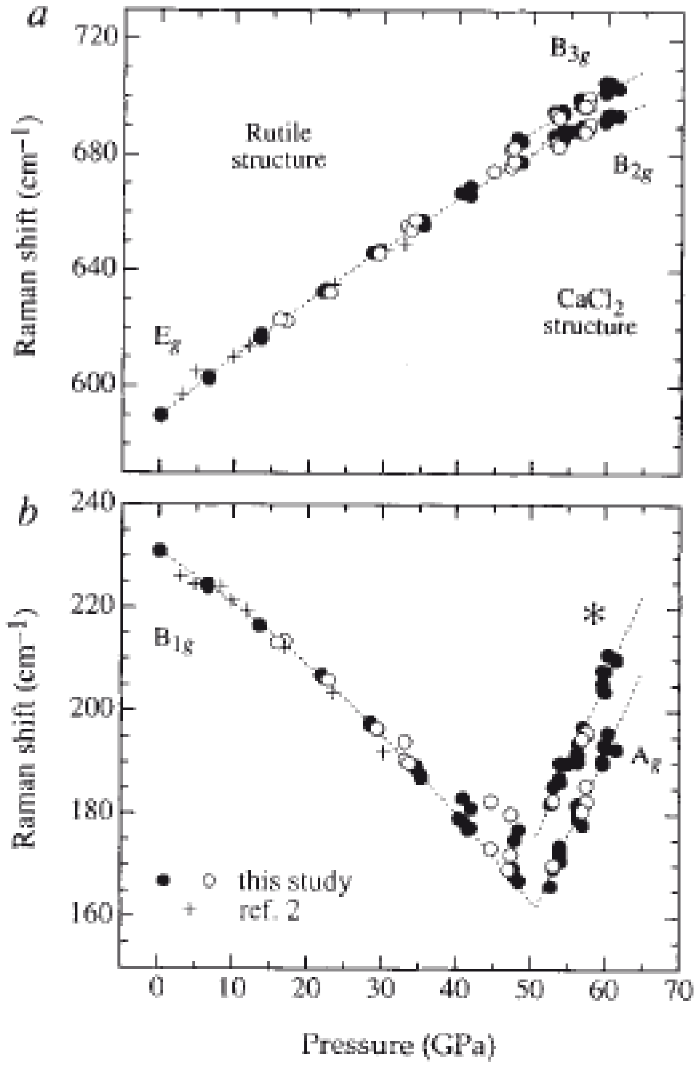


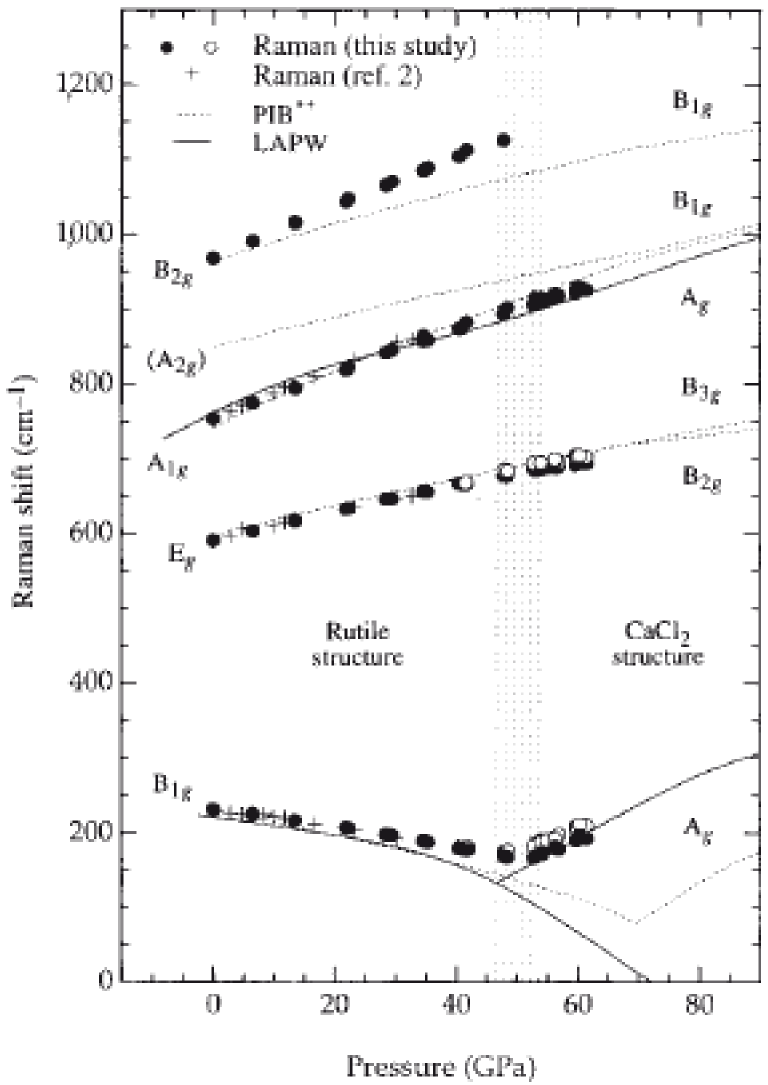




1st and 2nd order

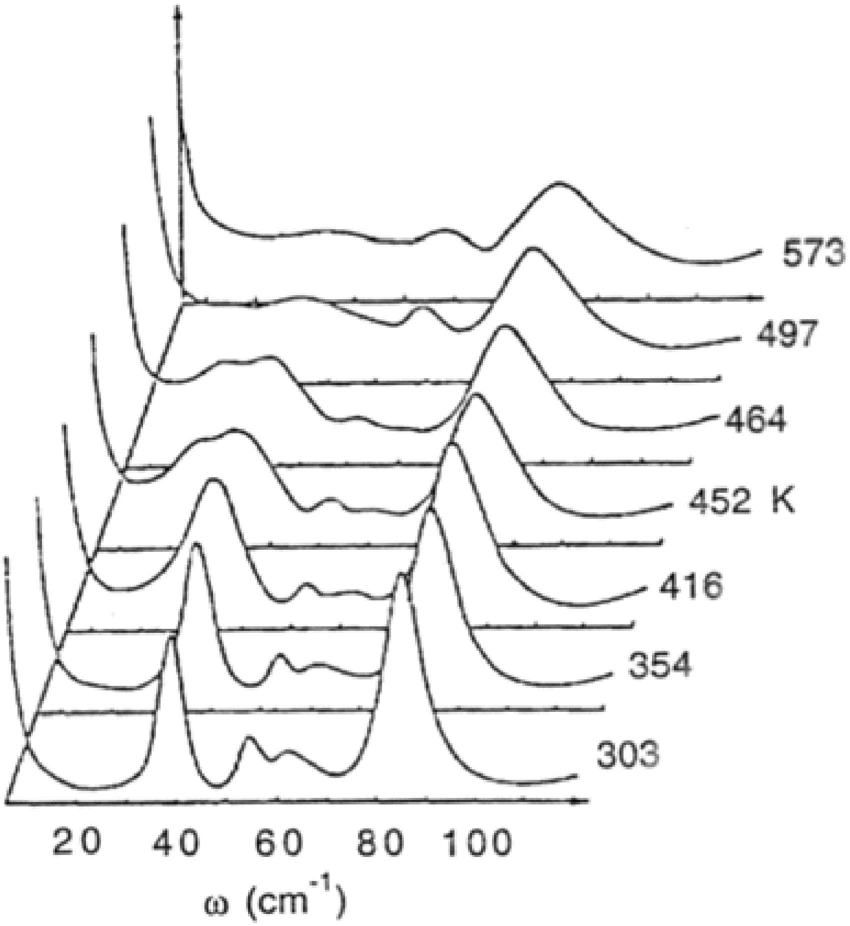
Stishovite

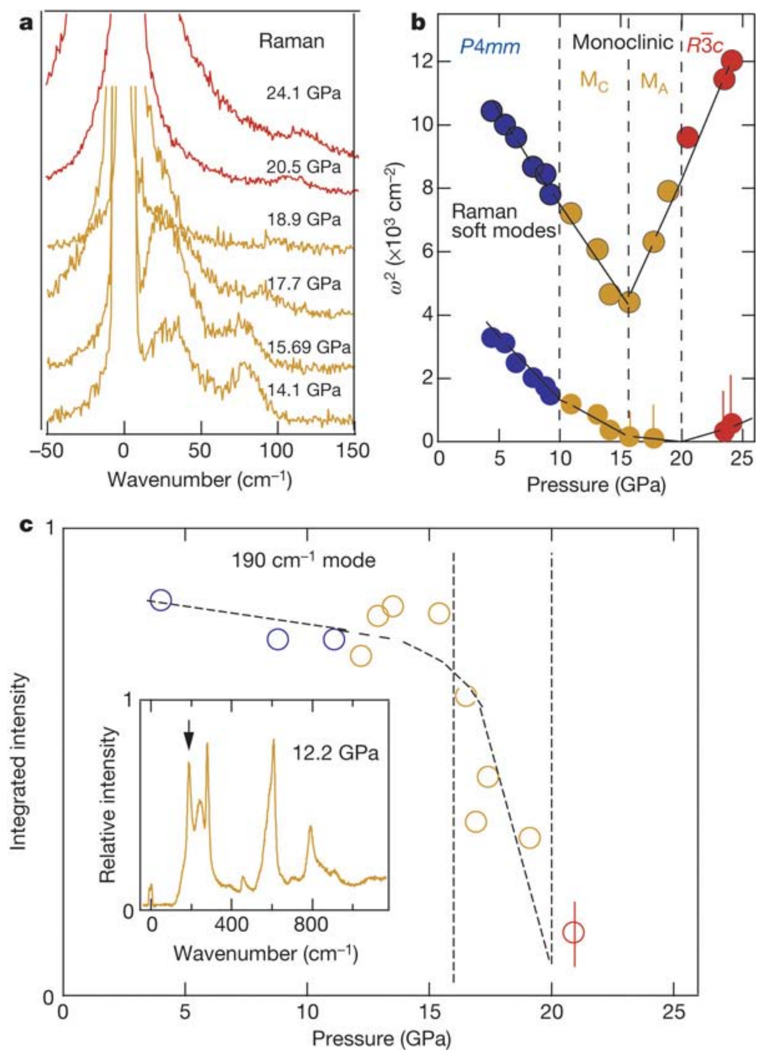




Kingma et al. Nature 1995

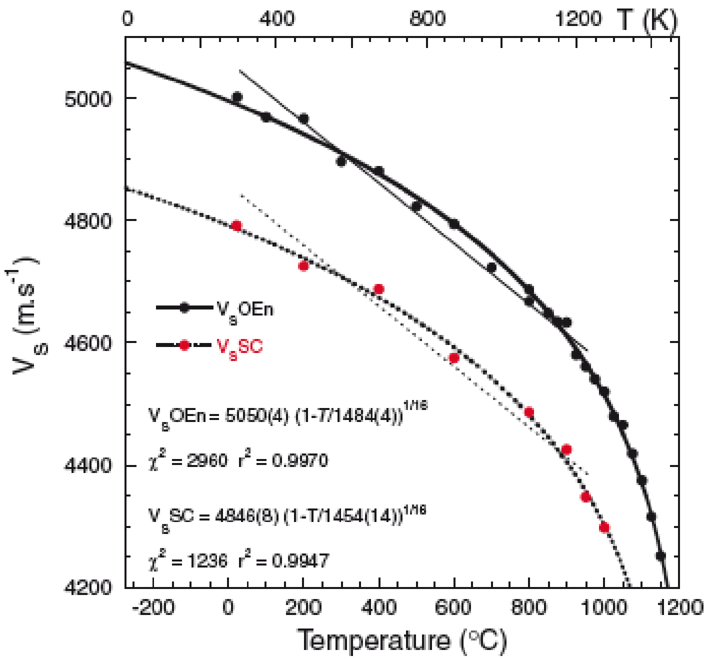
Second-order phase transition

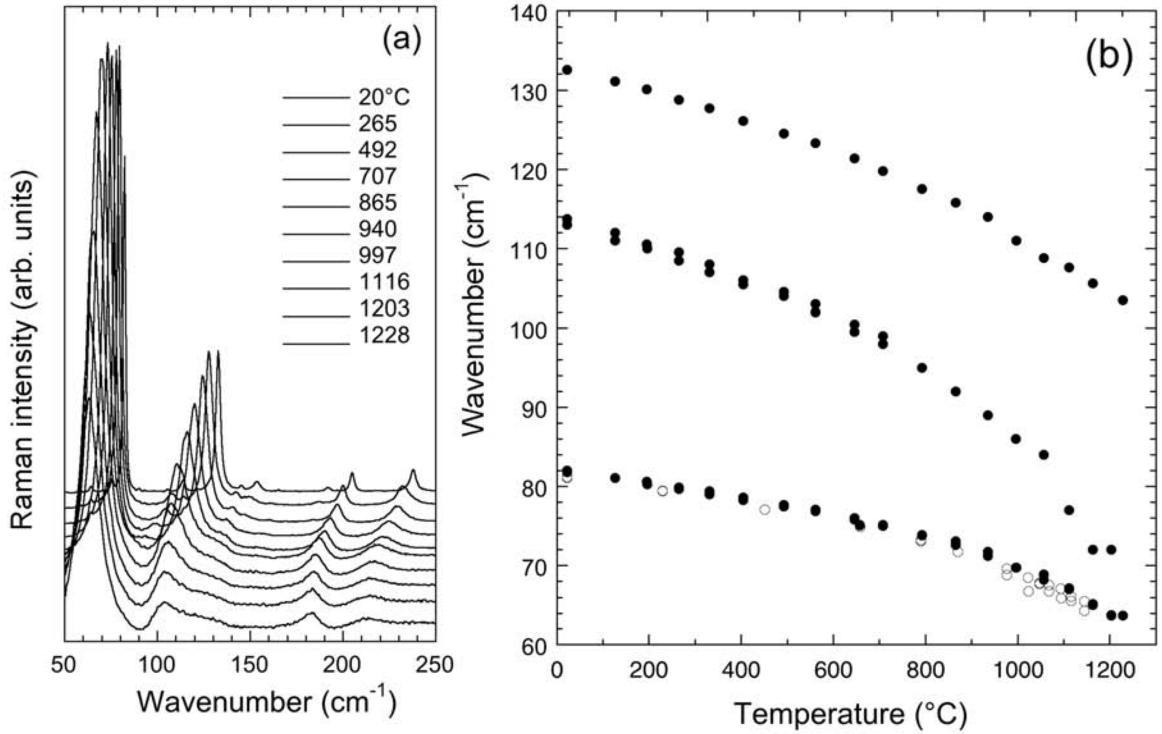




Critical softening at high order phase transition

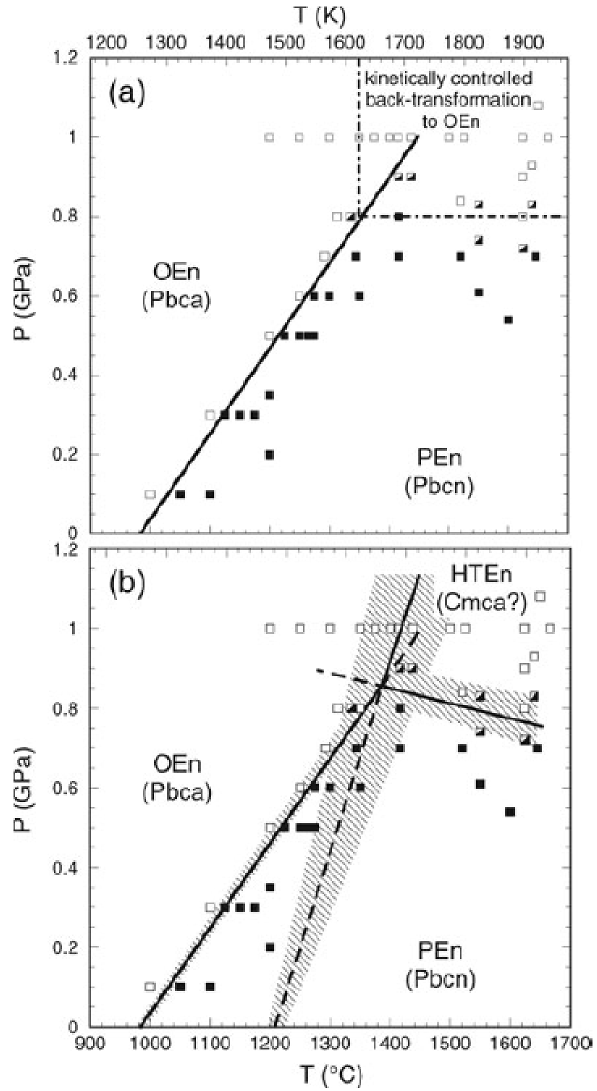
Elastic softening of orthopyroxenes above 600°C

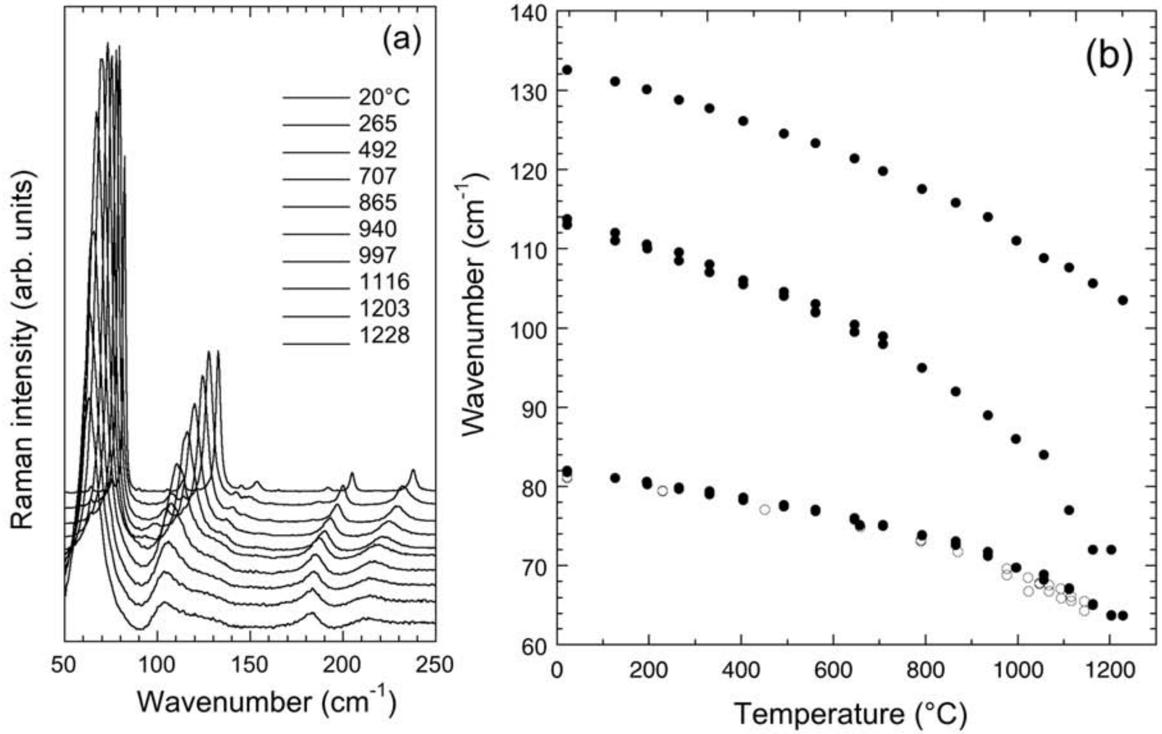




Low frequency Raman modes that derive from acoustic modes

Critical softening at high order phase transition

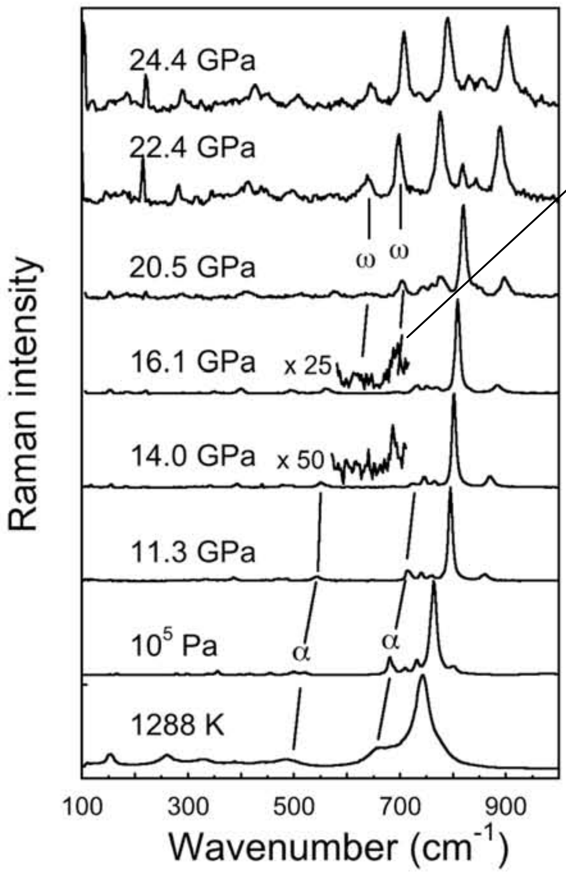




Softening of orthopyroxene Raman modes assigned to transition from Pnma to Cmcm

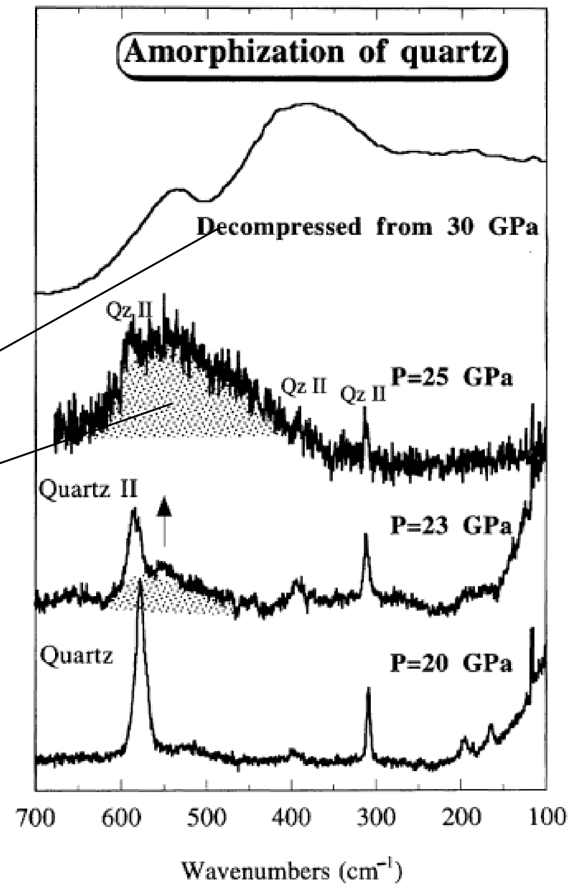
Metastable transformations

Mg_2GeO_4 Reynard et al 1994



Ge-O-Ge bonds

Richet and Gillet 1997

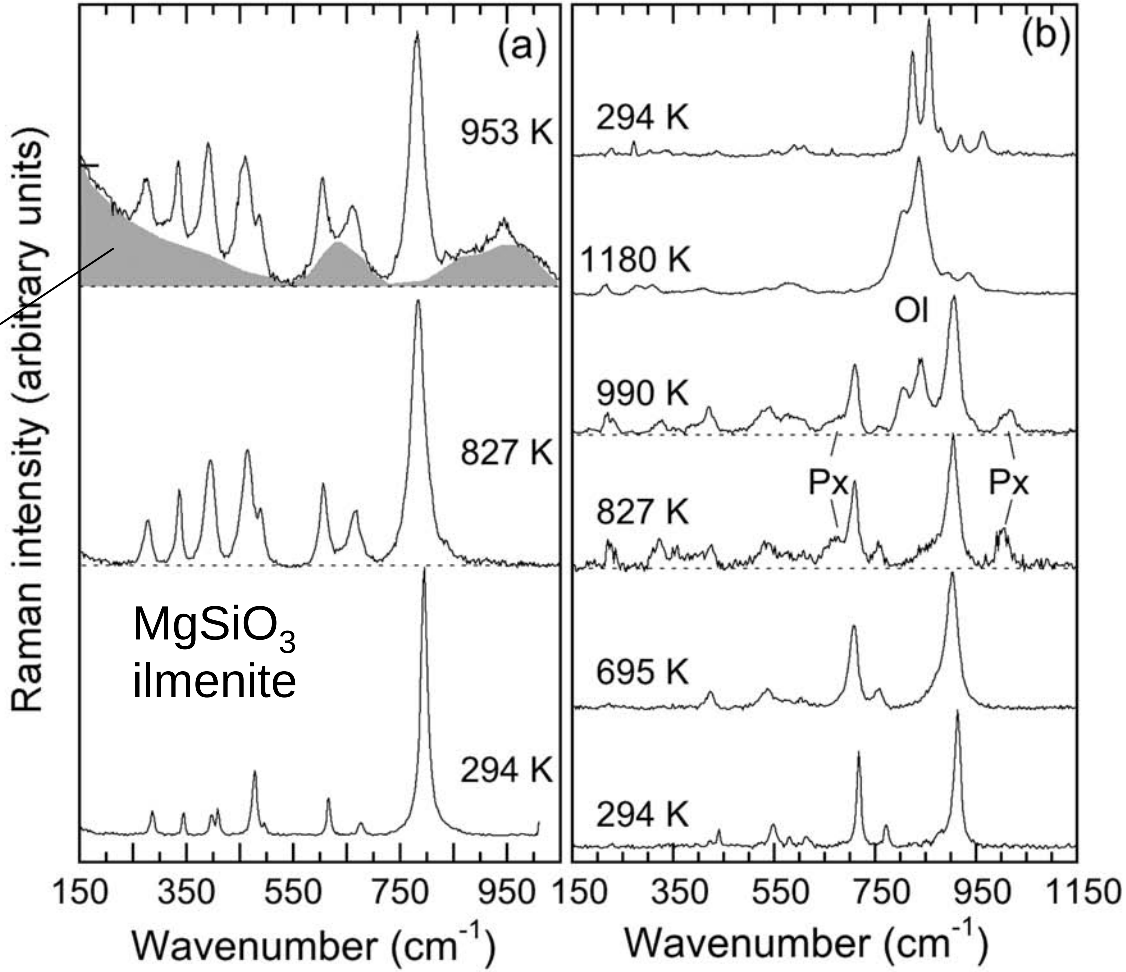


Densified
silica glass
PIA

Relevant to shock transformations in meteorites

Mirror effects of P and T

Heating of HP phase at room P



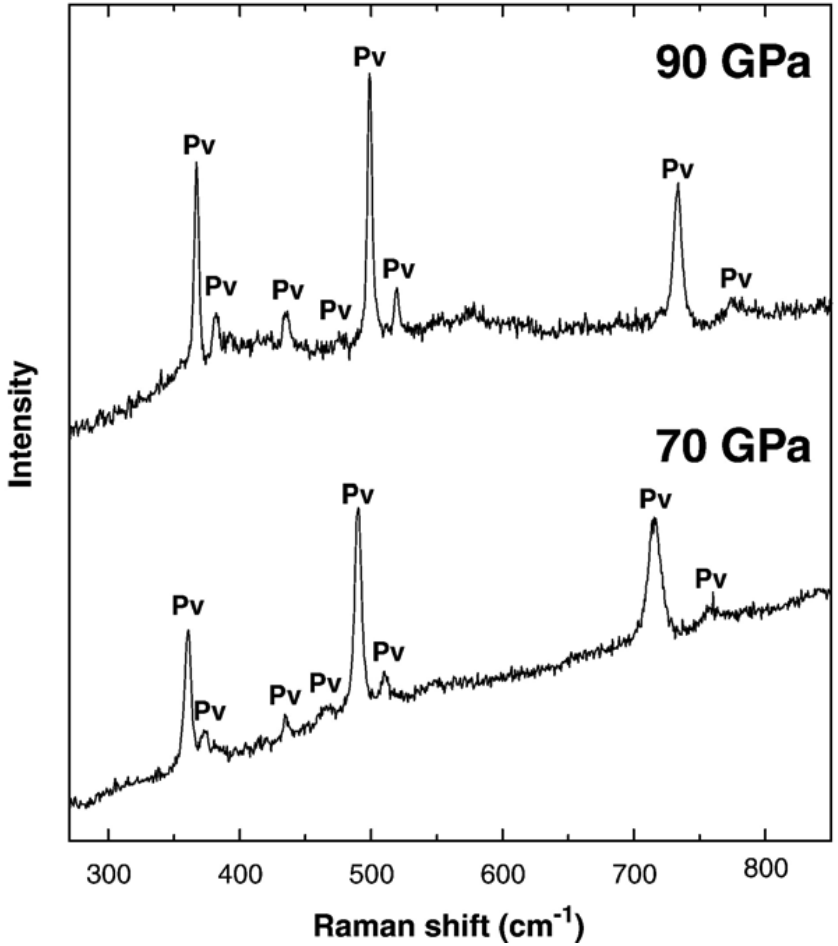
Low P glass

SiO_4 monomers
Olivine

SiO_3 chains!

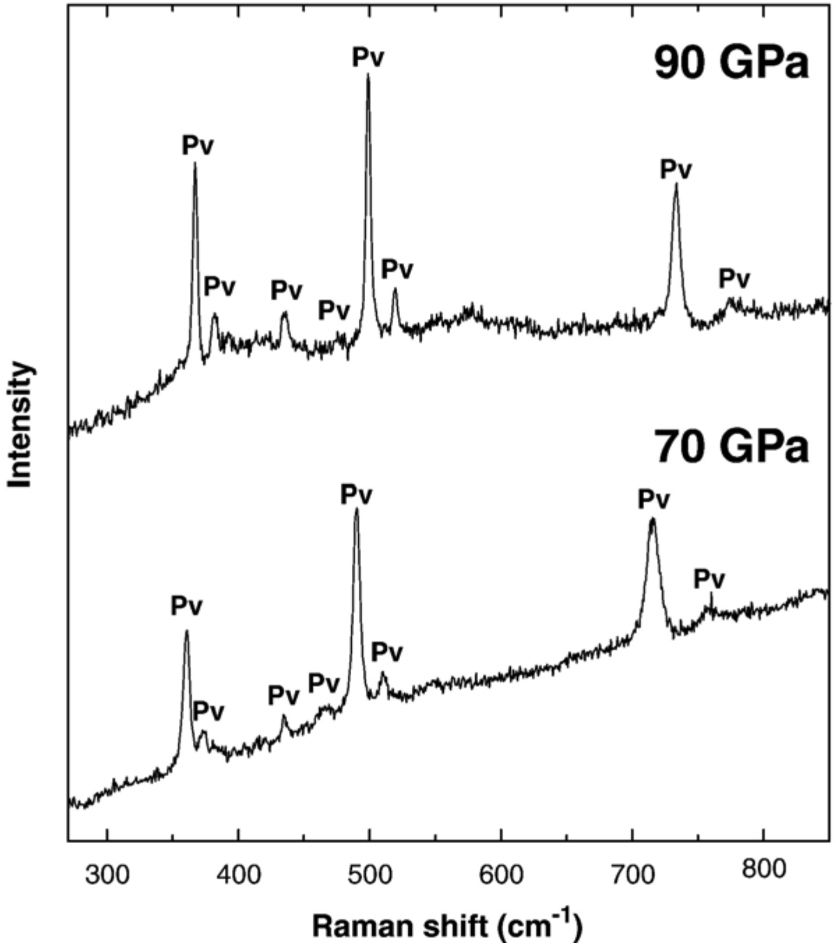
Si_2O_7 dimers
Wadsleyite

Should we keep doing Raman spectroscopy on solids at HP and HT?



Murakami et al 2007

Should we keep doing Raman spectroscopy on solids at HP and HT?



Murakami et al 2007

Why not…

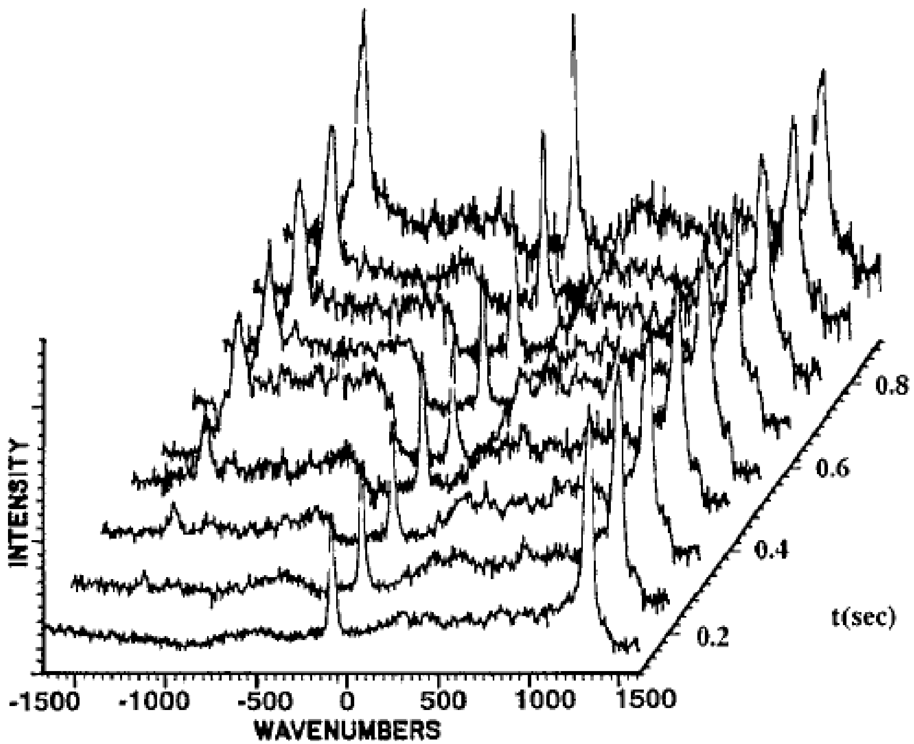
Easy to use technique

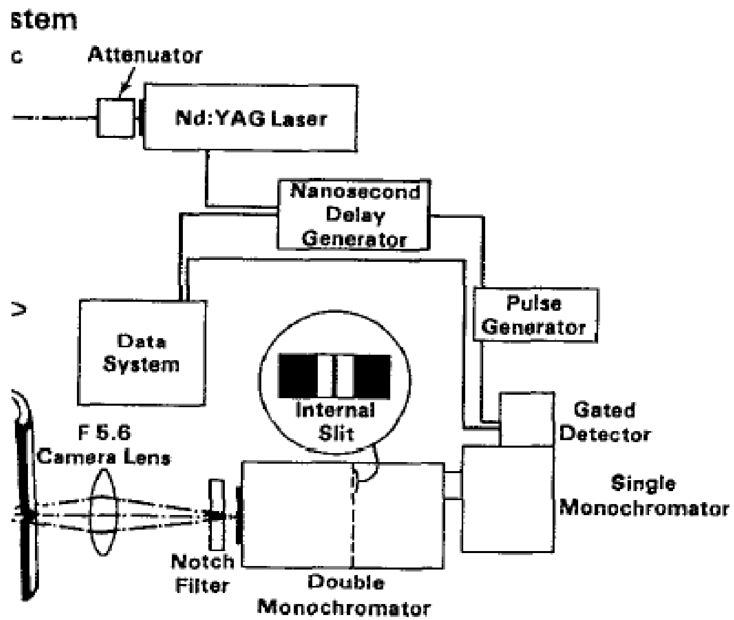
exploratory experiment before synchrotron runs or before using a more cumbersome technique (Brillouin, …)

Coupling with first-principles calculation necessary

Raman data provide a benchmark for extending predictions of elastic, thermodynamic and transport properties (thermal conductivity)

Complex systems (fluids, melts, …)


INTENSITY
WAVENUMBERS
-1500
-1000
-500
0
500
1000
1500
0.2
0.4
0.6
0.8
t(sec)


stem
Attenuator
Nd:YAG Laser
Nanosecond Delay Generator
Pulse Generator
Data System
Internal Slit
Gated Detector
F 5.6 Camera Lens
Single Monochromator
Notch Filter
Double Monochromator