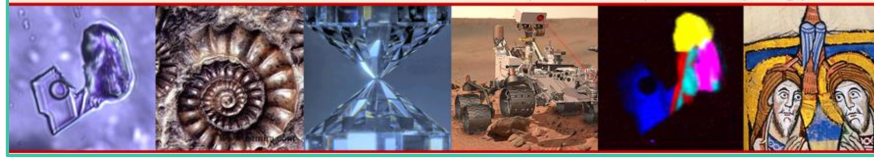
GeoRAMAN School for students and young scientists
June 15th, 2016

XII International Conference
GeoRAMAN – 2016
Novosibirsk, Russia, June 9-15, 2016



Stability and structure of high-pressure garnets: Raman approach

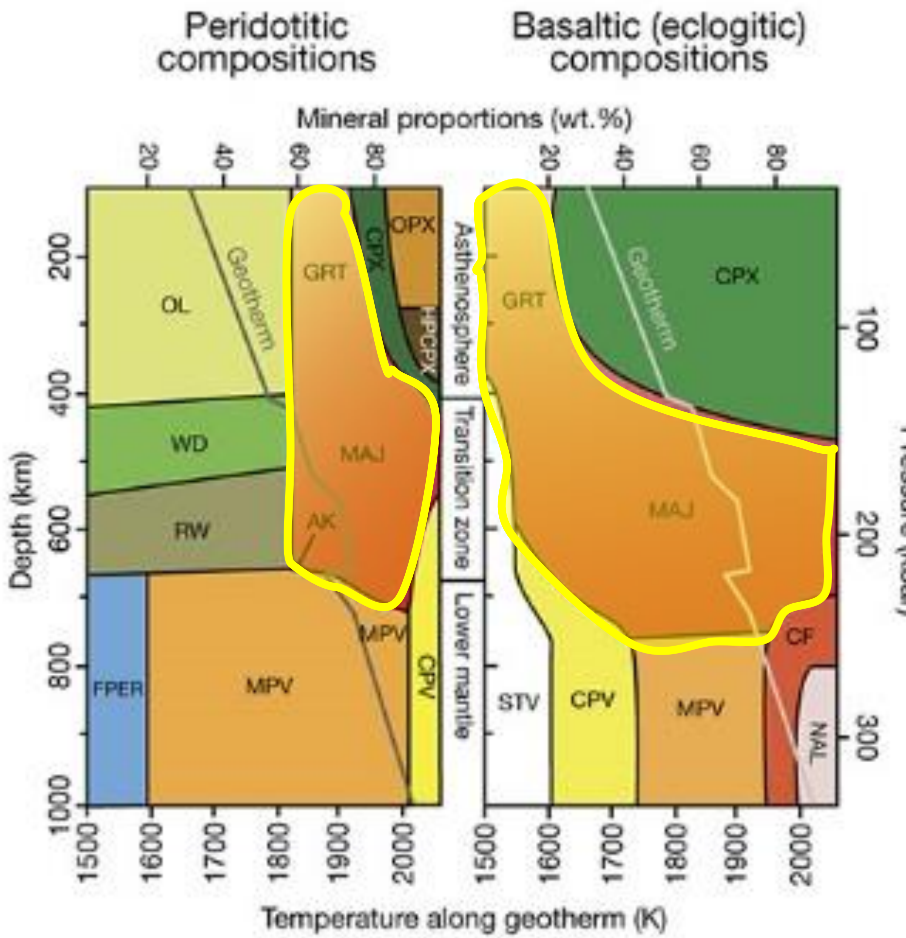
Anna Dymshits
a.dymshits@gmail.com

東北大学

SPring-8

INSTITUTE OF GEOLOGY AND MINERALOGY SB RAS

High pressure phases in the mantle

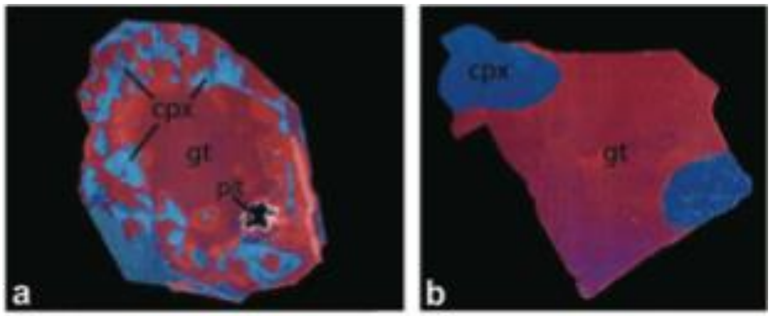


Harte, 2010

Garnet is one of the most abundant mineral in the upper mantle and transition zone

<u>Garnet (+ majorite)</u>

up to 40 vol.% of peridotitic lithology
up to 70 vol.% of eclogitic lithology



Dissolution of majoritic garnet

Harte, 2010
Mineralogical Magazine

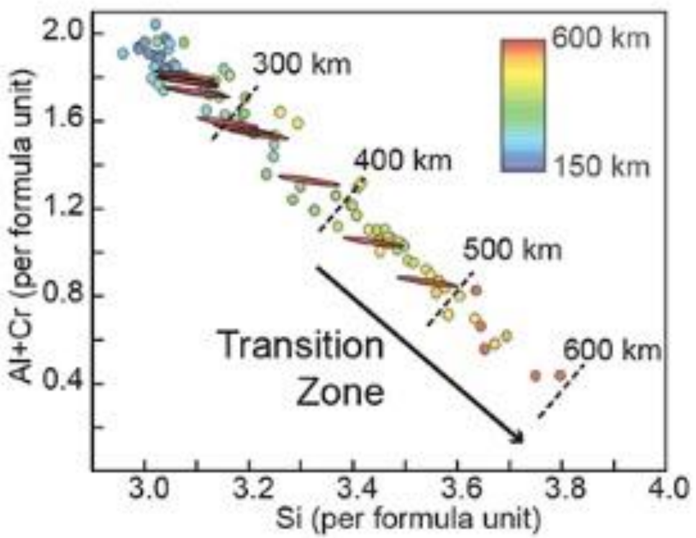
Synthetic pyrope-majorite garnet

Majorite

$Mg_3(Mg,Si)Si_3O_{12}$
$Mg_4Si_4O_{12}$

Majoritic garnet

$Mg_4Si_4O_{12}$ - $M_3Al_2Si_3O_{12}$
(M = Mg, Fe, Ca)



Iskert et al., 2015

- Silicon excess (Si = 3.07 – 3.26 f.u.)
- Isomorphic Na admixture
- $Na_2MgSi_5O_{12}$ – Na-majorite
- With increasing pressure garnet becomes progressively enriched in majorite component (Akaogi, Akimoto, 1977)

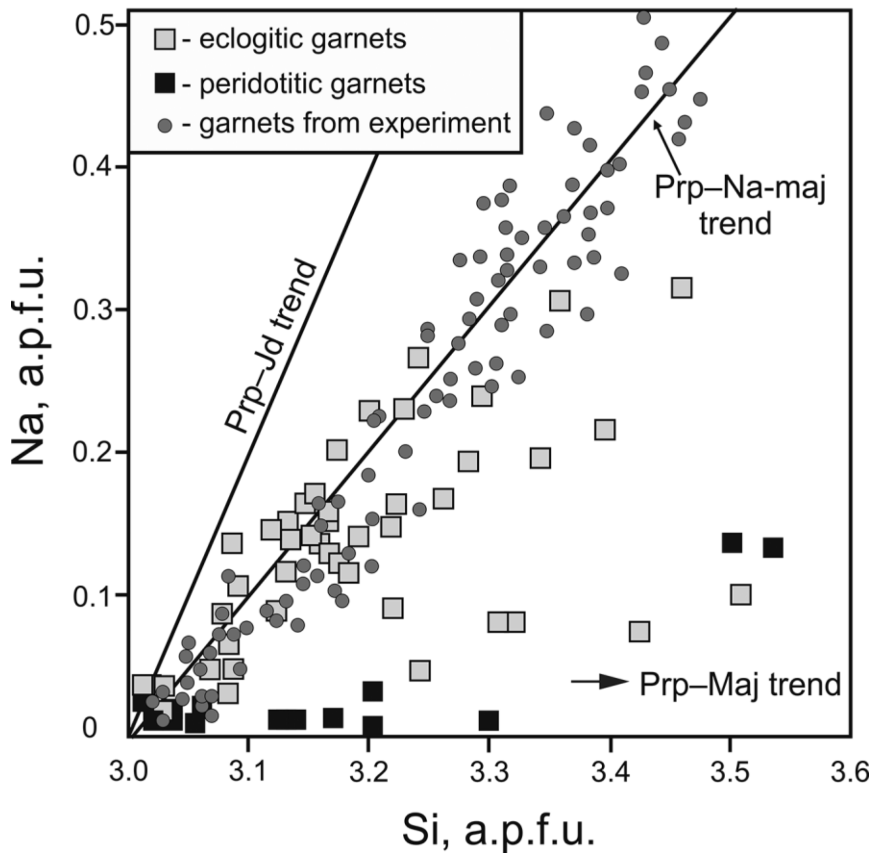

Majoritic garnet inclusion

Iskert et al., 2015

Na-bearing majoritic garnets in nature

South Africa (Moore, Gurney, 1985; Stachel, 2001); Brazil (Harte, Cayzer 2007); Guinea (Stachel et al., 2000), Russia (Sobolev et al., 1997; 2004 Shatskii et al., 2010); China (Wang et al., 2000); Canada (Davies et al., 2004; Pokhilenko et al., 2004)

Compositions of Na-rich majoritic garnets



Dymshits et al., 2015

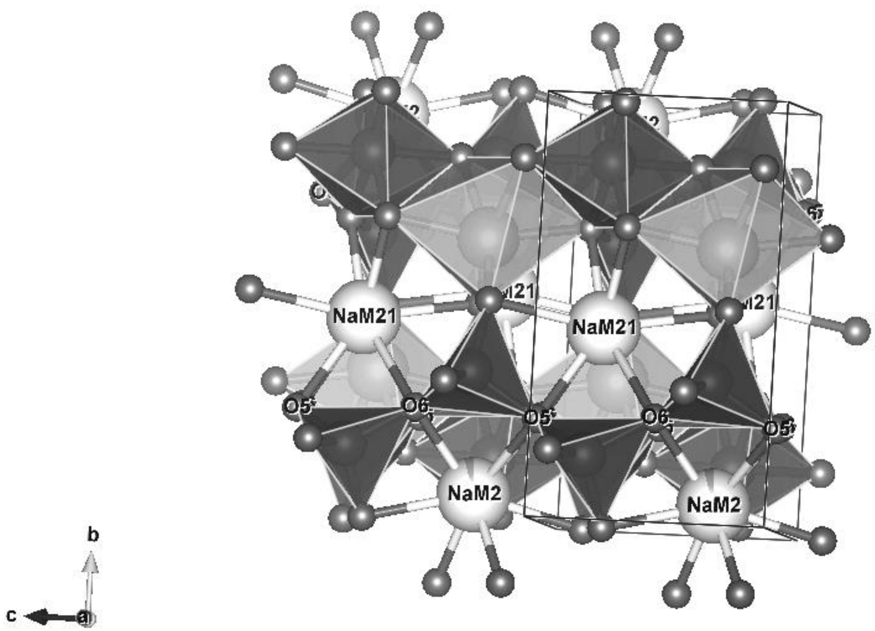
<u>Empirical geobarometers</u>:

Collerson et al., 2010

Kiseeva et al., 2016

Wijbrans et al., 2016

Na-bearing pyroxene (Na-Px) $Na_{0.5}MgSi_{2.5}O_6$

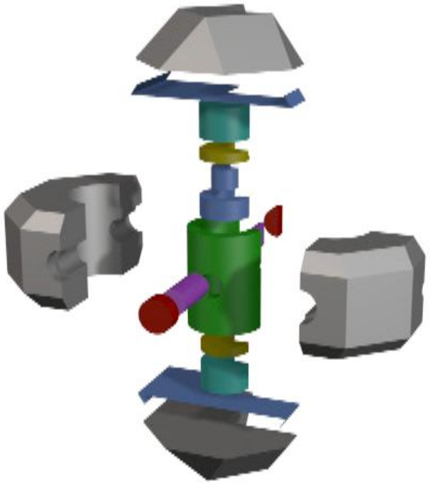


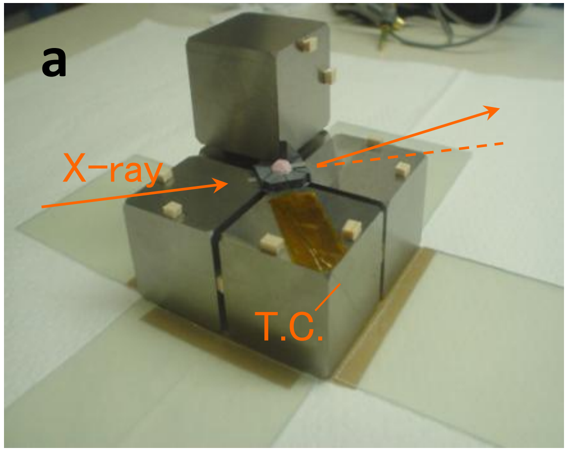
1. Low pressure modification of Na-majorite
2. Si occupies both tetrahedral and octahedral positions
3. Solid solutions were found in nature as inclusions in diamond (Pla Cid et al., 2014; Harte and Hudson 2013)
4. The formation pressure of such alkali-rich inclusion can be estimated based on Na-px–Na-maj transition

How to study phase transitions at high pressures and high temperatures?

***In situ* X-ray diffraction experiments**

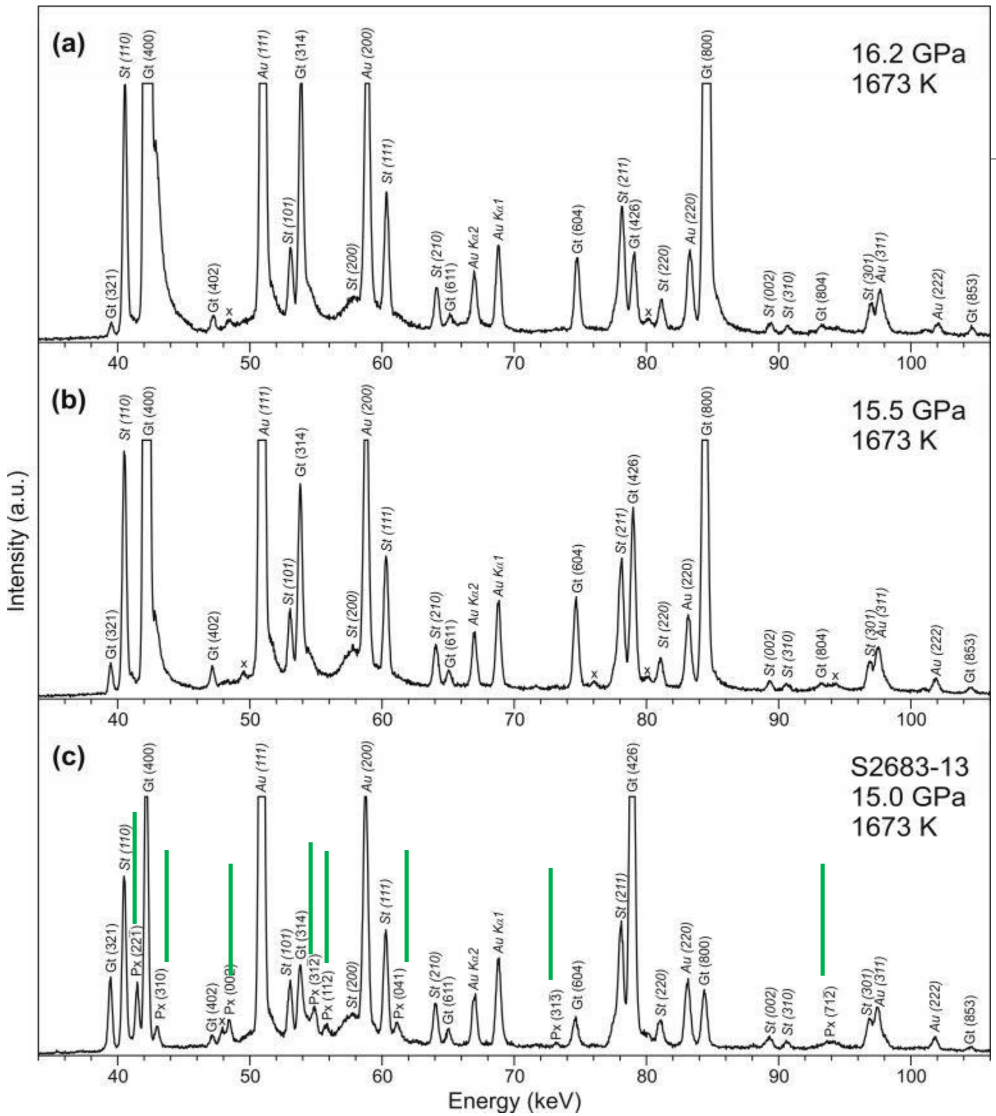
SPring-8 synchrotron radiation facility (Hyogo, Japan), using a 1500-tons and 700-tons Kawai-type multi-anvil apparatus





Furnace assembly for experiments

When a **phase transition** point is reached



Garnet stability field

Garnet stability field

Garnet + pyroxene stability field

How to obtain the boundary

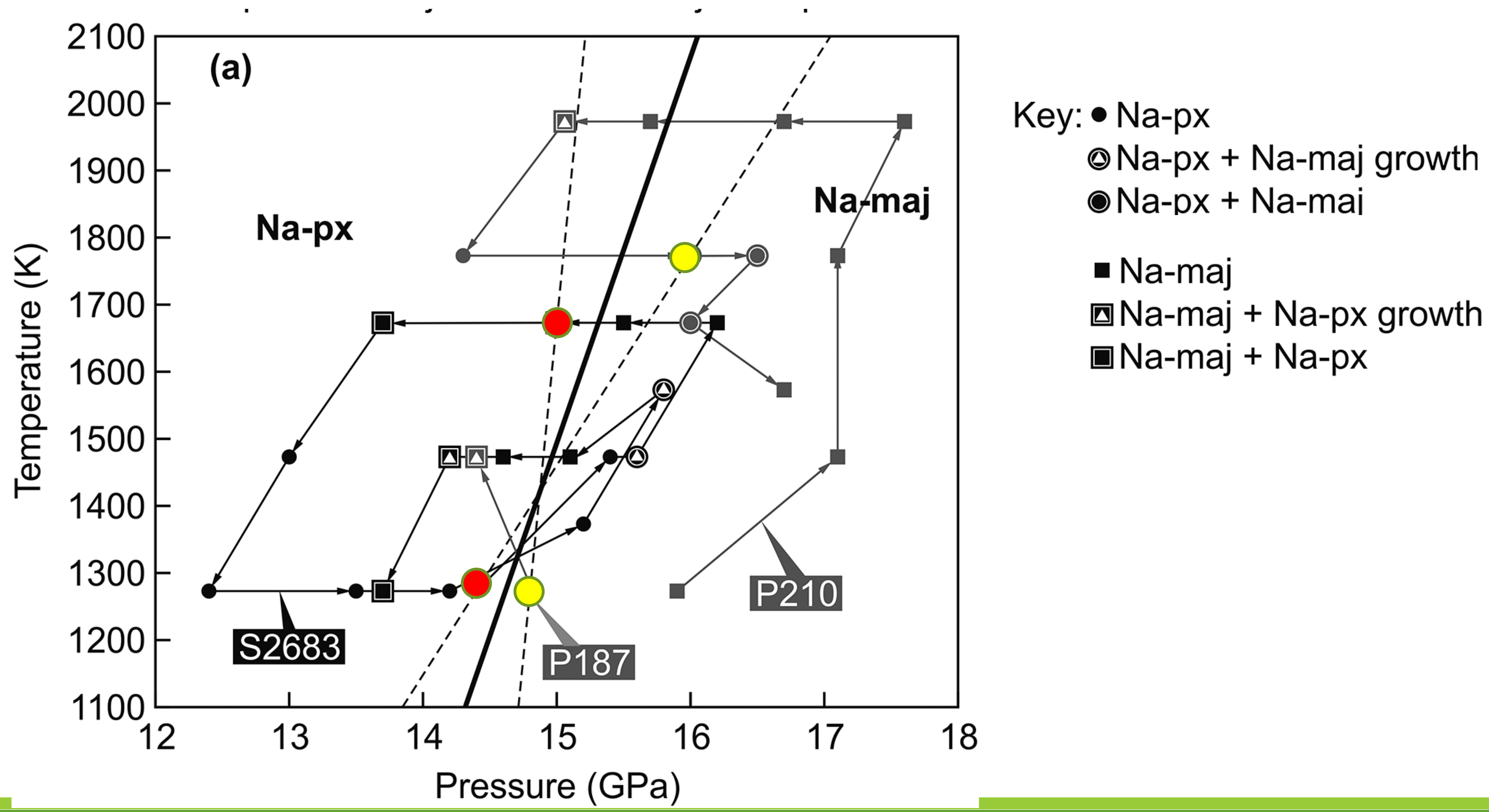
Run no.	V_{Au} (Å^3)	P_{Au} (GPa)	P_{Au} (GPa)	T (K)	X-ray observation
S2683	65.10(3)	14.4(1)	14.4 (1)	1,273	Na-px growth from starting material
S2683	65.15(4)	15.6(1)	15.5 (2)	1,473	Na-px → Na-maj growth after 10 min of annealing Na-maj only
S2683	65.78(2)	15.0(1)	14.9 (1)	1,673	Na-maj → Na-px growth
S2683	65.29(3)	15.8(1)	15.6 (1)	1,573	Na-px → Na-maj growth
S2683	65.59(3)	14.2(1)	14.1 (2)	1,473	Na-maj → Na-px growth
P187	64.96(4)	14.8(1)	14.6 (1)	1,273	Na-maj growth from starting material
P187	65.55(5)	14.4(2)	14.2 (2)	1,473	Na-maj → Na-px growth
P210	64.62(4)	15.9(1)	15.7 (1)	1,273	Na-maj growth from starting material
P210	66.51(5)	15.1(1)	15.1 (2)	1,973	Na-maj → Na-px growth
P210	65.67(3)	16.0(1)	16.0 (2)	1,773	Na-px → Na-maj growth

How to obtain the boundary

At low pressures **Na-maj** transforms to **Na-px**

The phase boundary Na-px /Na-maj

***P* (GPa) = 12.39 + 0.0018*T* (K).**

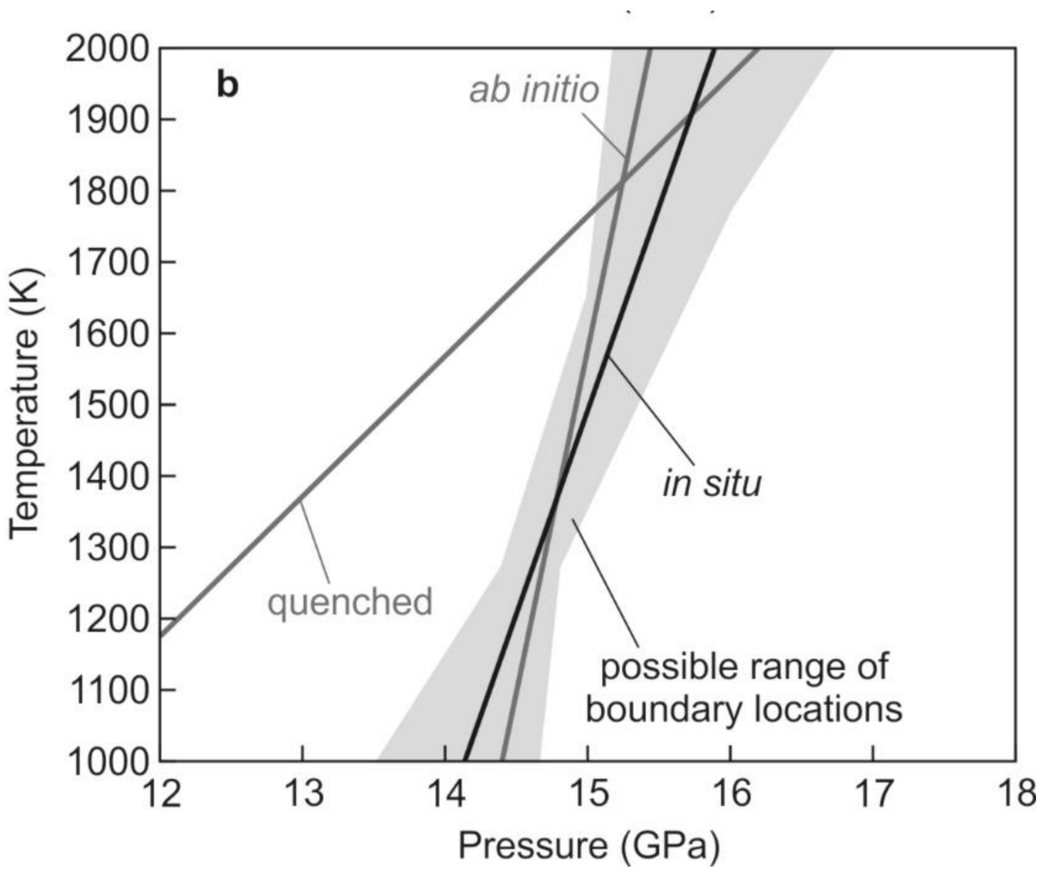


P-T diagram of Na-px/Na-maj

At low pressures **Na-maj** transforms to **Na-px**

The phase boundary Na-px /Na-maj

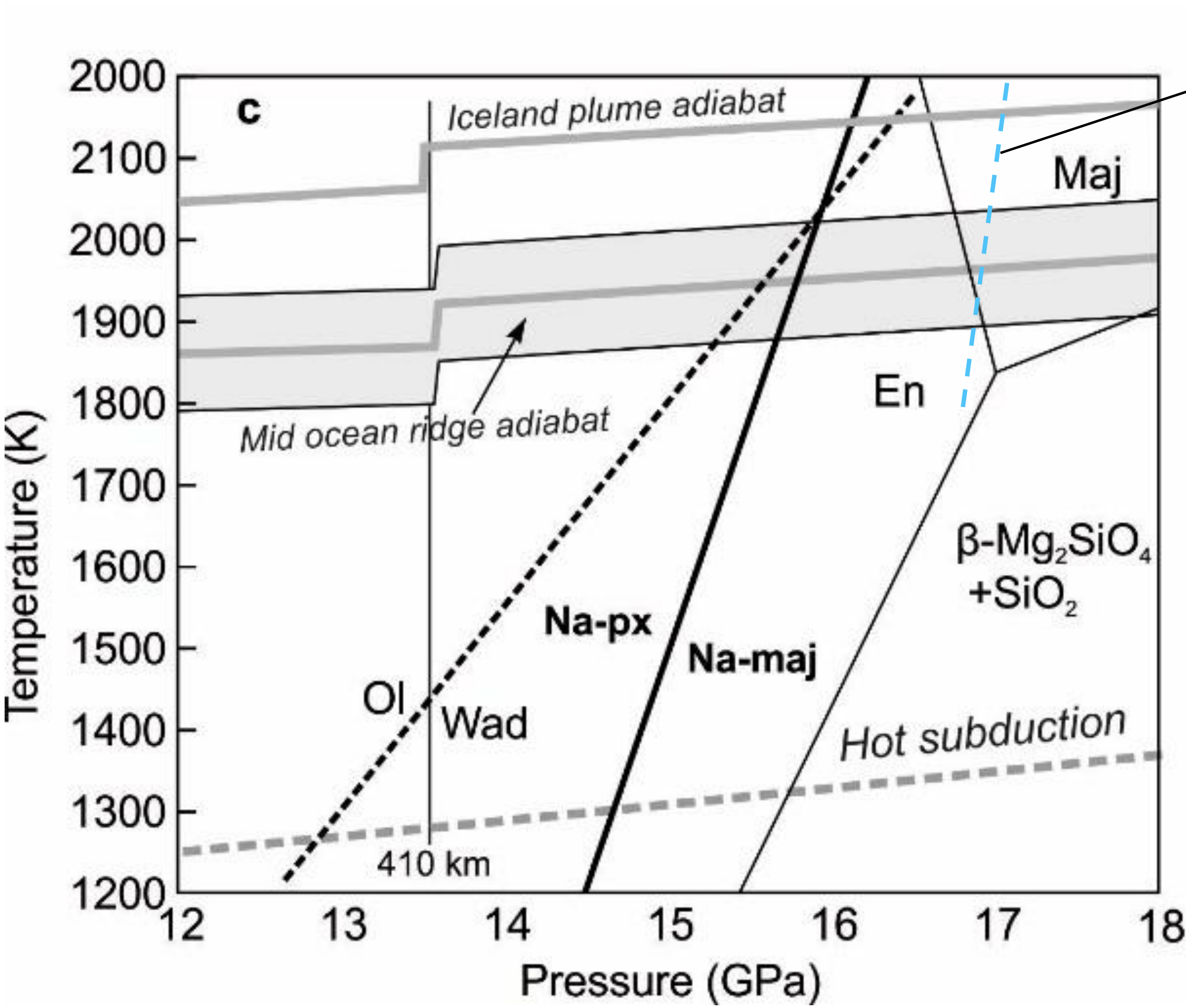
***P* (GPa) = 12.39 + 0.0018*T* (K).**



Ab initio:
Vinograd et al., 2011

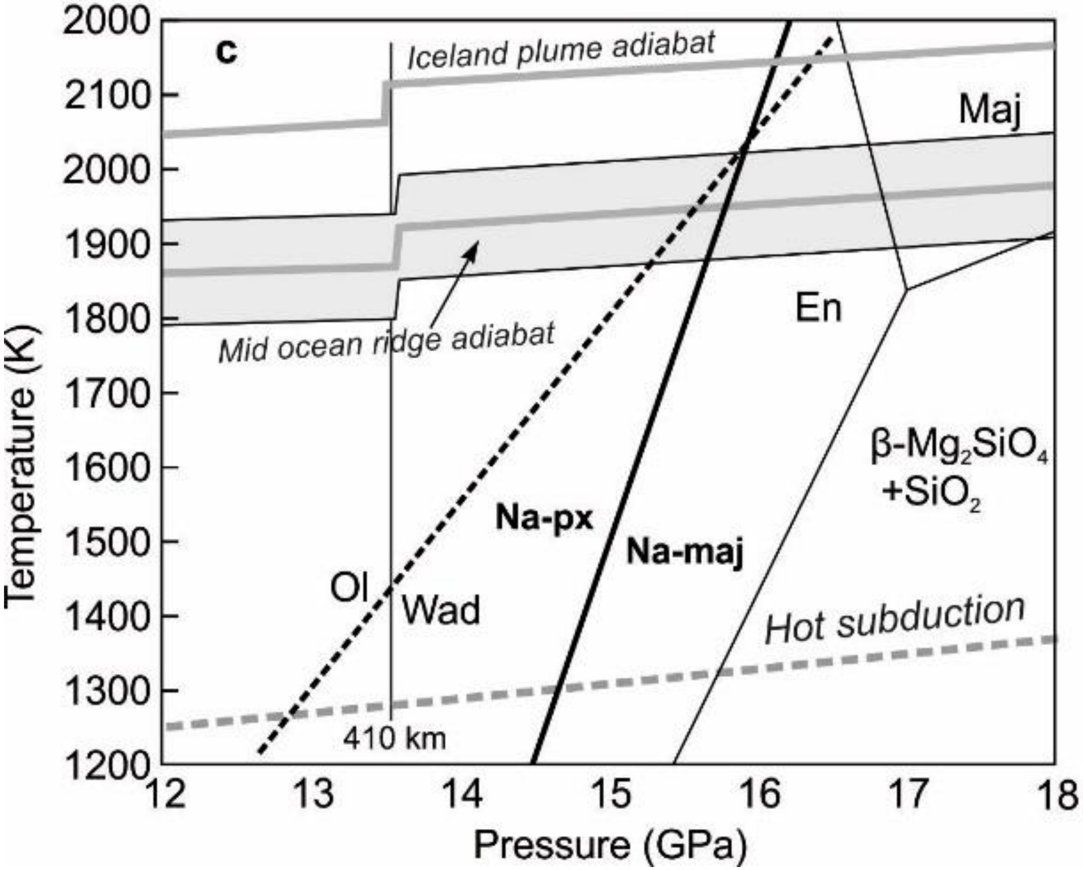
Quenched Experiments:
Dymshits et al., 2010

Majorite and Sodium-majorite systems



Sawamoto (1987)
En → Maj

Implication to natural majoritic samples



Na-rich Grt inclusion (China).

72 mol % Mg-maj – 18 mol % Na-maj
(Wang and Sueno, 1996)

Minimum pressure – 15.5 GPa

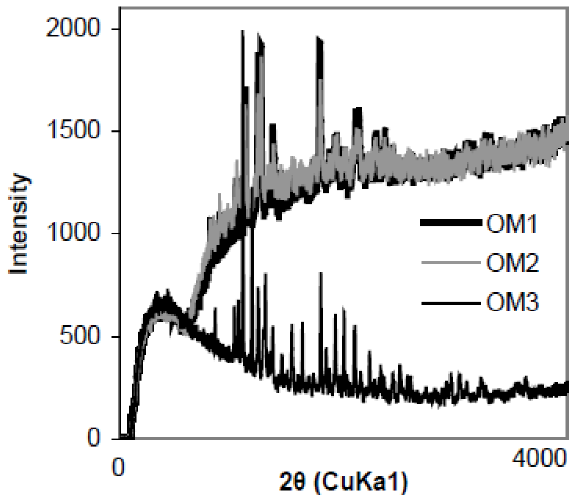
Na-rich Grt (?) inclusion (Brazil).

Highest possible Si excess (4.98 f.u.)
(Pla Cid et al., 2014)

Minimum pressure – 15.2 GPa

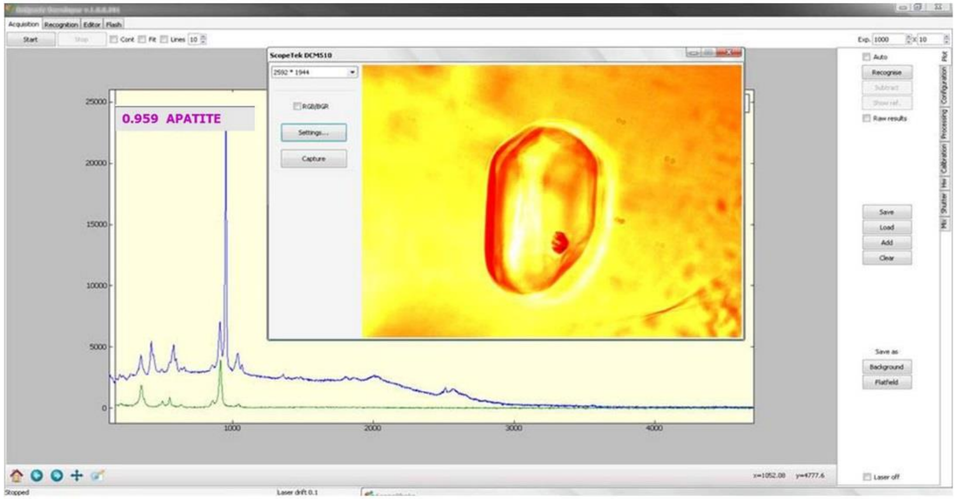
Diagnostic for mineral inclusions

X-ray diffraction



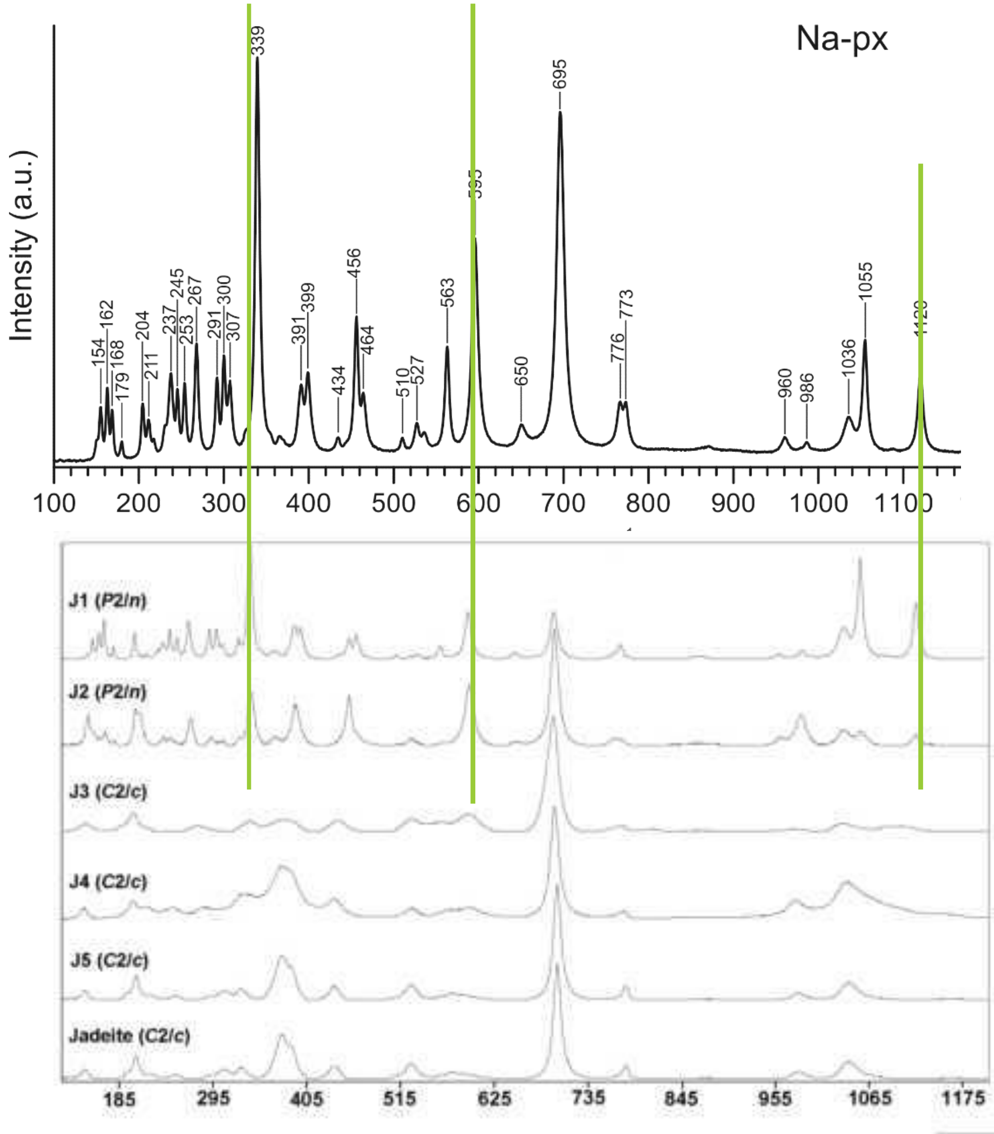
XRD patterns for three white inclusions from Allende. Menzies et al., 2003

Raman spectroscopy



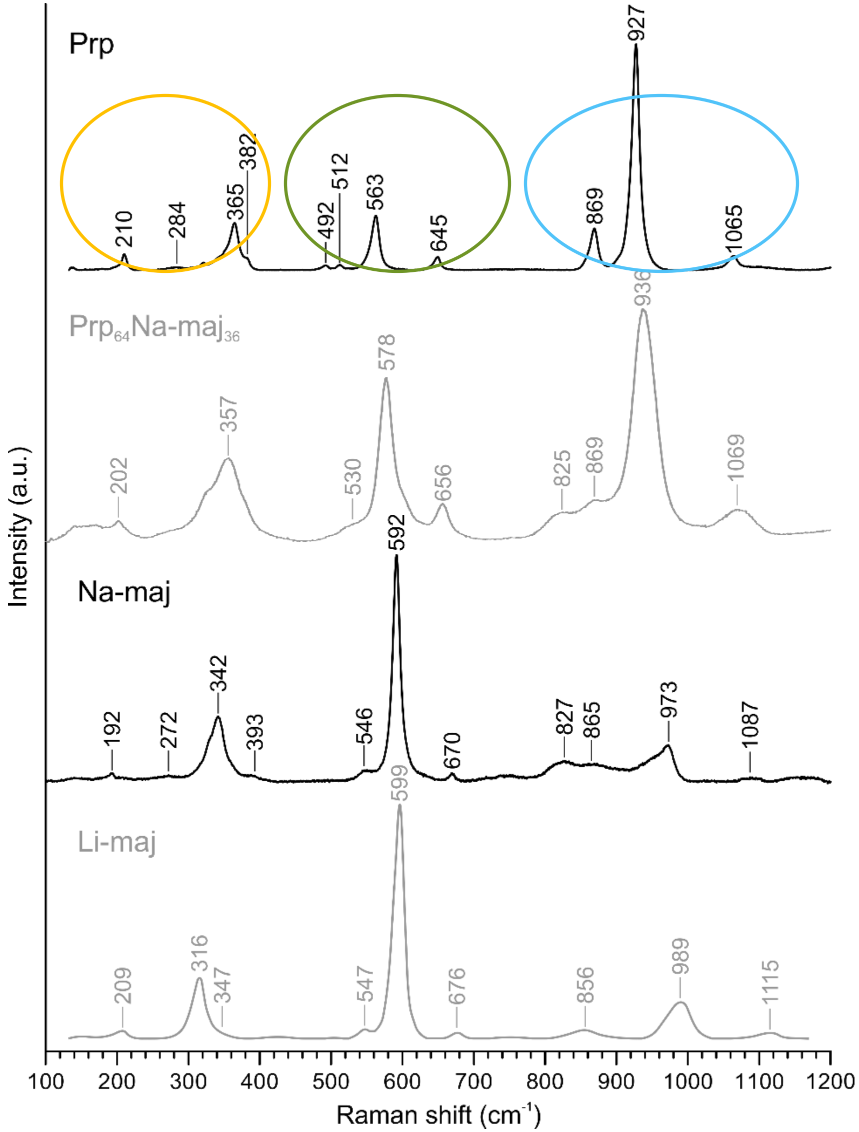
http://enspectr.com/rammics-m532/

Raman spectrum of Na-Px



Raman spectra of clinopyroxenes in the jadeite-NaPx system (Yang et al., 2009)

Raman spectrum of Na-Maj

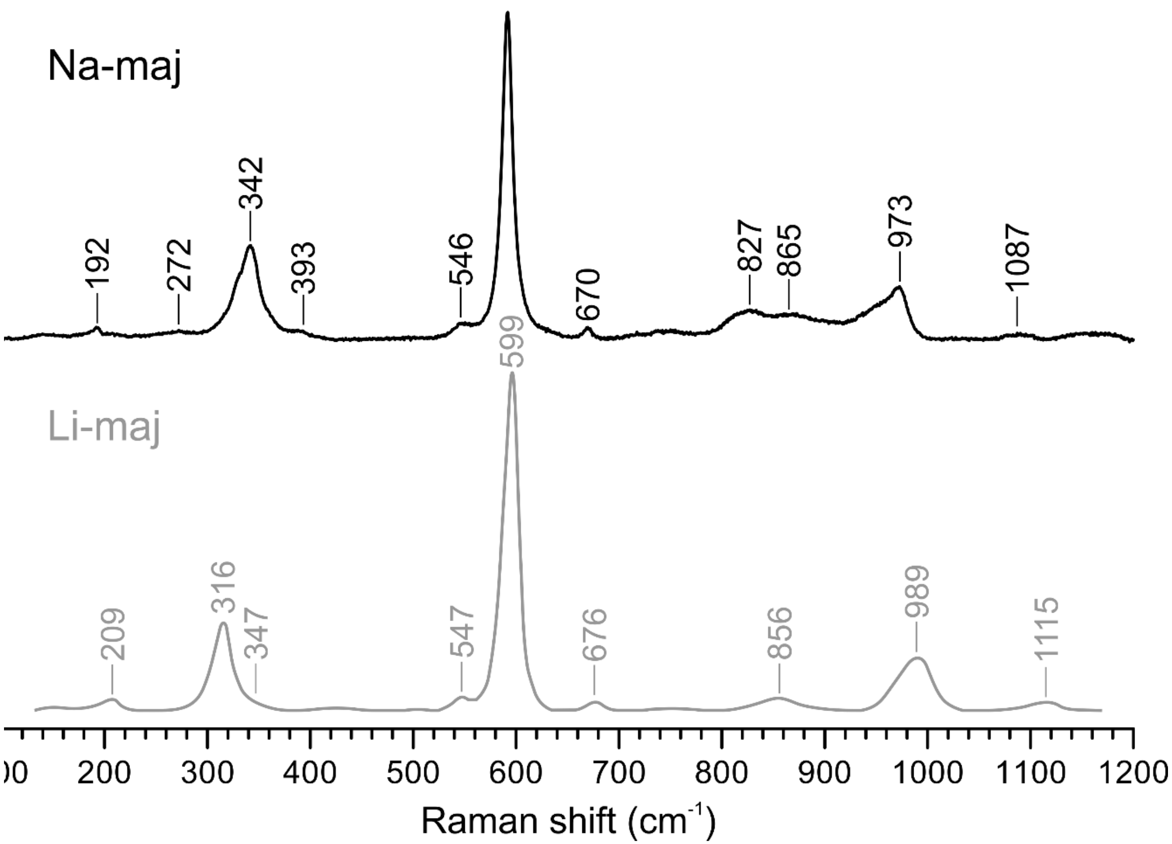


Prp from the RRUFF database (http://rruff.info/R080060)

Prp–Na-maj solid solution (our data)

Na-majorite (our data)

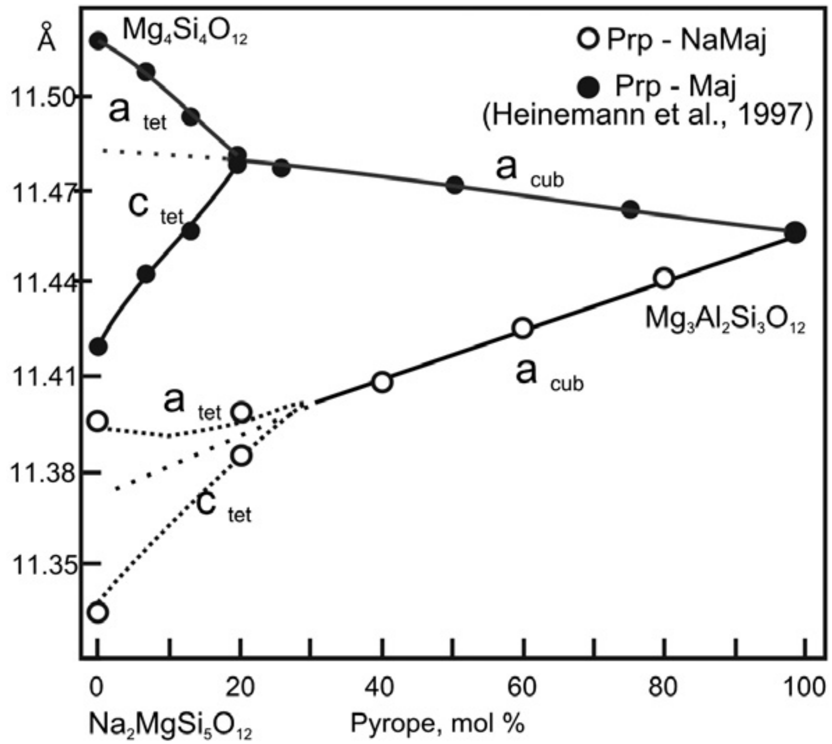
Li-majorite $(Li_2Mg)Si_2(SiO_4)_3$ (Yang et al., 2009)



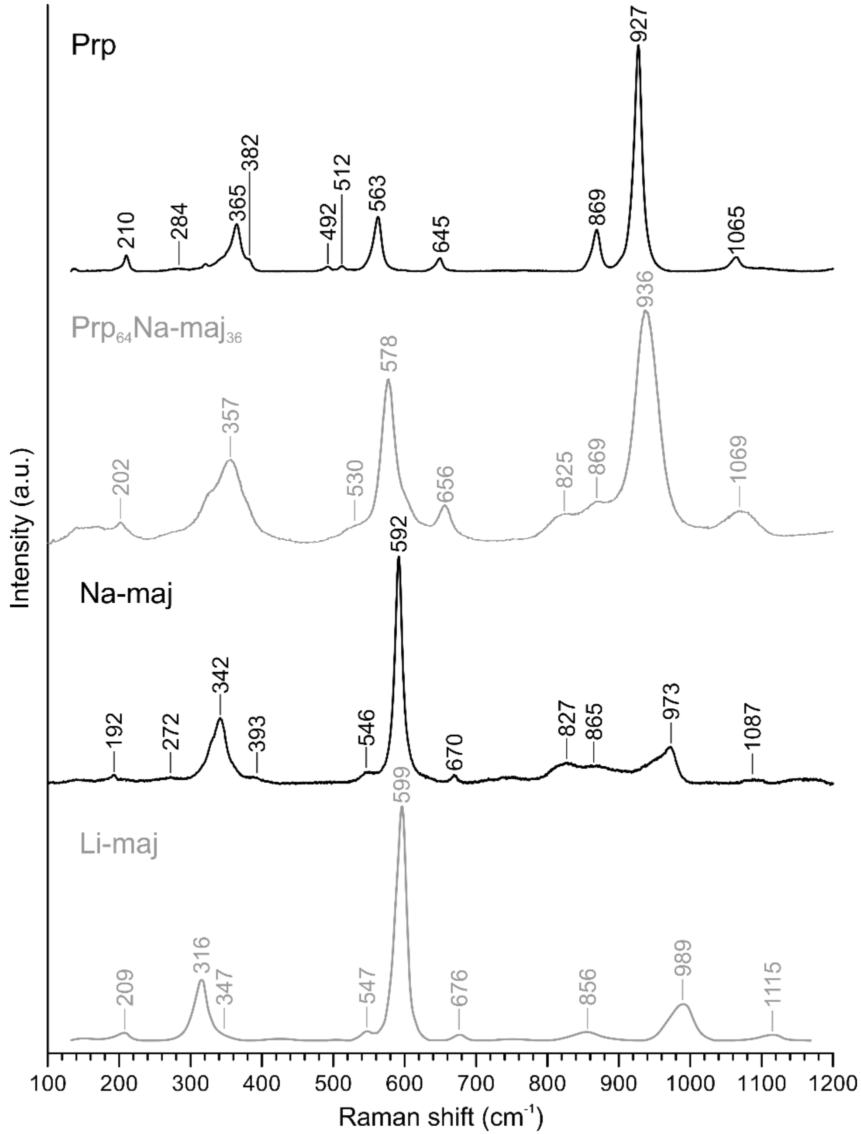
Tetragonal
space group $I4_1/acd$
(Bindi et al., 2011)

Cubic
space group *Ia*3*d*
(Yang et al., 2009)

Transformation from cubic to tetragonal



Variations of unit cell parameters as a function of composition for solid solutions
Dymshits et al., 2013



Mineral diagnostic and pressure estimation

Raman spectroscopy → pyroxene or garnet into the inclusion → pressure estimation

Microprobe analyses → Mineral composition → Pressure estimation

Barometer for majoritic garnets

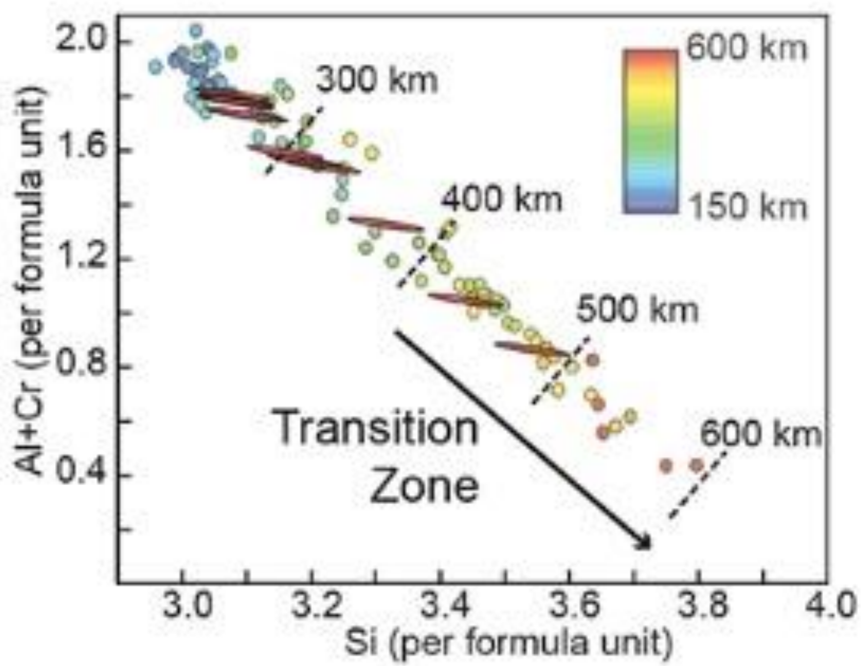
Akaogi and Akimoto (1979)

Empirical linear barometer based on Si and Al+Cr exchange

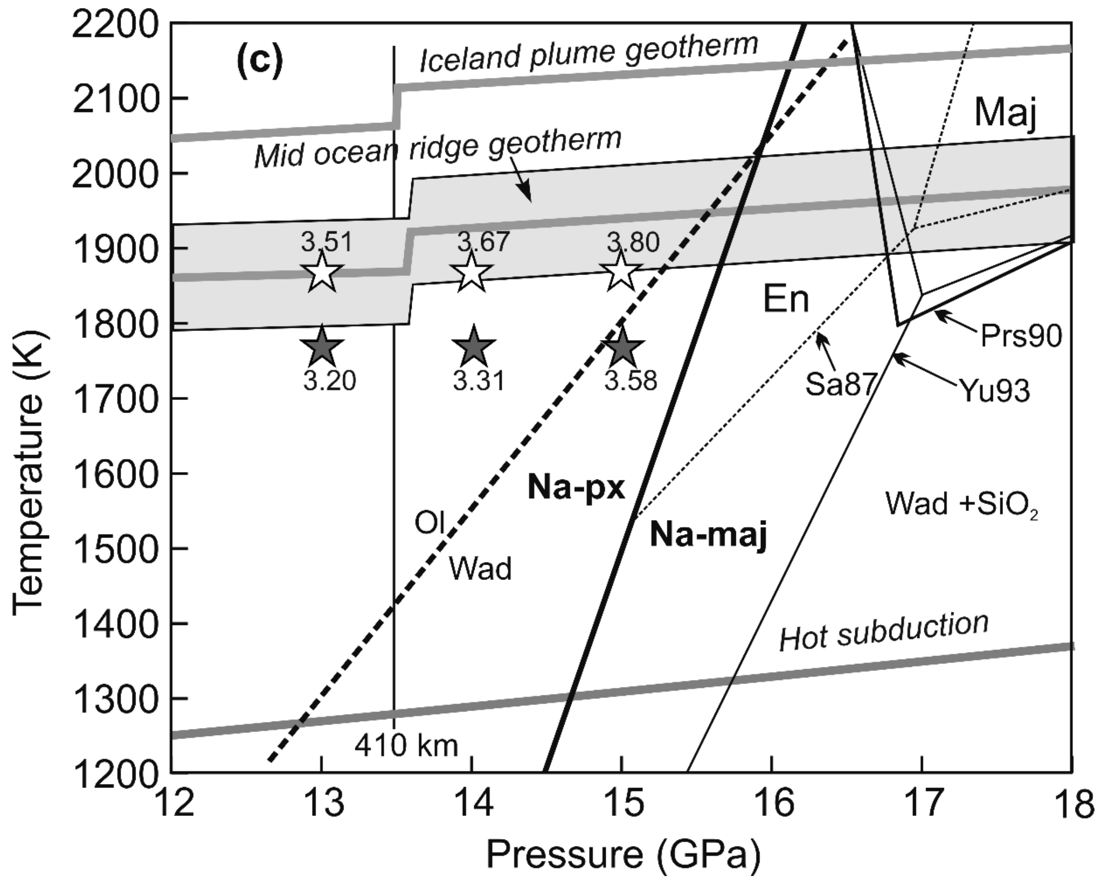
Keshav and Sen (2001)

Barometer based on experimental study of ultrabasic garnets (Irifune et al., 1987)

Stachel (2001)



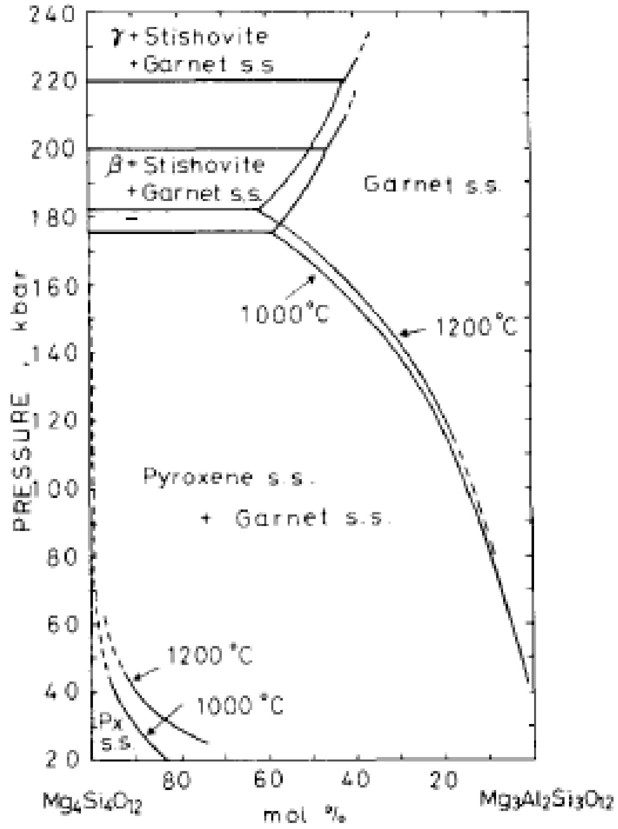
Barometer for majoritic garnets



Black stars - Si in f.u. in the garnets from Na-free systems (Gasparik 1992)

White stars – Si in f.u. in the garnets from Na-bearing systems (Dymshits et al. 2013)

Remember before you are going to create a new barometer



1. Good barometer = pressure dependent reaction (big volume effect of reaction)

2. Barometer is an exchange reaction (for example Px ↔ Grt)

3. Majorite barometer can be used up to 16.5 GPa (even for Na-free system)

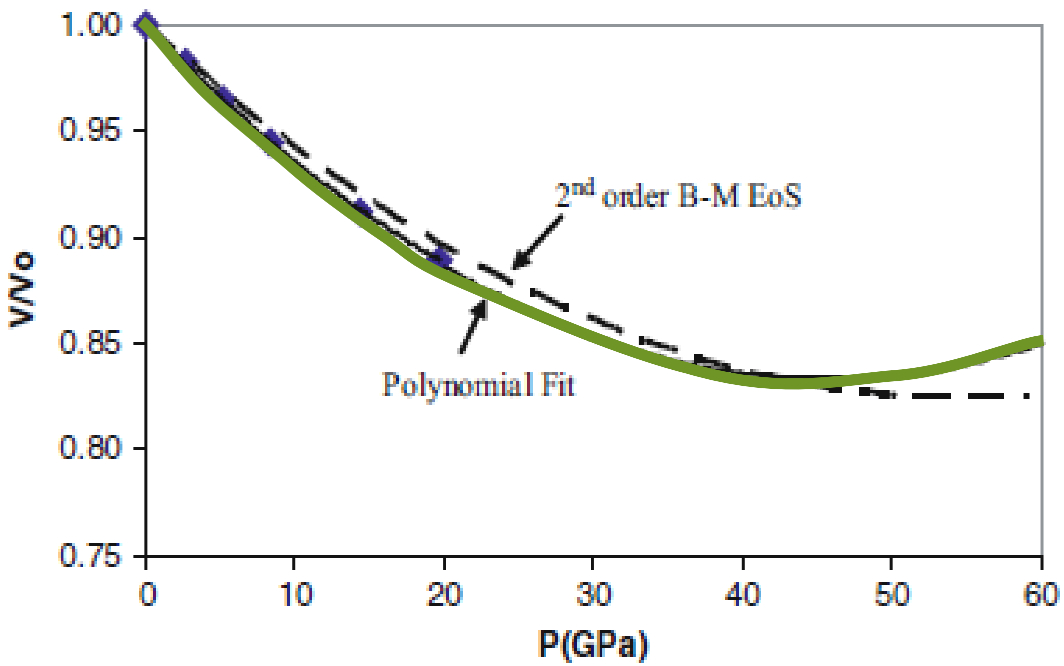
Equations of State

An Equation of State (EoS) = relation among V, P and T of a substance.

A **polynomial fit** of the measured P-V-T relation **is good for interpolation** of the experimental data

But a **polynomial** relation **can produce physically unacceptable behavior** on extrapolation beyond the range of experimental data.

Therefore, the experimental data need to be fitted by equations that have justifiable theoretical basis.



The ideal gas equation

PV = nRT

is the simplest example of such an equation.

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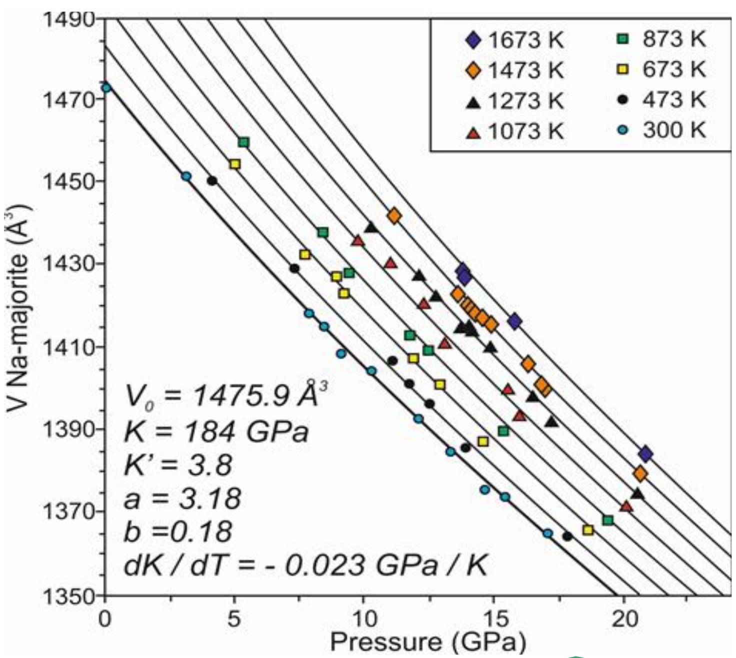
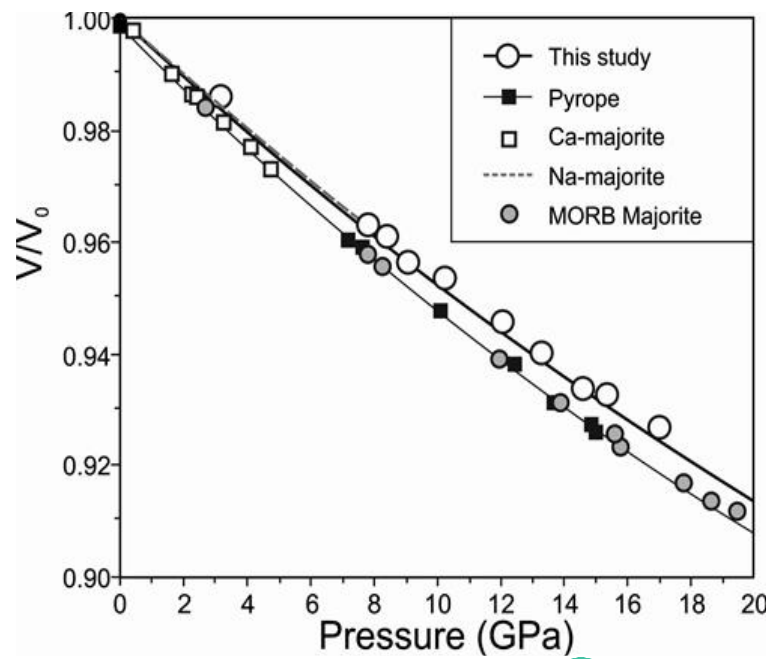
P–V–T equation of state of Na-majorite to 21 GPa and 1673 K

Anna M. Dymshits[a,b,*], Konstantin D. Litasov[a,b], Anton Shatskiy[a,b], Igor S. Sharygin[a,b], Eiji Ohtani[c], Akio Suzuki[c], Nikolay P. Pokhilenko[a], Kenichi Funakoshi[d]



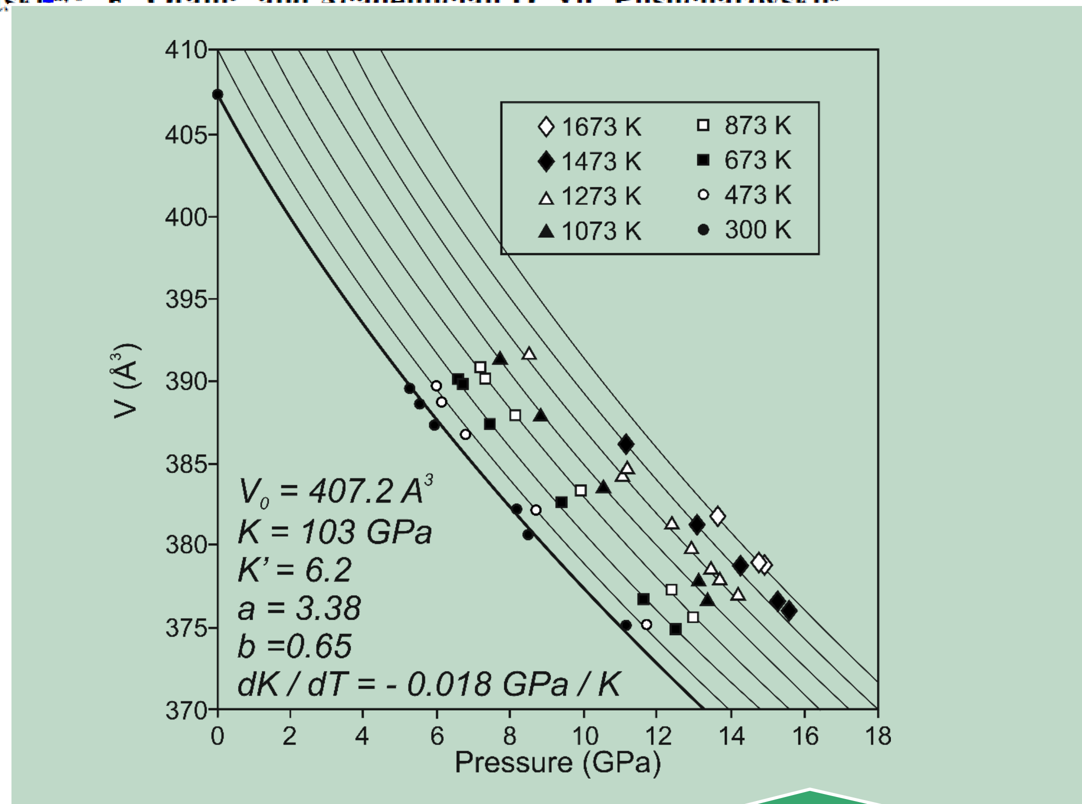


We have obtained the PVT equation of state of Na-majorite up to 21 GPa at high temperatures.

Na-majorite is the phase with the highest value of the bulk modulus among garnets

Thermal Equation of State of $NaMg_{0.5}Si_{2.5}O_6$ and New Data on the Compressibility of Clinopyroxenes

A. M. Dymshits[a, b], I. S. Sharygin[a, b], I. V. Podborodnikov[a, b], K. D. Litasov[a, b],
A. F. Shatskii[a, b], E. Otani[c], and Academician D. Yu. Pushcharovskii[d]



Despite the small volume of the cell, **Na-pyroxene** has a sufficiently **high bulk modulus**

It took Perchuk five years to develop ideas first formulated in his work into one of the most fruitful avenues of research in modern petrology: mineralogical geothermobarometry underlain by thermodynamic laws governing the distributions of isomorphic components between coexisting minerals.

Leonid Perchuk, an outstanding Russian petrologist and mineralogist.
November 1933 – June 2009

Thank you for attention!

V.S. Sobolev
Institute of Geology
and Mineralogy