The stability and water solubility of high pressure hydrous and nominally anhydrous minerals in the mantle

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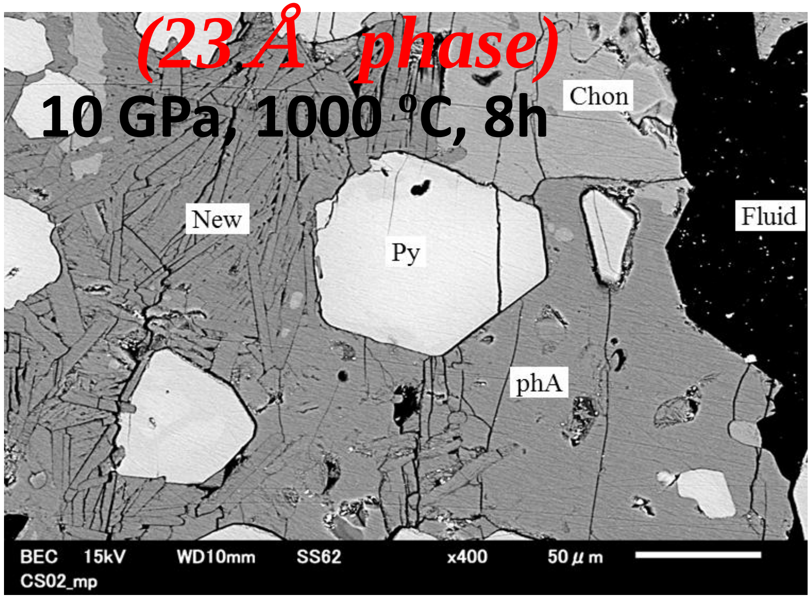
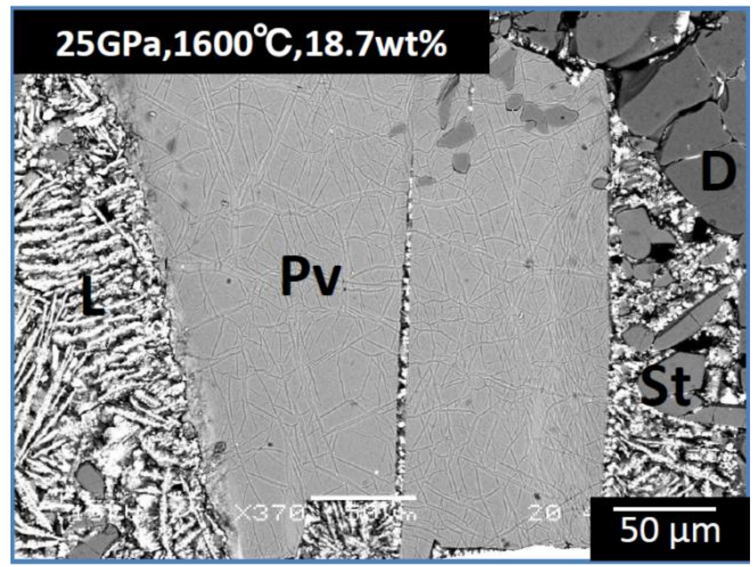
Aluminous new phase (23 Å phase)



$Mg_{11}Al_2Si_4O_{16}(OH)_{12}$
H_2O ~12 wt%

Cai et al. (2015)

hydrous bridgmanite (perovskite)



$MgAl_{0.1}Si_{0.9}O_3H_{0.1}$
H_2O ~0.8 wt%

Inoue et al. (in prep.)

Discovery of hydrous ringwoodite in diamond inclusion

(Pearson et al.,2014)

LETTER

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Hydrous mantle transition zone indicated by ringwoodite included within diamond

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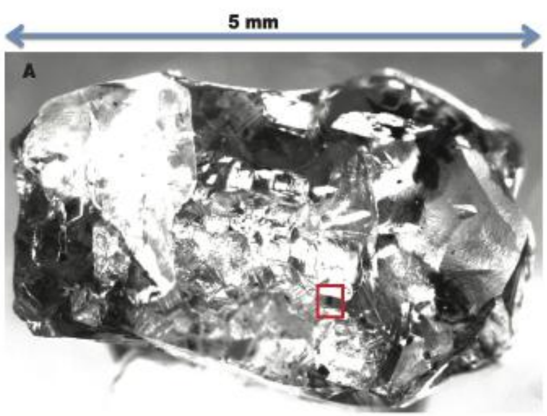
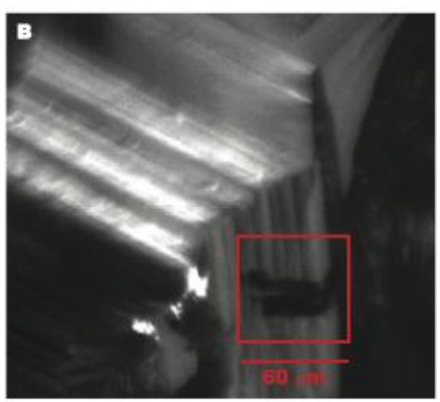




Extended Data Figure 1 | Image of JUc29 diamond and the ringwoodite-walstromite inclusion. a, Monochrome image of diamond JUc29 taken under incident light, with the ringwoodite-walstromite inclusion pair highlighted by a red square. The irregular shape and hexagonal pits in the diamond are signs of significant resorption. b, Enlarged view of the area of the host diamond (rotated 90° relative to a) containing the ringwoodite-walstromite inclusion pair. The shadow behind the rectangular area outlining the inclusion pair is probably a stress fracture in the diamond.

Discovery in diamond inclusion

~1.5 wt%H_2O included

The mantle transition zone is really hydrous condition, at least in some regions.

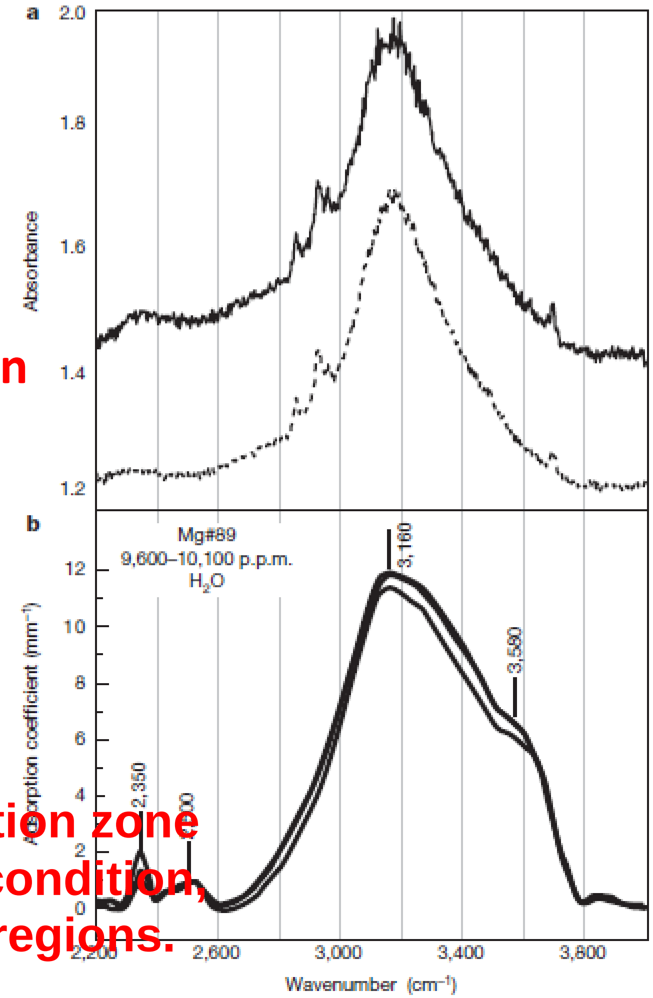
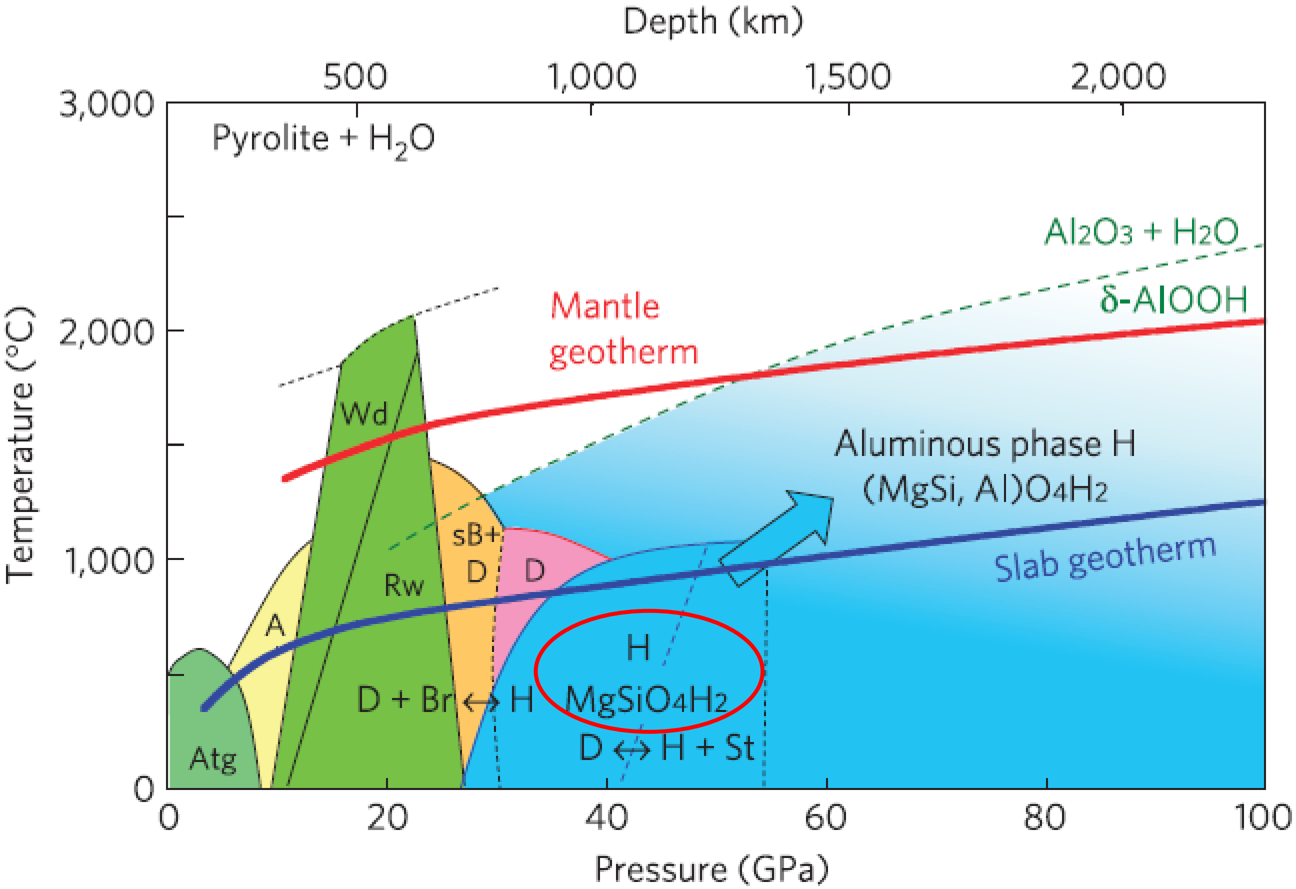


Figure 2 | FTIR spectra of ringwoodite inclusion in Juína diamond JUc29. **a**, Unpolarized FTIR spectra for ringwoodite inclusion in diamond JUc29 between 2,200 and 3,900 cm^{-1}. The two spectra were measured at ~90° degrees to each other and are unsmoothed, but were corrected for a background that includes the intrinsic response of the host diamond. Water contents calculated by integration of these two spectra are between 1.4 and 1.5 wt% (see Methods section on FTIR). **b**, Reference spectra for hydrous Fe-bearing ringwoodite (Mg# 89) containing ~1 wt% H_2O (ref. 27).

Hydrous peridotite (MgO-SiO_2-H_2O system)



Mg_2SiO_4

Wd: wadsleyite

H_2O= ~3.3 wt%

Rw: ringwoodite

H_2O= ~2.5 wt%

SiO_2

St: stishovite

Nishi et al. (2014)

Atg: antigorite $Mg_6Si_4O_{10}(OH)_8$ H_2O= 13 wt%

A: phase A $Mg_7Si_2H_6O_{14}$ H_2O= 11.8 wt%

sB: superhydrous B $Mg_{10}Si_3H_4O_{18}$ H_2O= 5.8 wt%

D: phase D $MgSi_2H_2O_6$ H_2O= 10.1 wt%

H: phase H $MgSiH_2O_4$ H_2O= 15.2 wt%

Br: brucite $Mg(OH)_2$

H_2O= 31 wt%

δ-AlOOH AlOOH

H_2O= 15 wt%

Our group has been conducting the study for the stability and water solubility of hydrous and nominally anhydrous minerals, and *the recent target is the effect of Al, trivalent cation.*
In this process, we found the new Al-bearing hydrous phase *(23 Å phase)* and Al-bearing hydrous bridgmanite.

Today's topic

1) Discovery of new Al-bearing hydrous phase *(23 Å phase)* stable in upper mantle condition (Cai et al., 2015)
2) Discovery of Al-bearing hydrous bridgmanite stable in lower mantle condition (Inoue et al., in prep.)

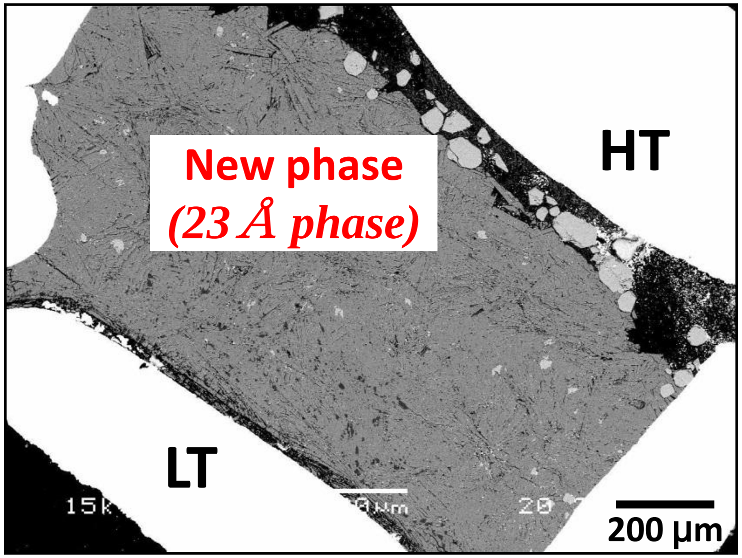
Al-bearing new hydrous phase
(23 Å phase)
in upper mantle condition

(Cai et al., 2015)

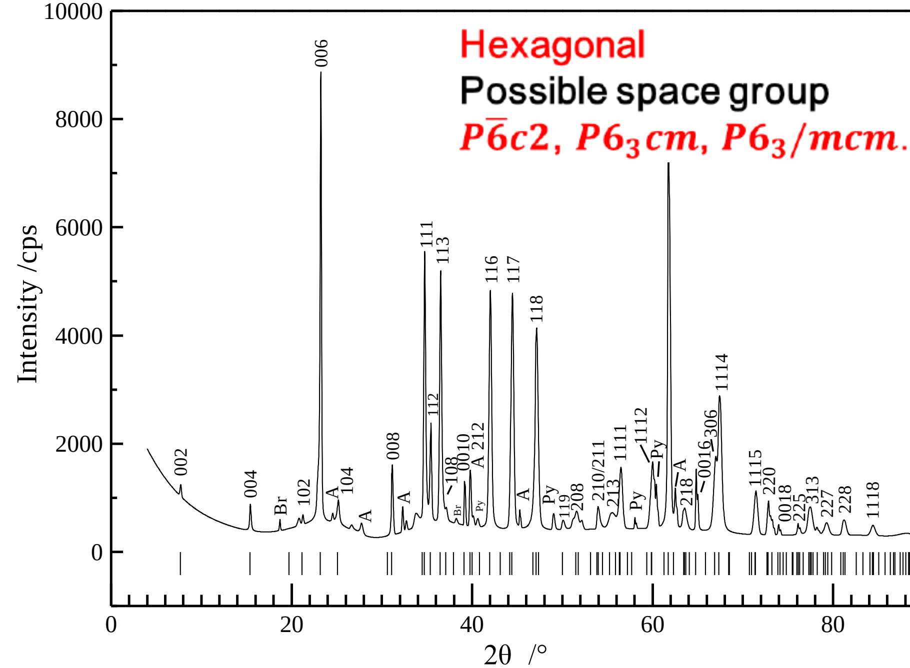
Al-bearing new hydrous phase *(23 Å phase)*

Starting composition: $Mg_{11}Al_2Si_4O_{15}(OH)_{14}$

P&T: **10 GPa, 1000 ºC**



Fitting the XRD pattern by assuming a hexagonal structure

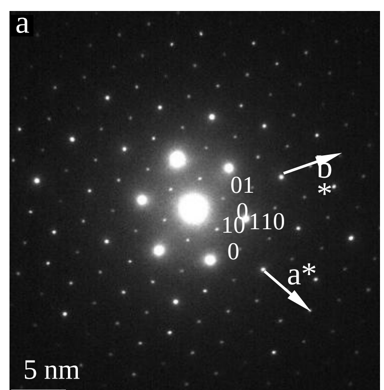


Chemical Composition (wt%)

MgO	Al_2O_3	SiO_2	H_2O	Total
49.84	11.75	26.46	11.95	100

New phase *(23 Å phase)*	phA
$Mg_{11}Al_2Si_4O_{16}(OH)_{12}$	$Mg_7Si_2O_8(OH)_6$
H_2O 12.1 wt%	H_2O 11.8 wt%

TEM observation

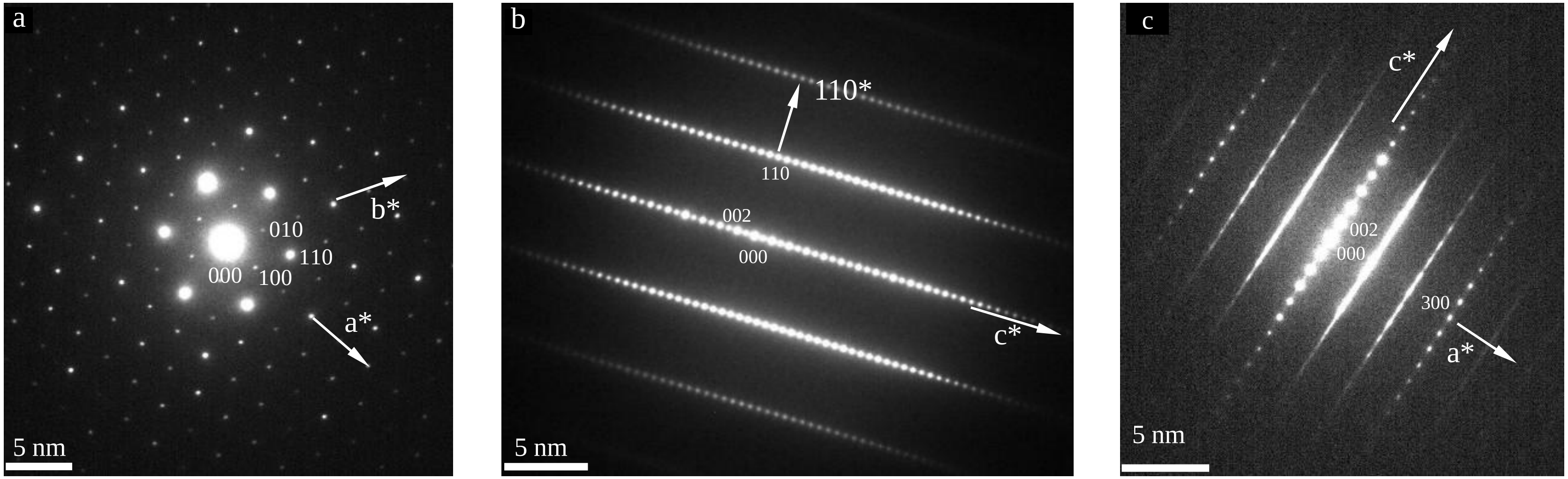


Lattice parameter

	new phase	phase A*
a	5.1972(9) Å	7.8603(2)
c	*22.991(4) Å*	9.5730(2)
V	537.8(2) Å^3	512.22
ρ	2.760	2.959

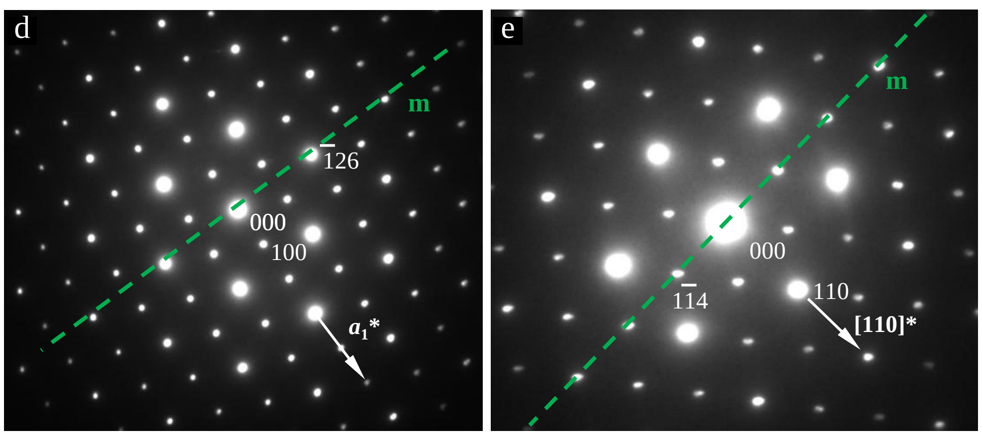
*Horiuchi et al., 1979

TEM observation



hhl spots

$h\bar{h}l$ spots



Mirror planes exist at every 30º.

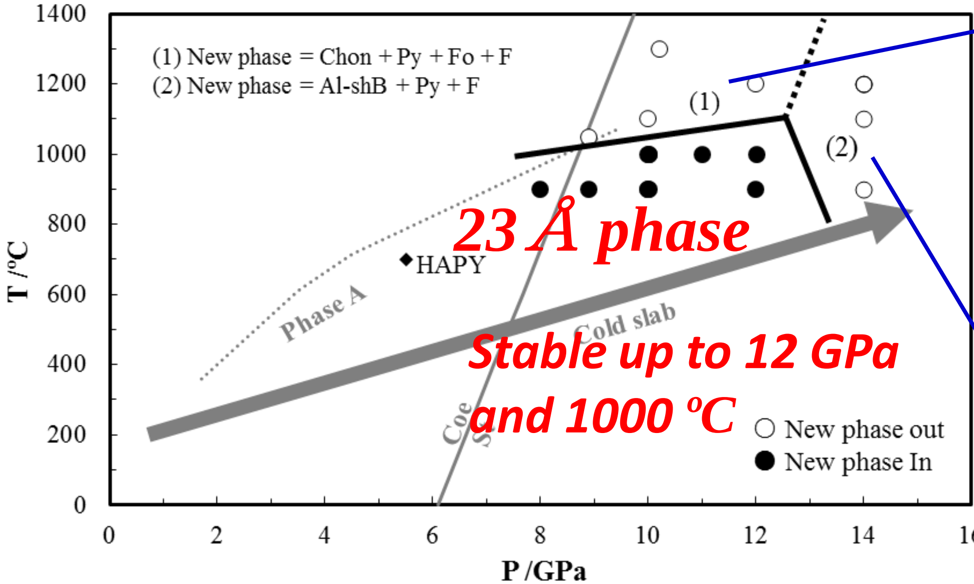
- **Hexagonal** structure;
- hhl not extinct;
- $h\bar{h}l$ (l = 2n+1) extinct;
- $00l$ (l = 2n+1) extinct;
- **Mirror planes**.

Possible space group:

$P\bar{6}c2$, $P6_3cm$, or $P6_3/mcm$

a = 5.23(6) Å, c = 23.2(2) Å

Stability region of *23 Å phase*

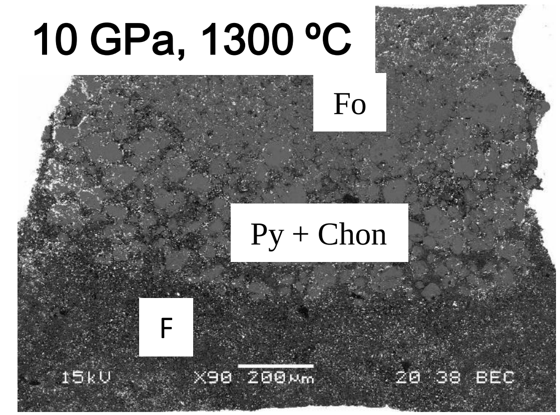


Break down:

<13 GPa

23 Å phase → **Chon + Py + Fo + F**

10 GPa, 1300 °C

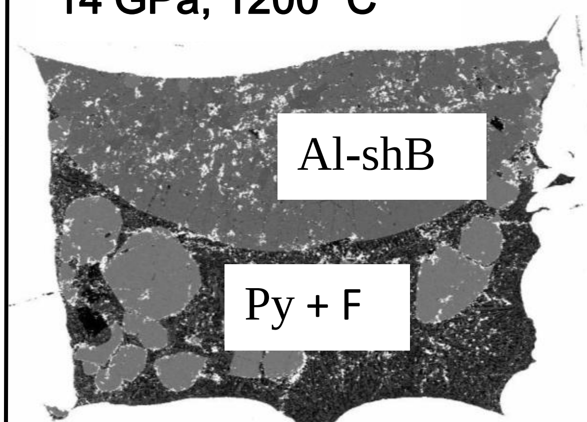


500 μm

>13 GPa

23 Å phase → **Al-shB + Py + F**

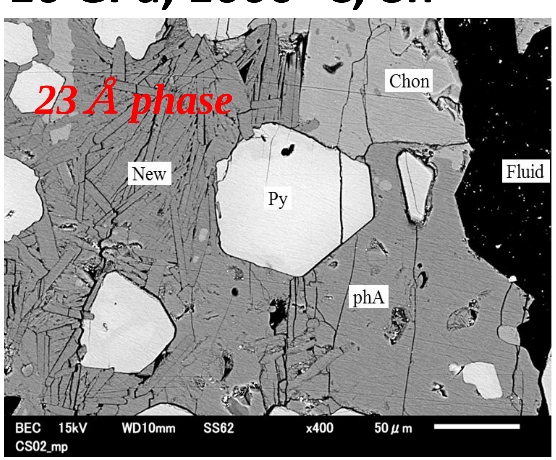
14 GPa, 1200 °C



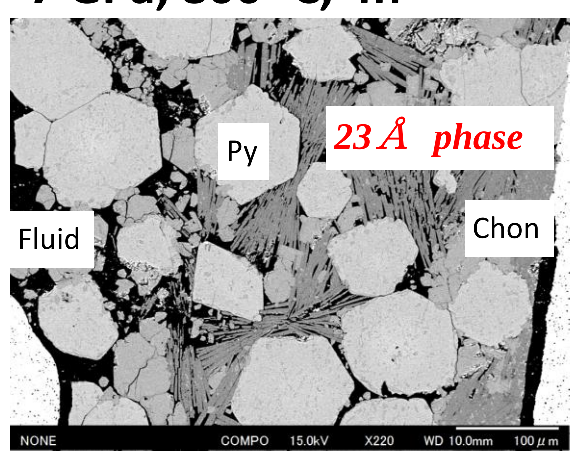
Fo: forsterite; Chon: chondrodite; Py: pyrope; Al-shB: Al-bearing superhydrous B; F: fluid

23 Å phase is stable *in Chlorite composition*

10 GPa, 1000 °C, 8h



7 GPa, 800 °C, 4h



Al-bearing hydrous bridgmanite stable in lower mantle condition

(Inoue et al., in prep.)

This PPT was modified from my oral presentation because before publication.

Chemical composition of Bridgmanite

Table. Chemical compostion of Perovskite (mol)

P (GPa)	25	26	26
H_2O (wt%)	18.7	18.7	11.3
Mg	0.99	1	0.99
Al	0.09	0.09	0.11
Si	0.94	0.93	0.93
Cation sum	2.02	2.02	2.02
measured number	8	3	7

(T=1600℃) Oxygen=3

No Mg deficit

DRY (Akaogi et al., 2002)

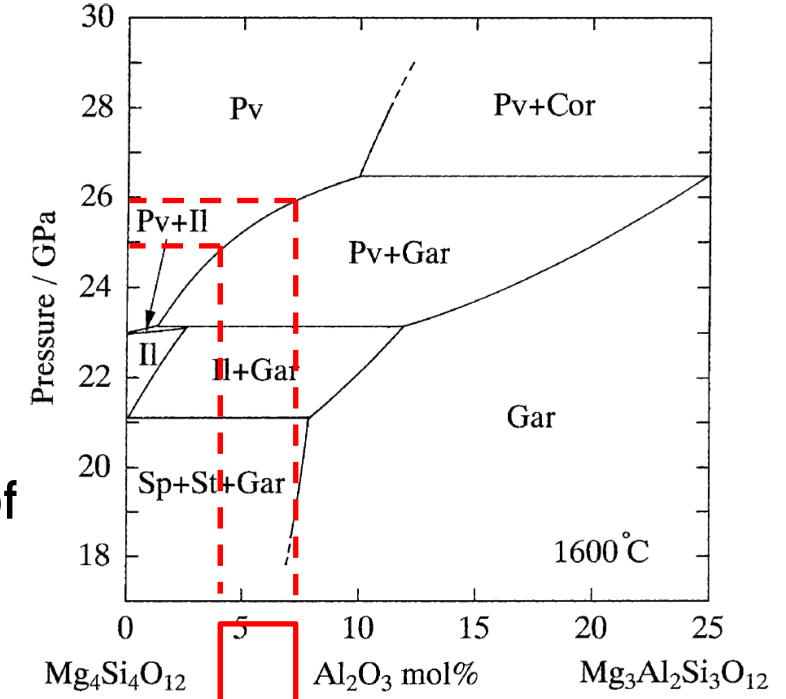


Fig. 3. Phase boundaries in the system $Mg_4Si_4O_{12}$–$Mg_3Al_2Si_3O_{12}$ at 1600 °C up to 30 GPa determined by Kubo and Akaogi (2000). Abbreviations are the same as in Fig. 1.

Al incorporates into perovskite by the substitution of $Mg^{2+} + Si^{4+} \Leftrightarrow 2Al^{3+}$ in anhydrous condition, but in hydrous condition, only Si deficit is observed.

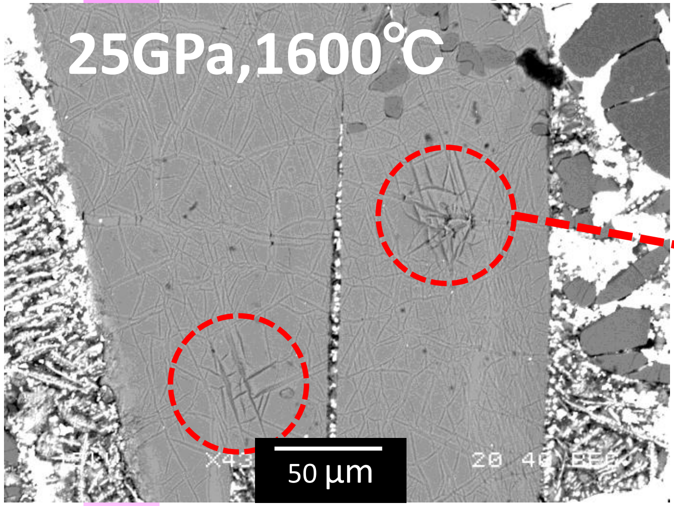
Al-perovskite in DRY condition (1600℃)

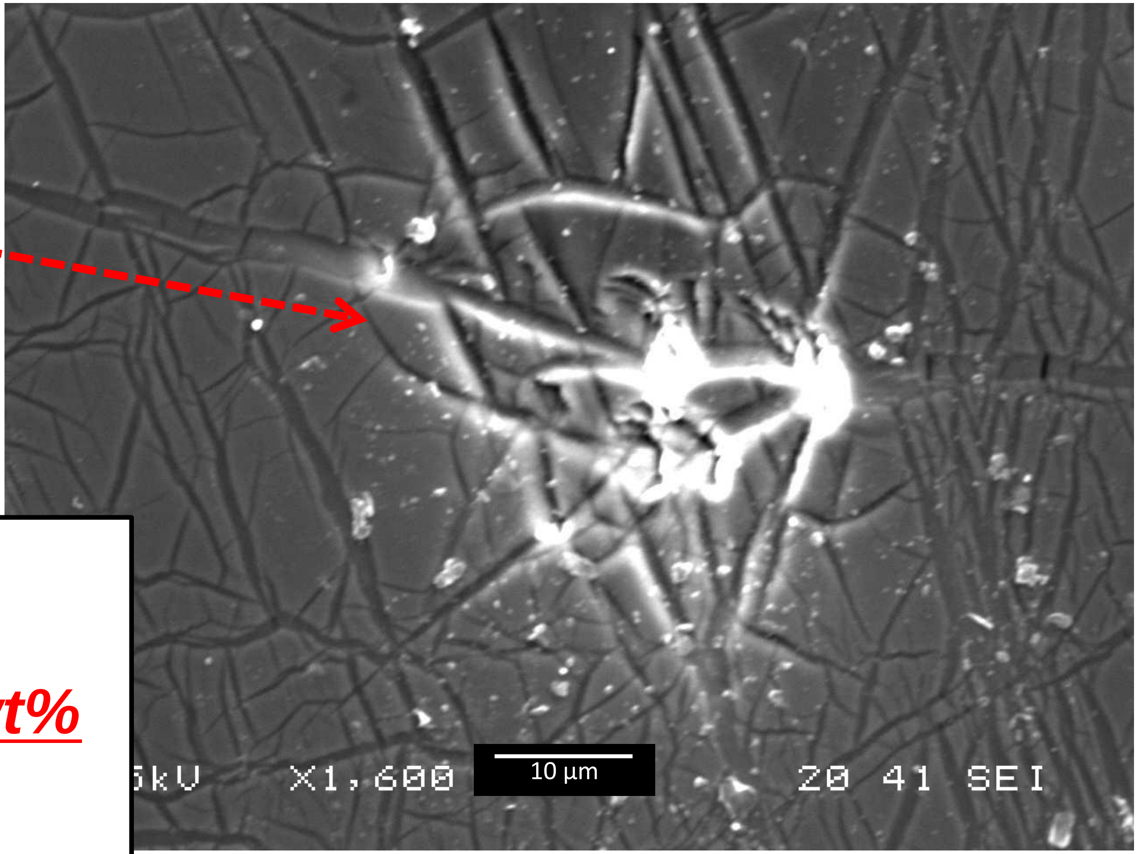
25 GPa: $Mg_{0.96}Al_{0.08}Si_{0.96}O_3$

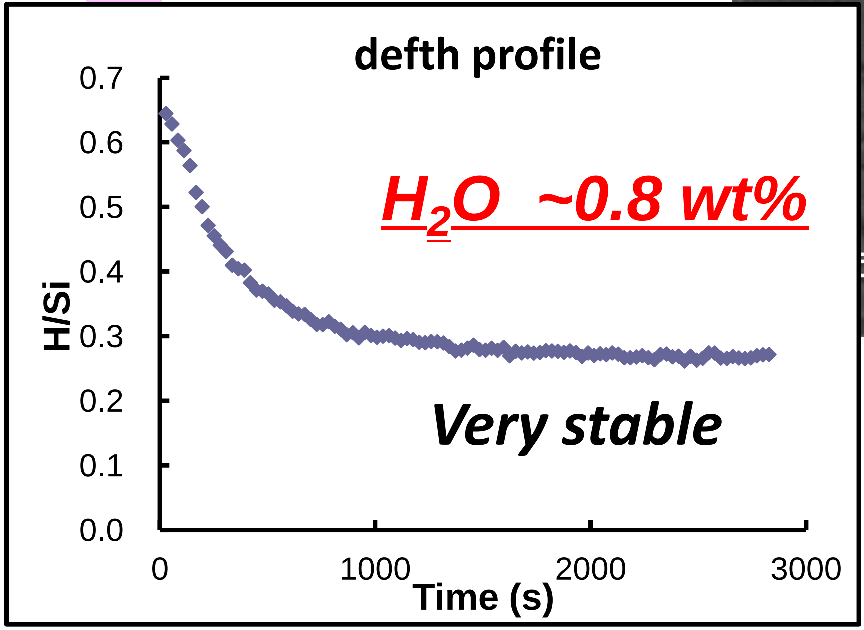
26 GPa: $Mg_{0.93}Al_{0.14}Si_{0.93}O_3$

H_2O measurement by SIMS

Hydrous bridgmanite

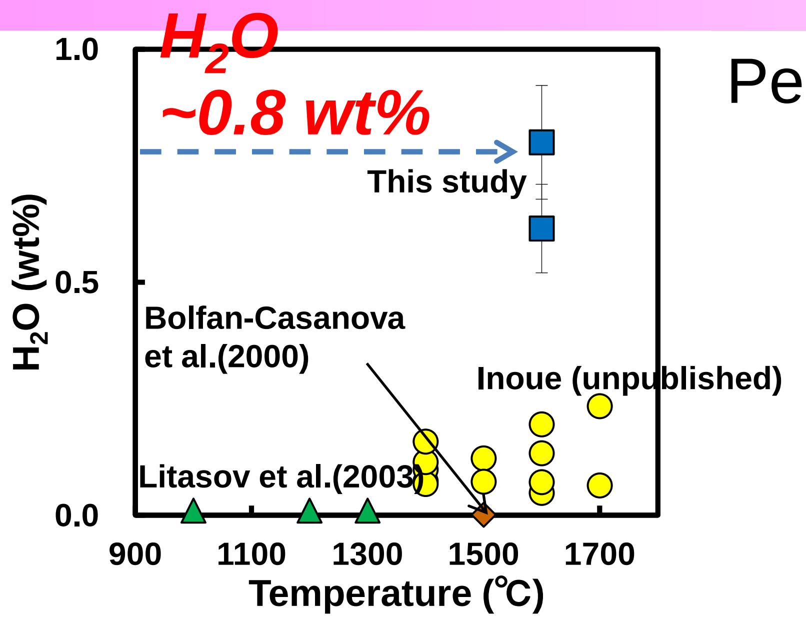






Amphibole crystal (H_2O ~1.66 wt%) was used as standard.

perovskite($MgSiO_3$) $Mg_{0.97}Si_{0.92}Al_{0.09}H_{0.09}O_3$



Perovskite includes Al_2O_3 (~5 wt%)

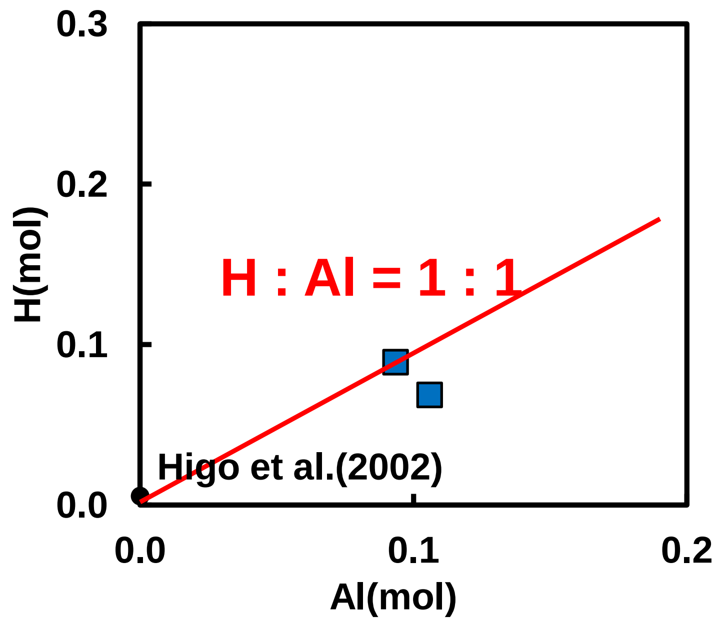
⇩

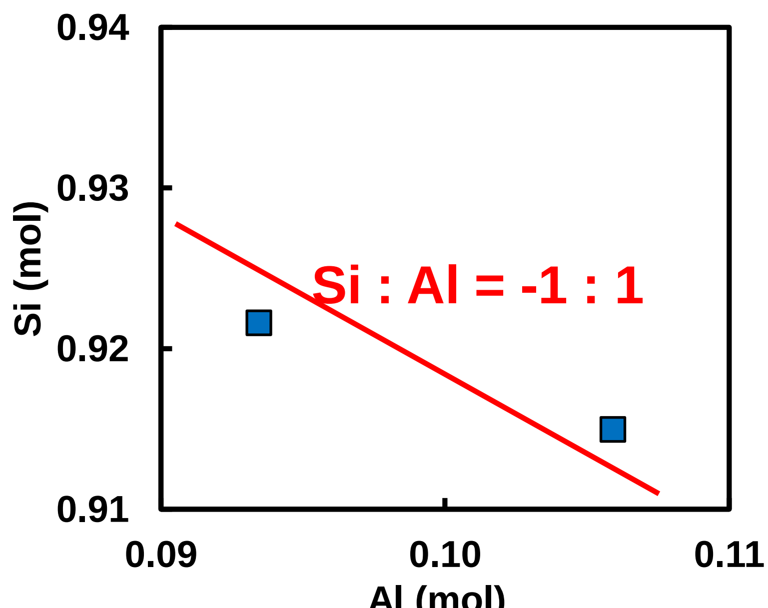
$Al^{3+} + H^{+} \Leftrightarrow Si^{4+}$

⇩

H : Al = 1 : 1→ H ↑, Al ↑

Si : Al = -1 : 1→ Si ↓, Al ↑





Single crystal X-ray diffraction study

Automated four-circle diffractometer at BL-10A, PF, KEK

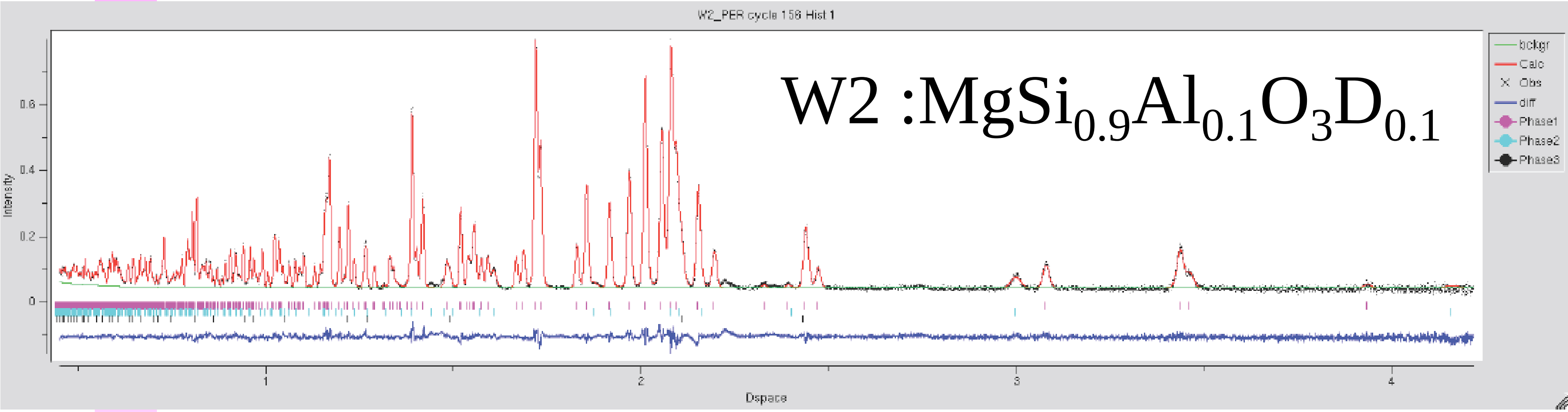
Structure refinement

1) SHELXL97 with WinGX software was used for all structural refinements (Scheldrick and Schneider 1997; Farrugia 1999).
2) Initial structural parameters of non-hydrogen atoms were taken from Horiuchi et al. (1987).
3) The averaged scattering values for dodecahedral (A) and octahedral (B) sites were modeled by the scattering factor of Mg^{2+} for A-site and that of Si^{4+} for B-site, respectively.
4) After the values were refined, the distributions of Mg, Al and Si at both A- and B-sites were evaluated by the optimization to minimize the summation of the squared residuals between the calculated and observed data such as <u>the site scattering power (electron number) of each site</u>, <u>total amount of each atom in the unit cell</u>, and <u>the mean bond valence distance</u> in each polyhedron within the restrictions of its bulk chemical formula.

Rietveld analysis for neutron diffraction study

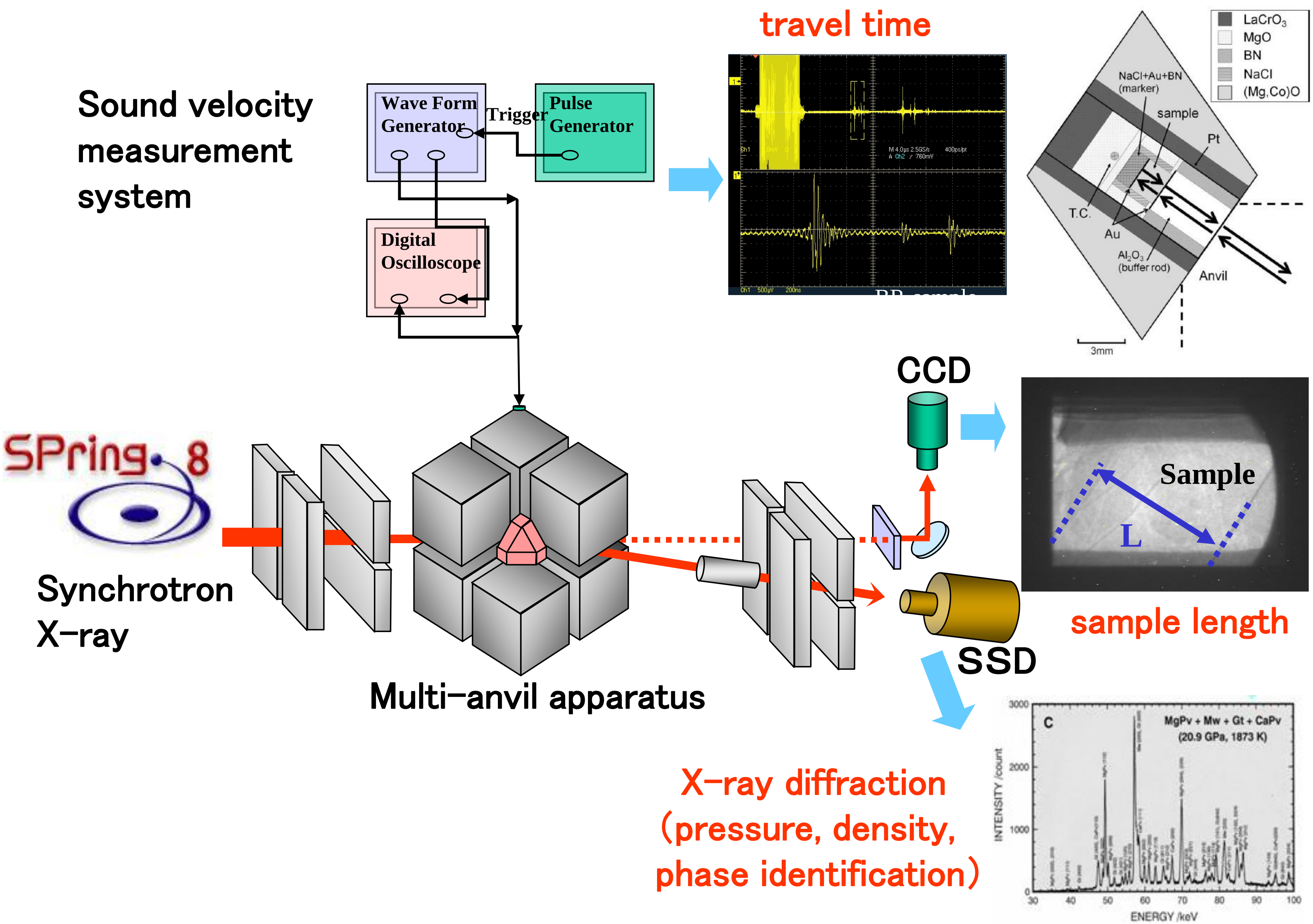
Slit size: 5 x 5 mm
Measurement time: 5 hr

Z-Rietveld program was used.



The above analysis was done by Pv : phase D: periclase = 90:8:2.
Still small amount of the other phase (δ-AlOOH) may exist.

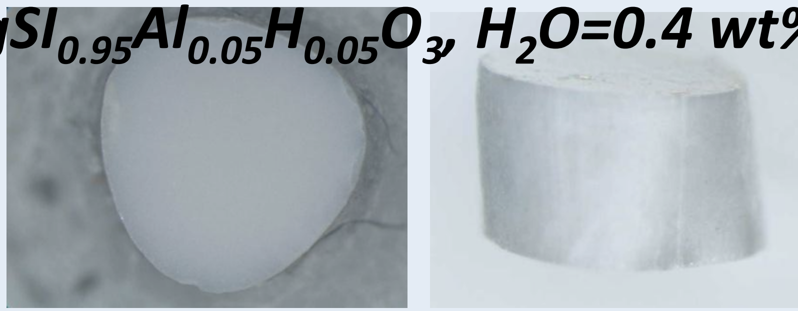
Sound velocity measurement under high P-T in SPring-8



Ultrasonic velocity (Vp, Vs) measurement

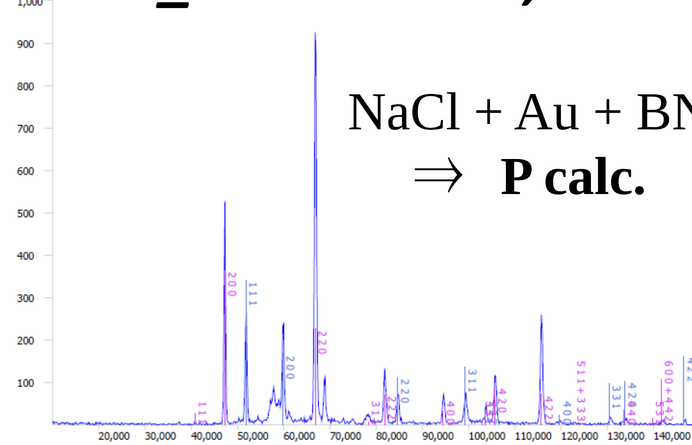
hydrous bridgmanite:

$MgSi_{0.95}Al_{0.05}H_{0.05}O_3$, H_2O=0.4 wt%



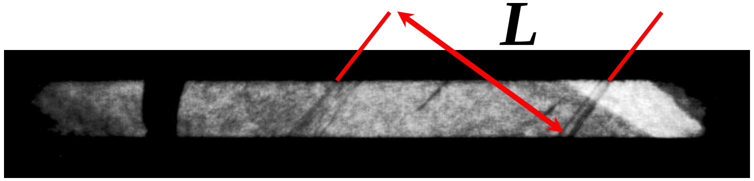
2 mm

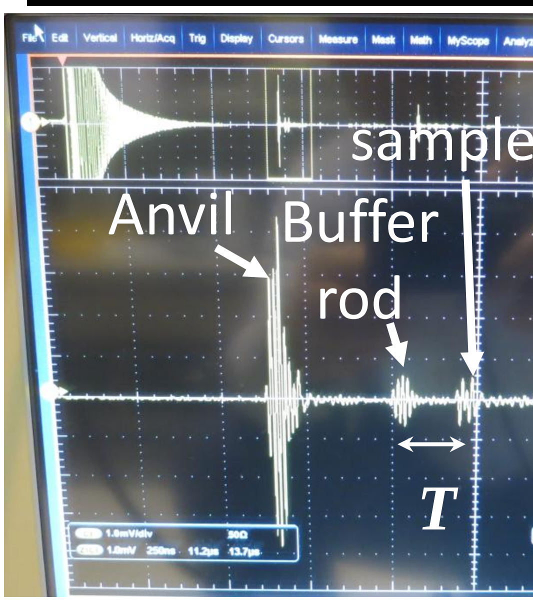
S2961_30: 19.7 GPa, 27°C



NaCl + Au + BN

⇒ **P calc.**





Sample length: ***L***

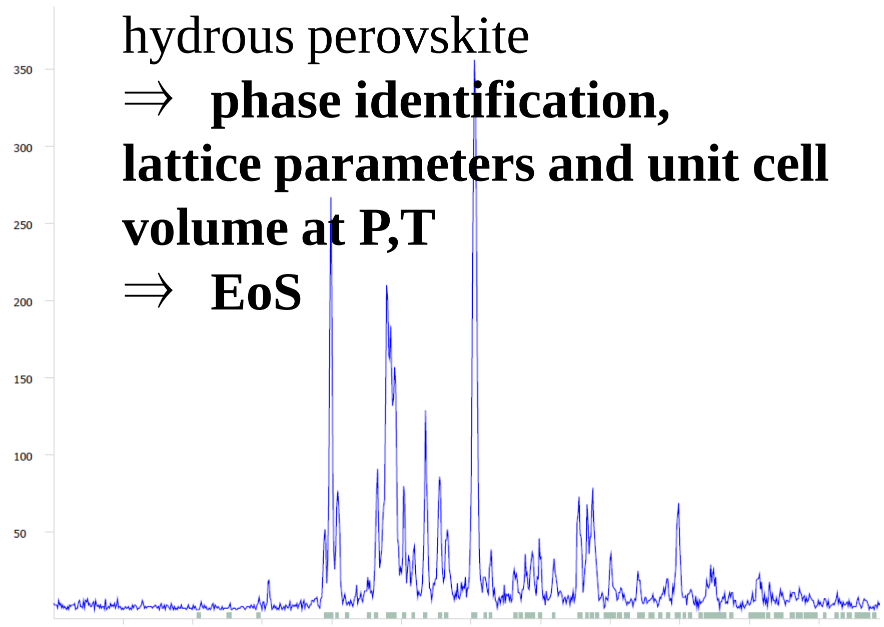
Travel time: ***T***

⇒ ***2L/T***

⇒ ***Vp, Vs***

Vp: 60 MHz

Vs: 40 MHz



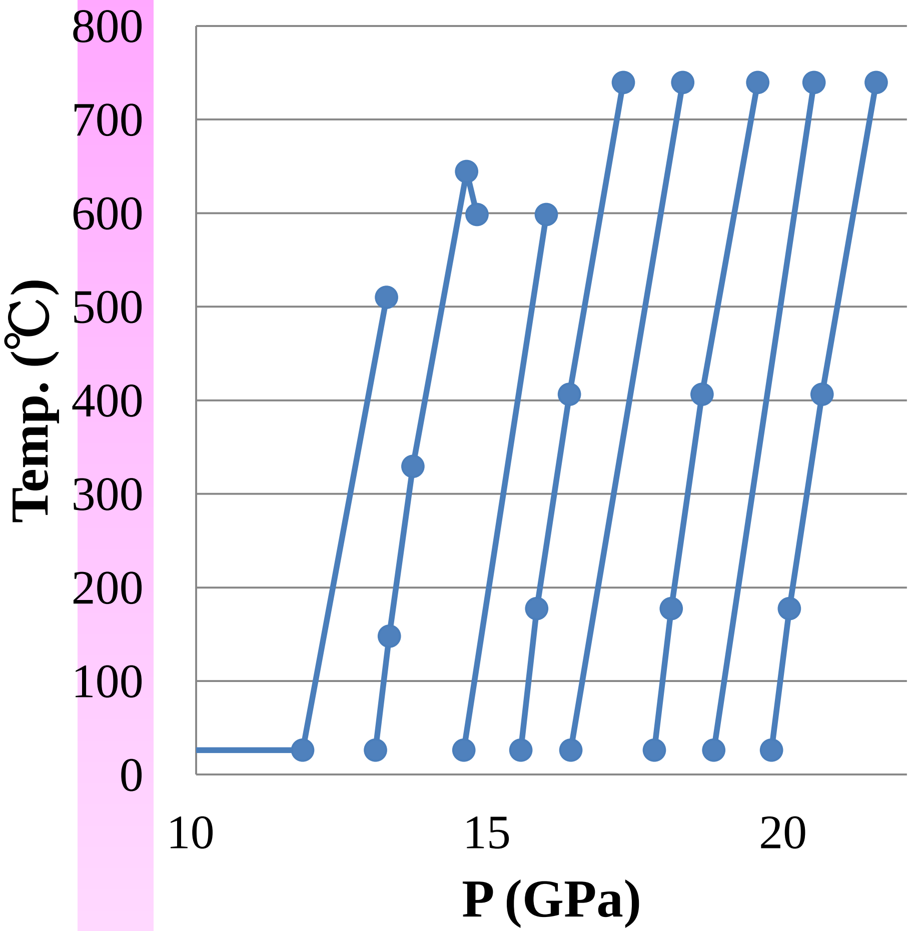
hydrous perovskite

⇒ **phase identification, lattice parameters and unit cell volume at P,T**

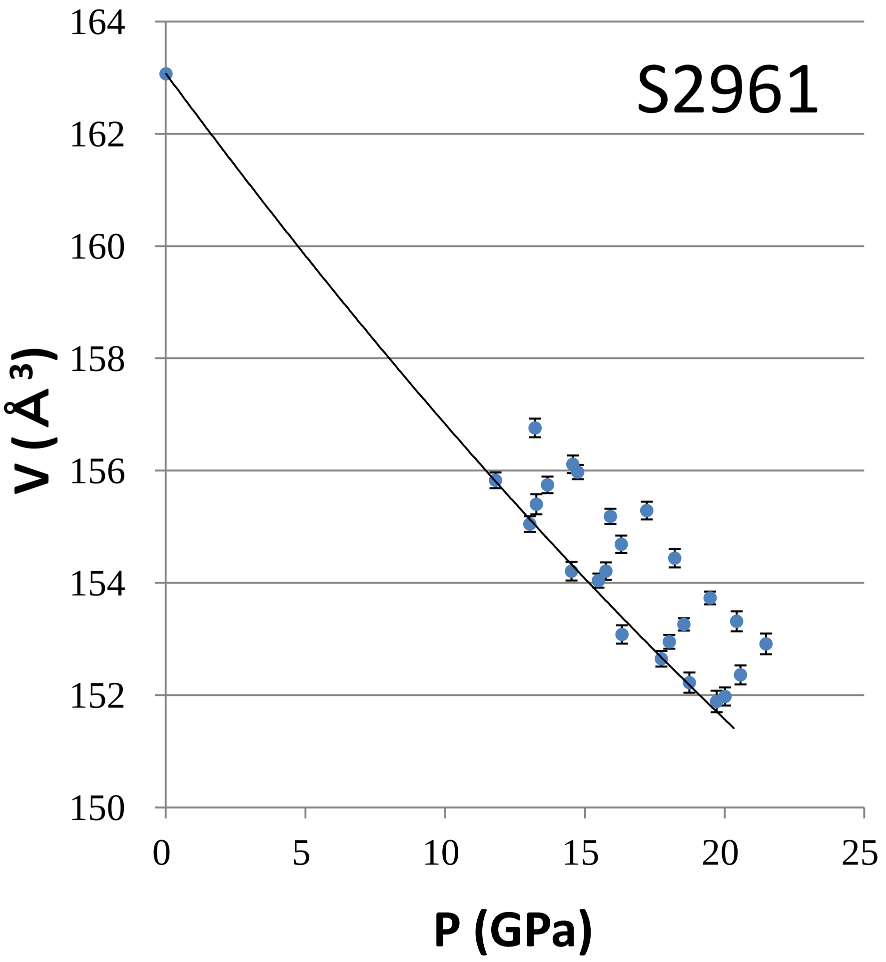
⇒ **EoS**

PVT of hydrous bridgmanite

Pressure-Temperature path



Pressure-Volume



Summary

1) New Al-bearing hydrous phase (23 Å phase) was found in chlorite composition in upper mantle condition. This structure is very unique, which shows elongated structure to c-direction.

   $Mg_{11}A_{l2}Si_4O_{16}(OH)_{12}$ H_2O ~12 wt%

   Hexagonal a=5.1972(9) Å, c=22.991(4) Å

2) Al-bearing hydrous bridgmanite was found, which formula is ~$MgSi_{0.9}Al_{0.1}O_3H_{0.1}$ H_2O ~0.8 wt%

   The lattice parameters and unit cell volume were larger than those of dry bridgmanite

3) The crystal structure was investigated by single crystal X-ray and powder neutron diffraction methods. These show that Al prefer B-site, and hydrogen position between O2-O2 which is c-direction could be the strong candidate.

4) The elastic velocity measurement was conducted. The preliminary analysis shows that bulk modulus , Vp and Vs are lower than those of dry bridgmanite.

Future plan

1) Determination of hydrogen position precisely.
   Then investigation of the effect of pressure
2) Determination of elastic wave velocity precisely, especially under high temperature.
3) Determination of EoS precisely,
4) The effect of pressure in the maximum water solubility in perovskite.
5) Investigation of the effect of Fe^{3+}.

Thank you for your attention.