Earth Science

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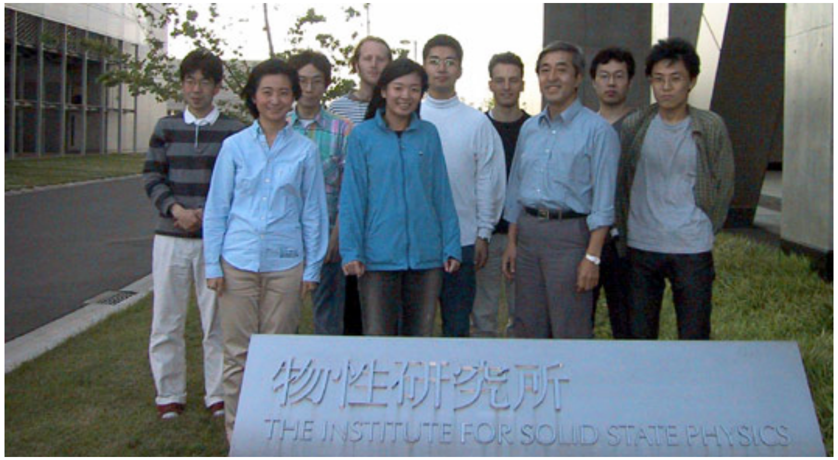
Acknowledgments

I had been a heavy user of synchrotron radiations (PF and SPring-8) for these more than 35 years to do high P-T X-ray diffractions.

1971 – 2012 : Institute for Solid State Physics, Univ. Tokyo



2012 – 2014: Geodynamic Research Center, Ehime Univ.

2014 – present : Geochemical Research Center, Univ. Tokyo

Outline

Introduction

Materials under pressure

Earth’s interior viewed by seismic wave

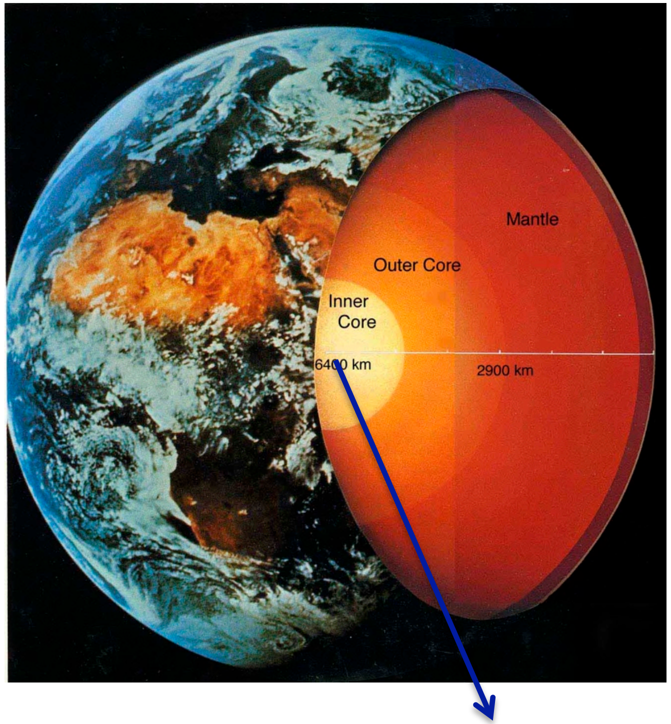
High-pressure experiments on minerals

High-density minerals discovered by these experiments

Present view of the dynamic Earth

Application to the study of novel materials

Pressures in the universe

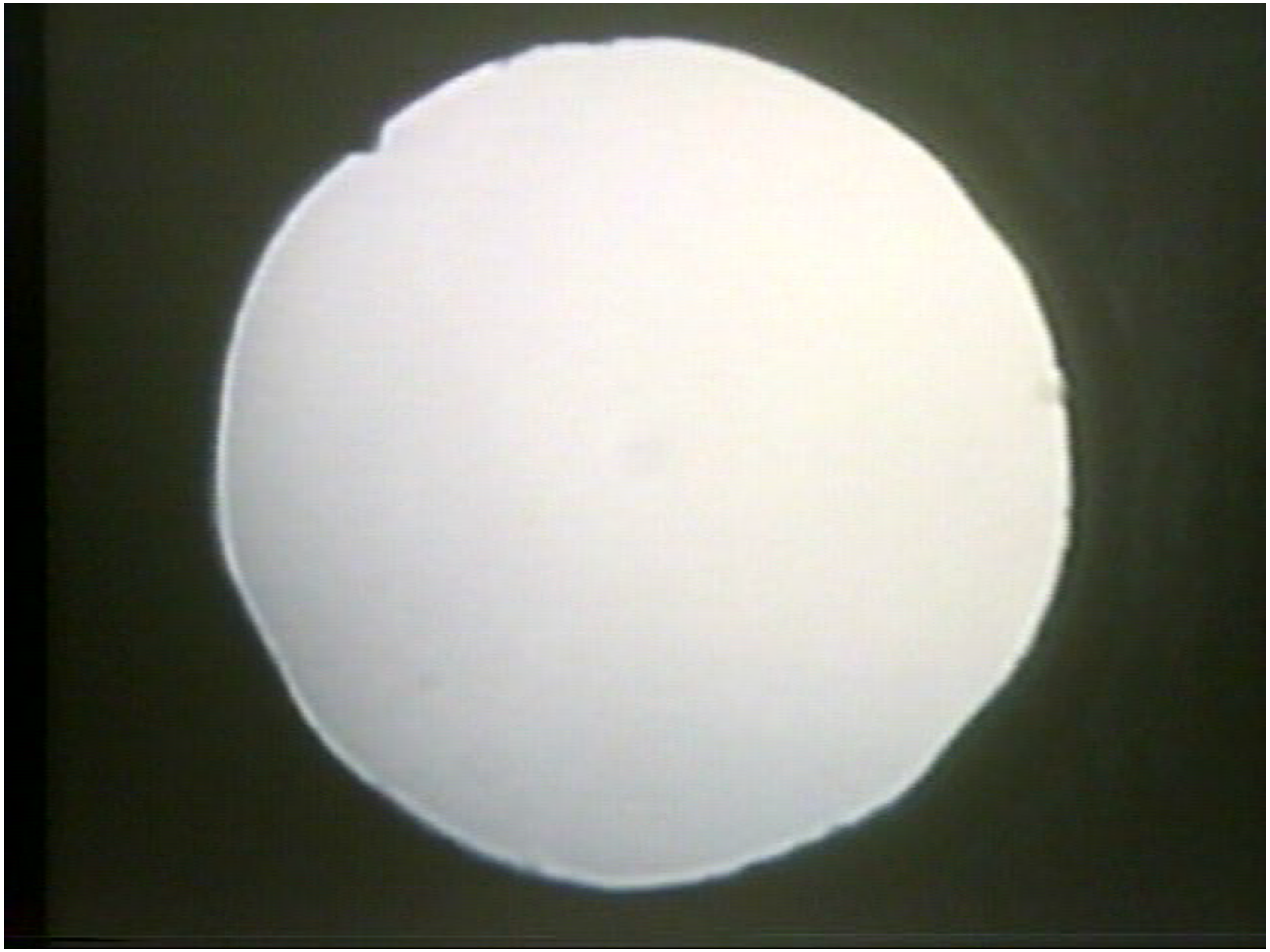


1 atm (0.1 MPa)

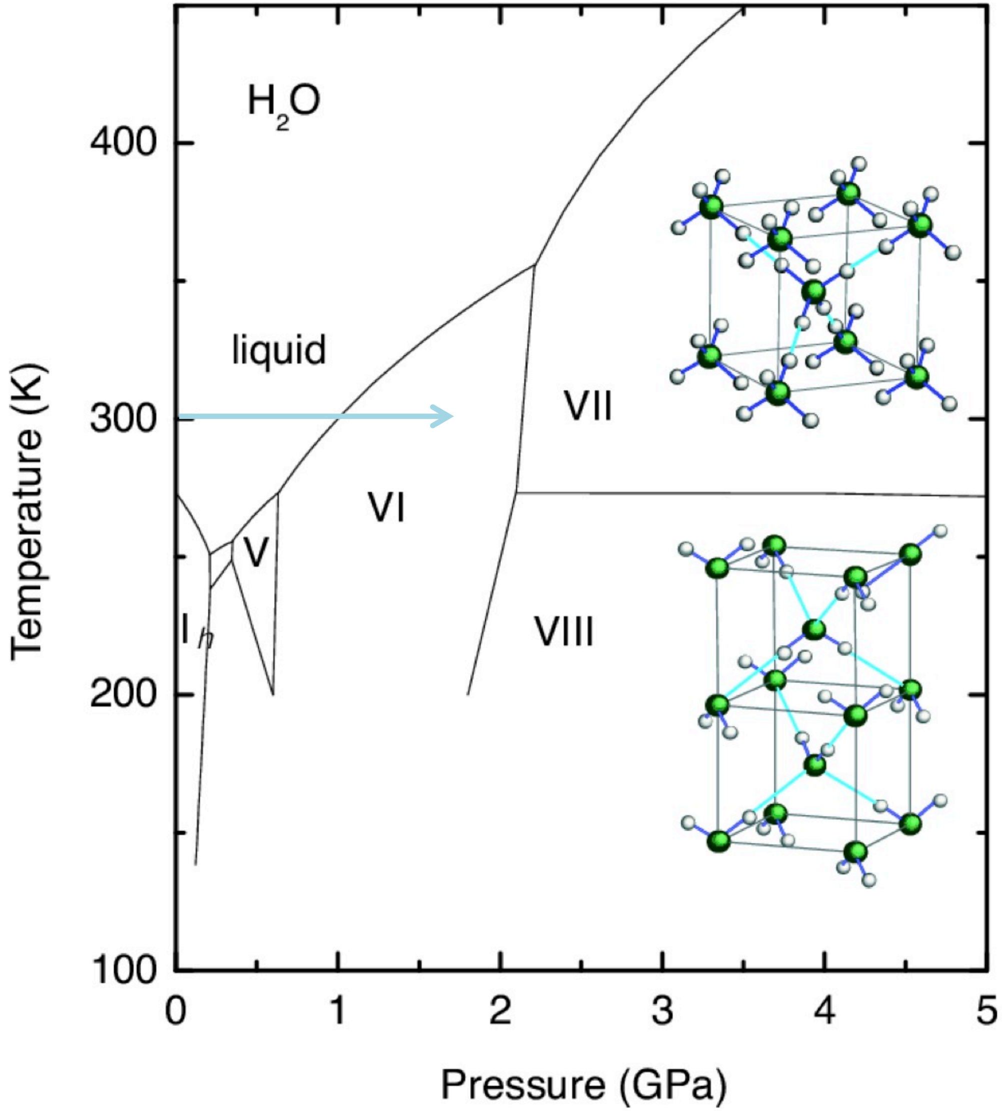
360 GPa

Bottom of the deepest sea: 0.1 GPa
Center of the Earth: 360 GPa
Center of Jupiter: 4.5 TPa (10^{12} Pa)
Center of the sun : 2.4 x 10^{16} Pa

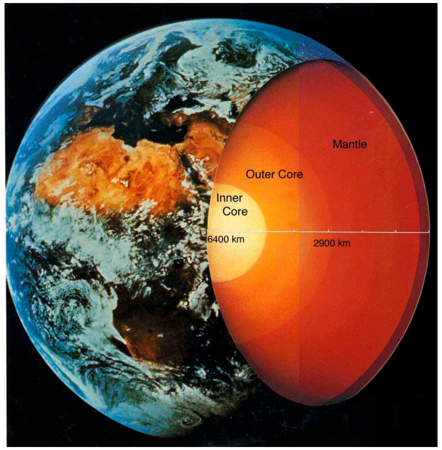
Behavior of H_2O at 300 K & high pressure



Phase diagram of H_2O ice



Earth's interior observed by seismology



Velocity, km/sec

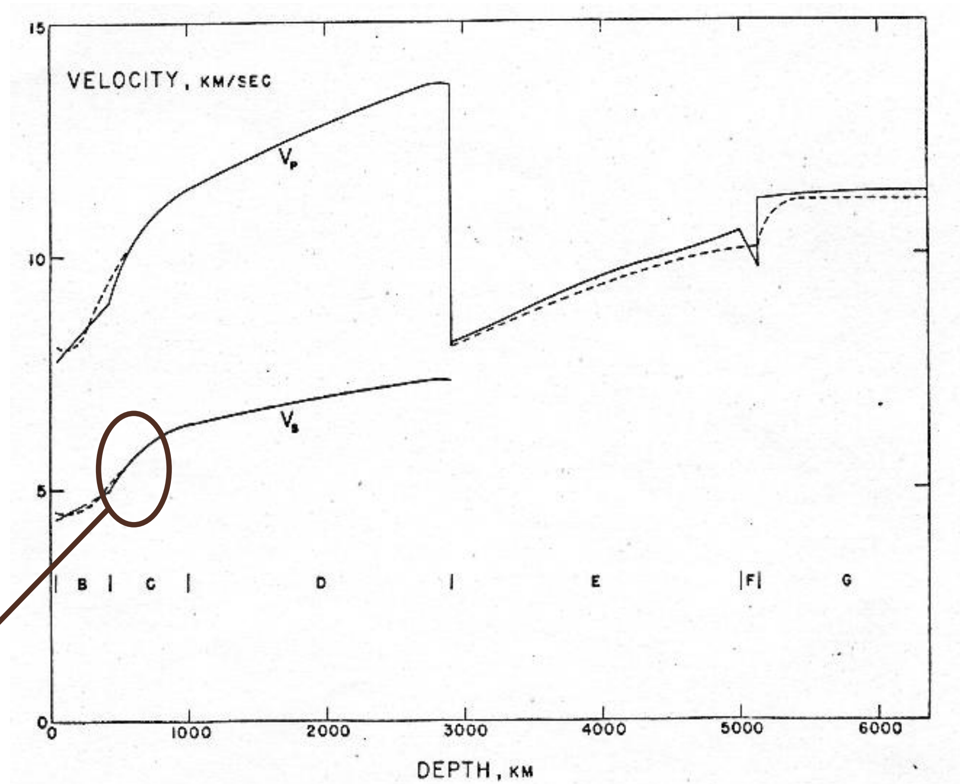


FIG. 1—SEISMIC VELOCITIES AS FUNCTION OF DEPTH

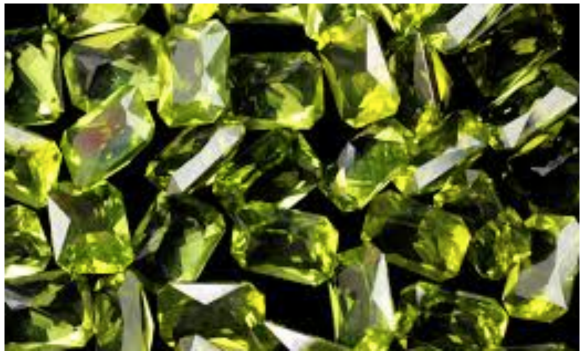
"transition zone"

Depth, km

F. Birch (1952)
"Elasticity and constitution of the Earth's interior"

Most abundant mineral in the upper mantle

Olivine: $(Mg,Fe)_2SiO_4$



"peridot"

Mg_2GeO_4 (at 1 bar)

olivine structure

810 °C

Temperature

spinel structure

Olivine - Spinel transition hypothesis

Bernal. J. D. (1936)

Jeffery H. (1937)

Experimental proof of Olivine-Spinel transition (I)

Ringwood (1958) Fe_2SiO_4, 600℃, 38 kbar

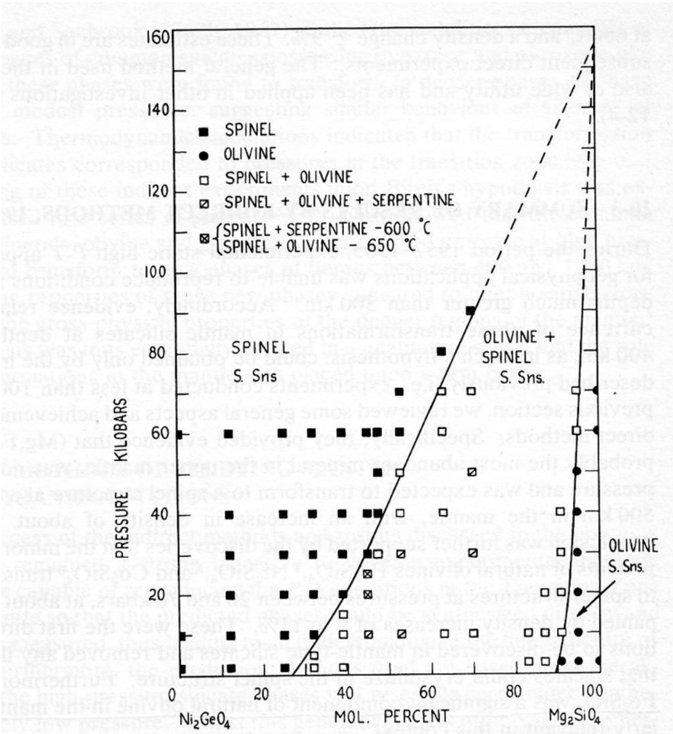
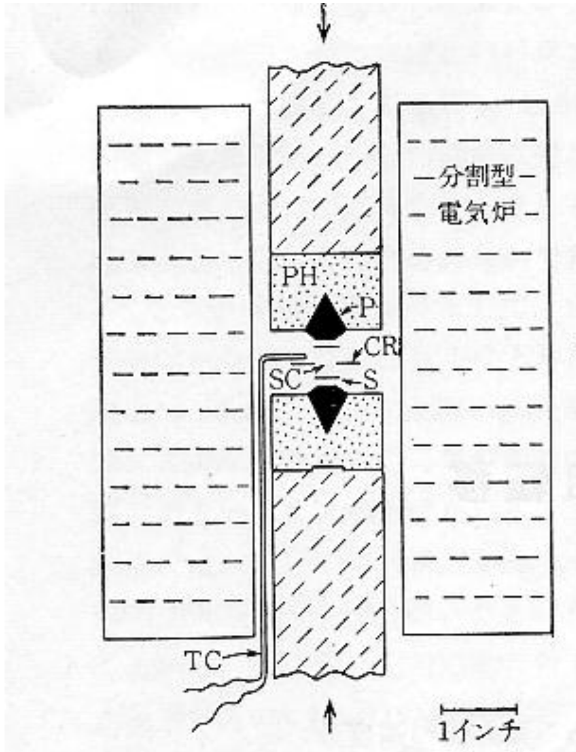


FIGURE 10-1
The system Ni_2GeO_4-Mg_2SiO_4 at 600°C and 0 to 90 kbars. *(From Ringwood and Seabrook 1962a, with permission.)*

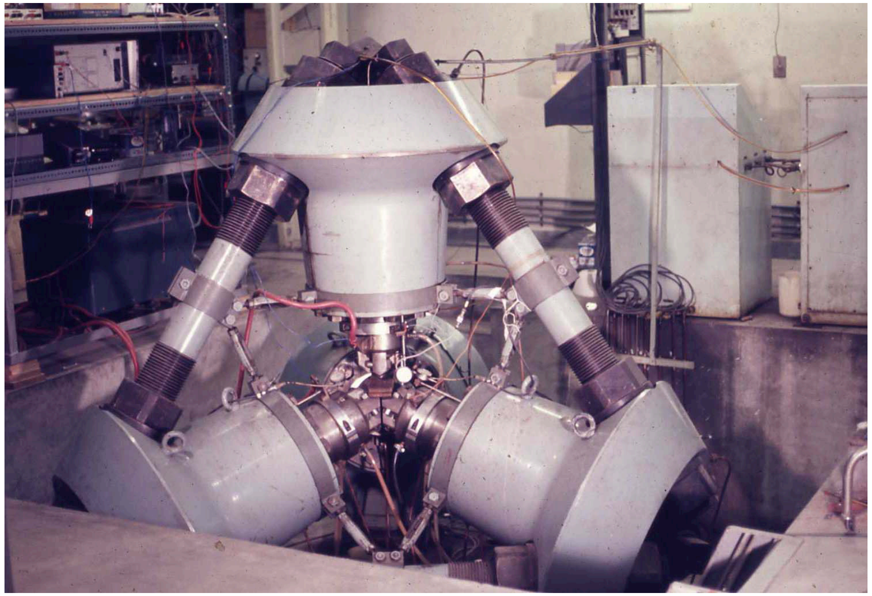
Ni_2SiO_4-Mg_2SiO_4 system



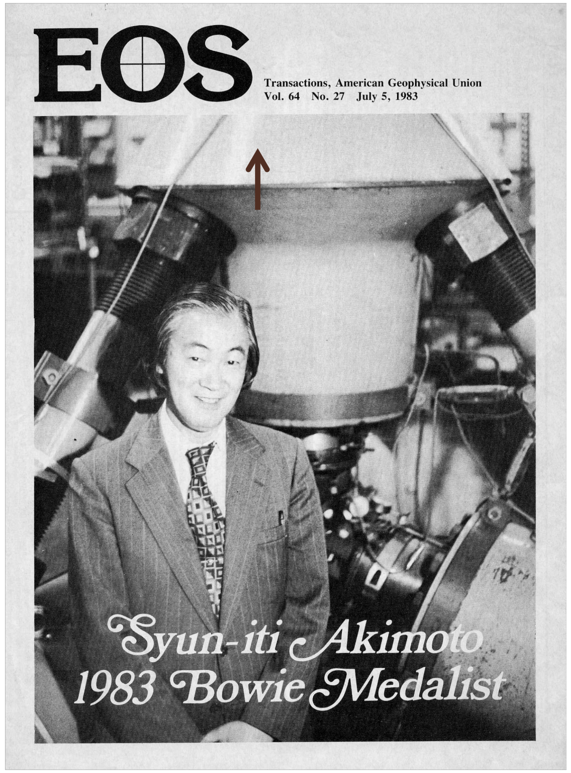
(simple squeezer apparatus)

Experimental proof of Olivine-Spinel transition (II)

Akimoto (1963)



Tetrahedral press at ISSP



Detailed study of Olivine-Spinel transition

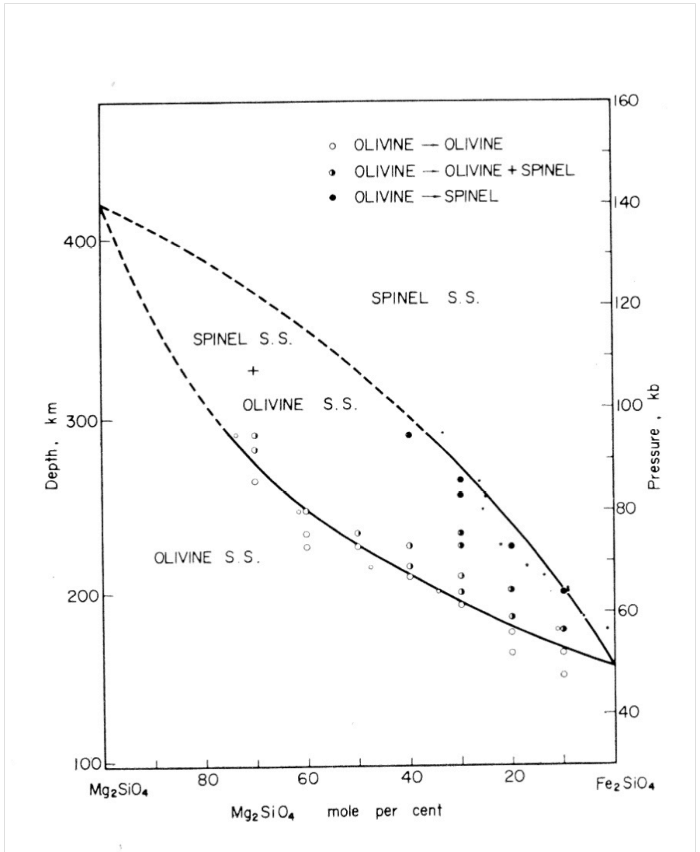
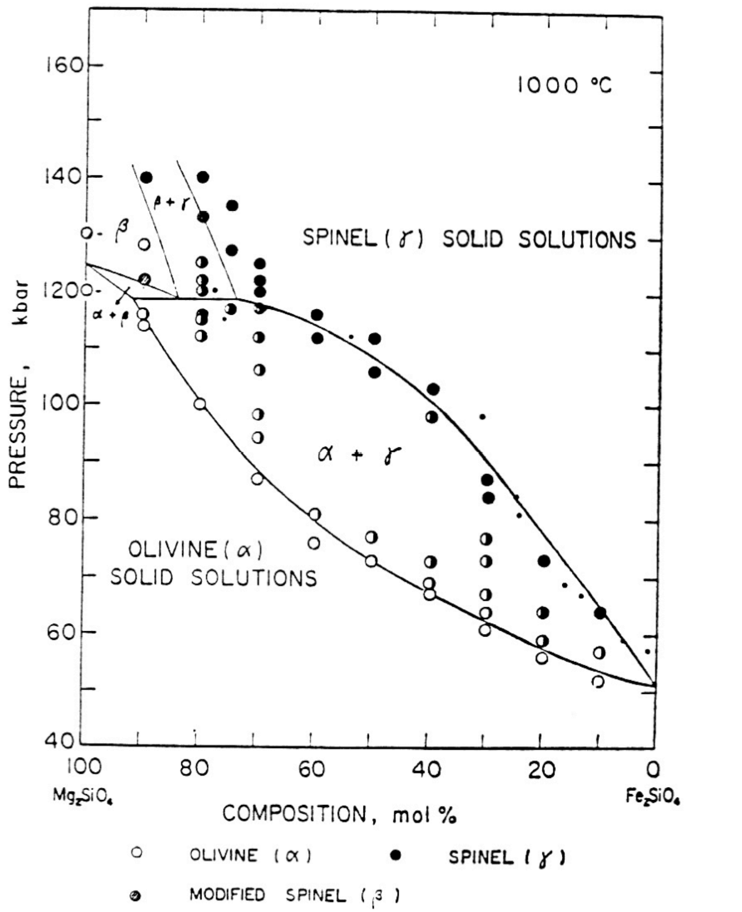


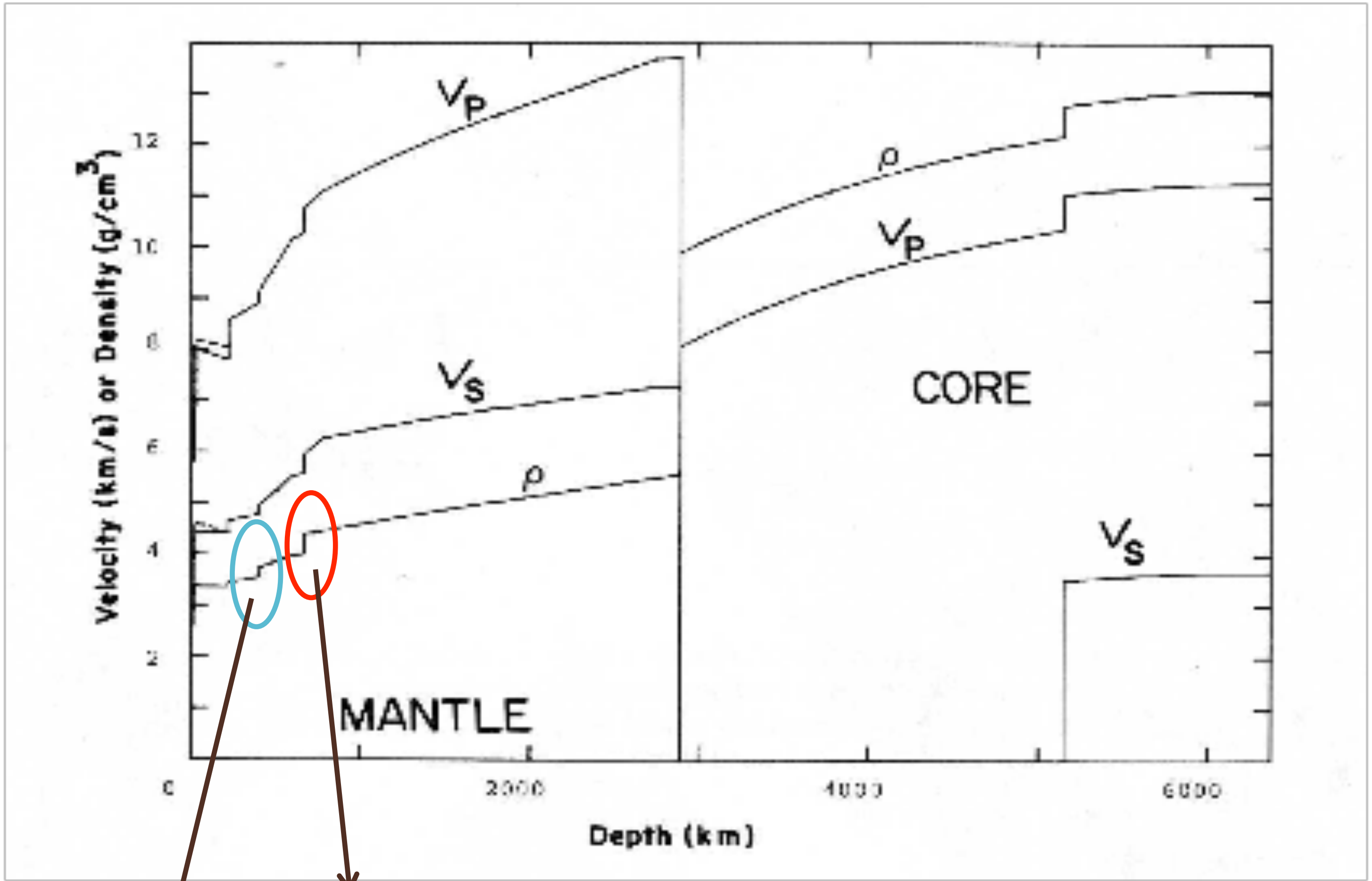
Fig. 4. Phase diagram for the olivine-spinel transition of the system Mg_2SiO_4-Fe_2SiO_4 at 1000°C.

Akimoto& Fujisawa(1968)



Akimoto et al.(1972)

Seismic Discontinuities in the Mantle



660 km : spinel → "post spinel transition" ?

410 km : olivine → spinel

Origin of the 660 km Discontinuity

Possibilities for the “post-spinel phase”

A_2BO_4 with denser structure

(K_2NiF_4 type, Sr_2PbO_4 type, ・・・)

ABO_3 + AO

(ilmenite, perovskite, corundum) + rocksalt

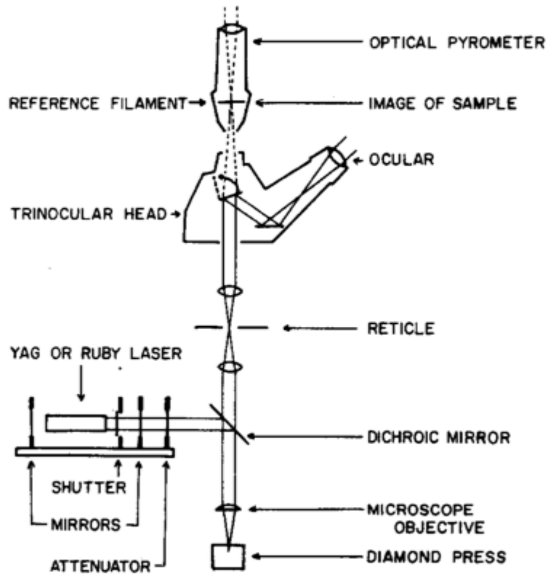
2AO + BO_2

rocksalt + rutlie

Finding of Silicate Perovskite

Liu (1974)
"silicate perovskite from garnet"

(laser heated diamond anvil)



$Mg_2SiO_4 \rightarrow MgSiO_3$ perovskite + MgO

$MgSiO_3 \rightarrow MgSiO_3$ perovskite

$Mg_3Al_2Si_3O_{12} \rightarrow (Mg_3Al)(AlSi_3)O_{12}$ perovskit

perovskite (cation : anion = 2 : 3)

Origin of the 660 km Discontinuity

Possibilities for the “post-spinel phase”

A_2BO_4 with denser structure

(K_2NiF_4 type, Sr_2PbO_4 type, ・・・)

$\boxed{ABO_3 + AO}$

(ilmenite, $\boxed{\text{perovskite}}$, corundum) + rocksalt

$2AO + BO_2$

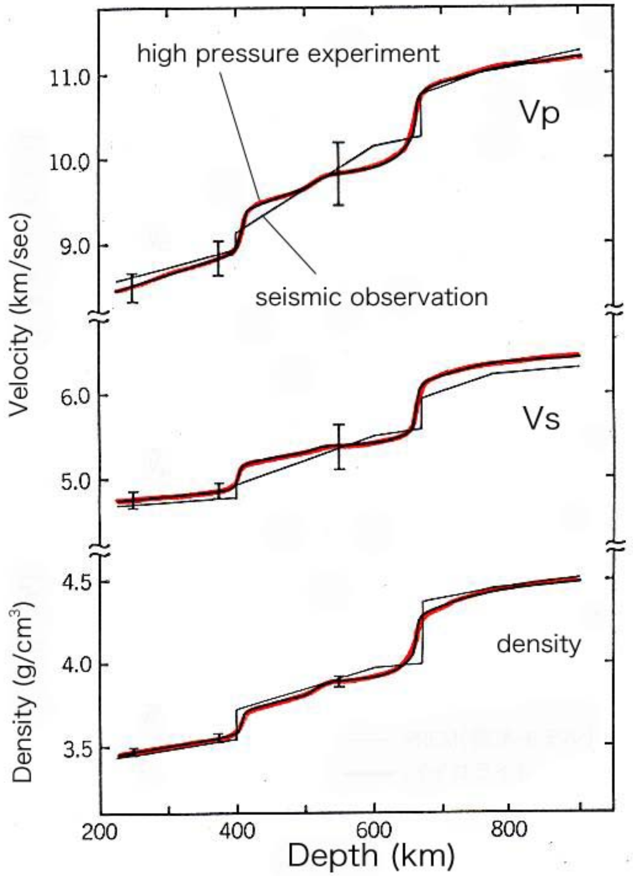
rocksalt + rutlie

Constitution of the mantle

Upper mantle		Lower mantle
olivine	→	perovskite + rocksalt
pyroxene	→	perovskite
garnet	→	perovskite

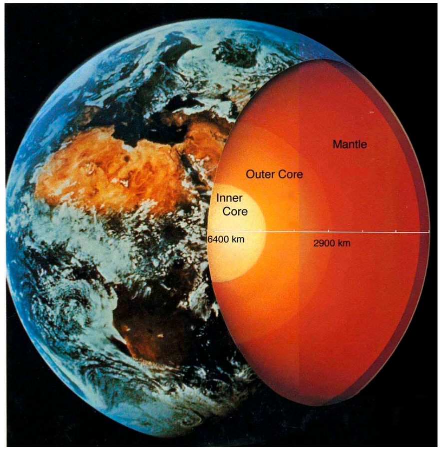
(transition zone: spinel, ilmenite)

Lower mantle : complicated solid solution with perovskite structure

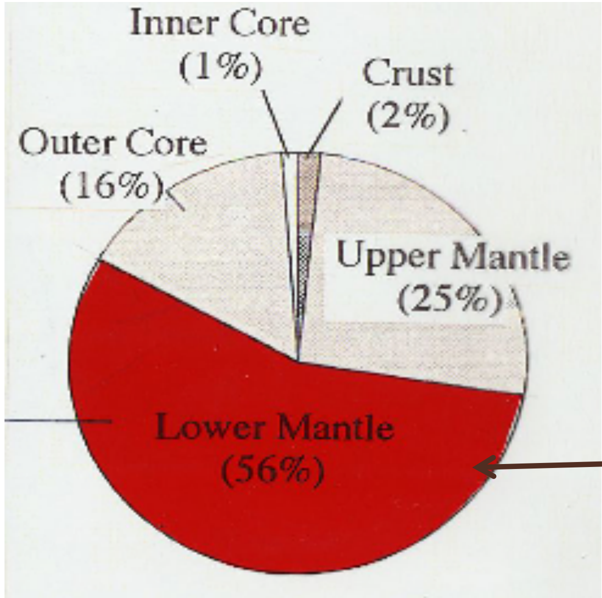


Comparison of calculated property and seismic observation

“The most abundant mineral” of the Earth



Volume ratio of the Earth



> 50 %

Perovskite : the most abundant mineral of the Earth

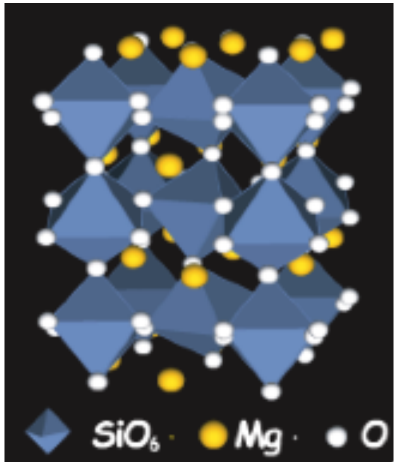
perovskite-type $(Mg,Fe)SiO_3$

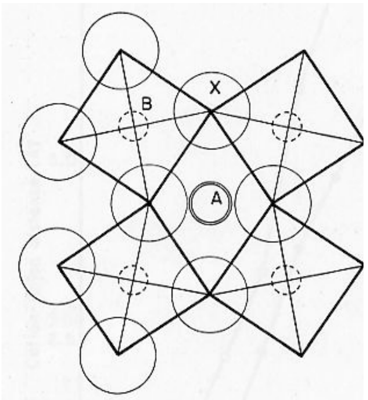
mineral name : “bridgmanite” after P. W. Bridgman

Crystal Structure of Silicate Perovskite

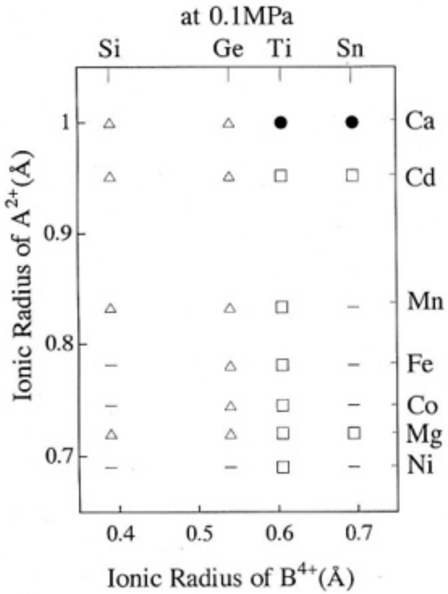
perovskite structure: fcc close packing of O and A cation

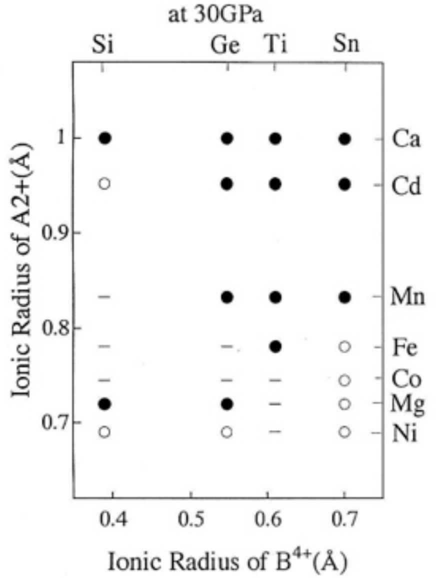
→ unusually dense packing





stable structures of ABO_3-type compounds





● : perovskite

Stability of Silicate Perovskite

Experiments

Knittle and Jeanloz (1987) ; Experiments up to 127 GPa

"silicate perovskite is stable throughout the lower mantel"

Kesson et al. (1998) ; Experiments up to 135 GPa

"MgPv was found to be present and no additional phases or disproportionations were encountered"

Theoretical consideration

perovskite structure : ultimate dense form of ABO_3-type compounds

⇒ perovskite is stable to the bottom of the mantle

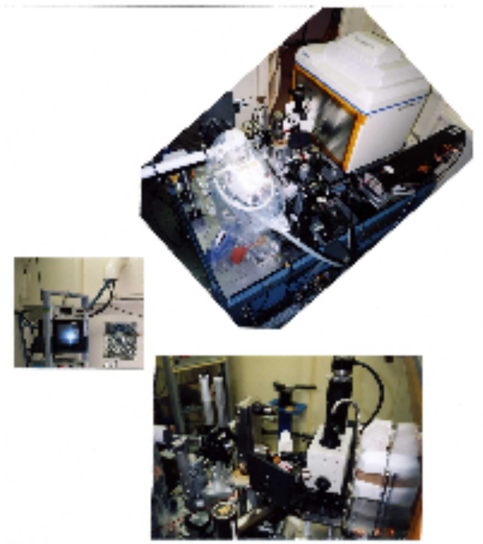
Construction of Laser Heated DAC combined with Synchrotron Radiation (I)

Big grant from the government (1995 - 1999)

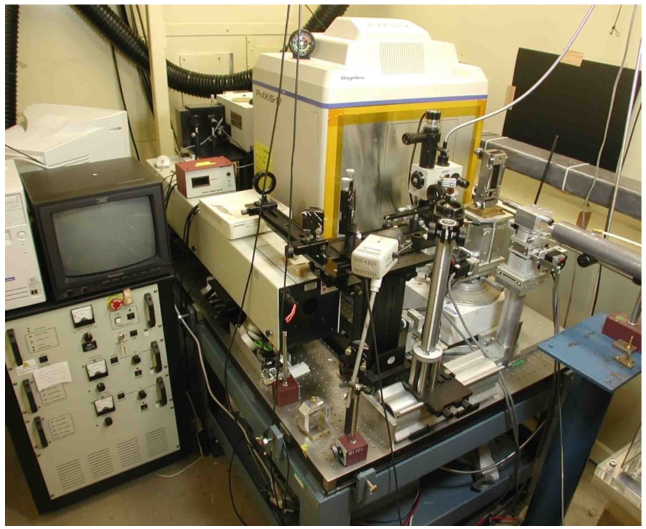
"Study of the Structure and Properties of the Lower Mantel based on High Pressure and High Temperature experiments"

Photon Factory BL-13

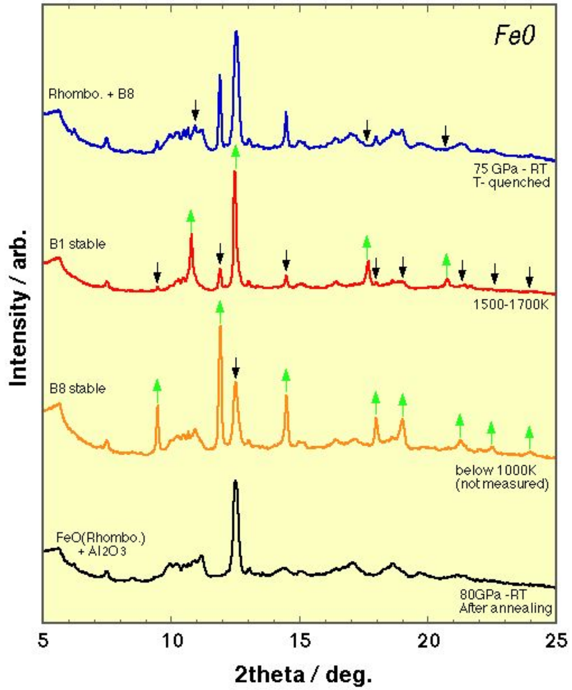
CO_2 laser

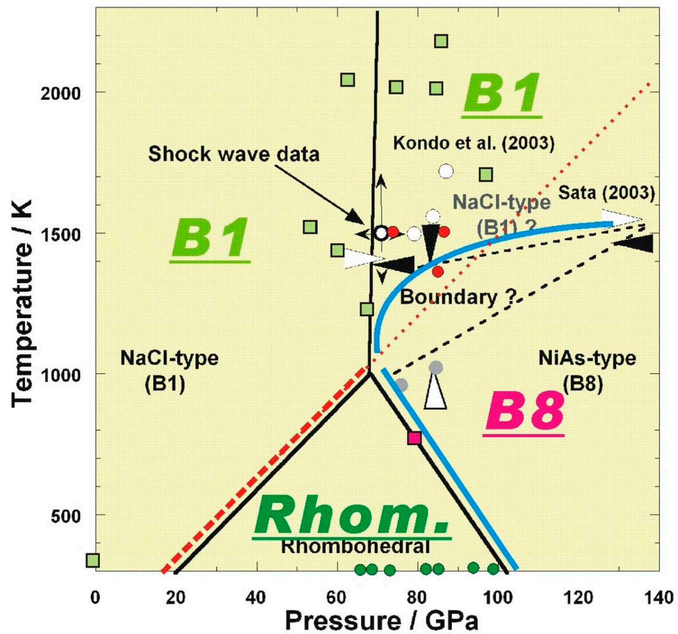


YAG laser



Study of the Minerals in the Lower Mantle



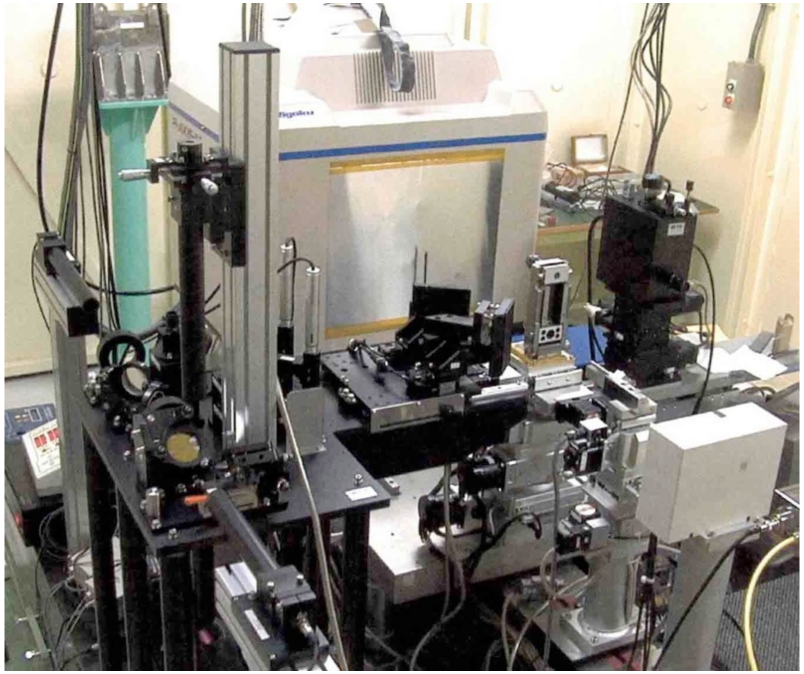


Funamori et al. (1997) ***Science*** "Transformation in garnet from orthorhombic perovskite …."
Miyajima et al. (1999) ***Phys. Earth Planet. Inter*** ."Garnet-perovskite transformation ….."
Kondo et al. (2000) ***J. Appl. Phys.*** "Phase transitions of MnO to 137 GPa."
Miyajima et al. (2001) ***Am. Mineral.*** "Potential host phase of aluminum and potassium …."
Kondo et al. (2004) ***Phys. Earth Planet. Inter.*** "Phase transitions of (Mg, Fe)O at megabar….."

Construction of Laser Heated DAC combined with Synchrotron Radiation (II)

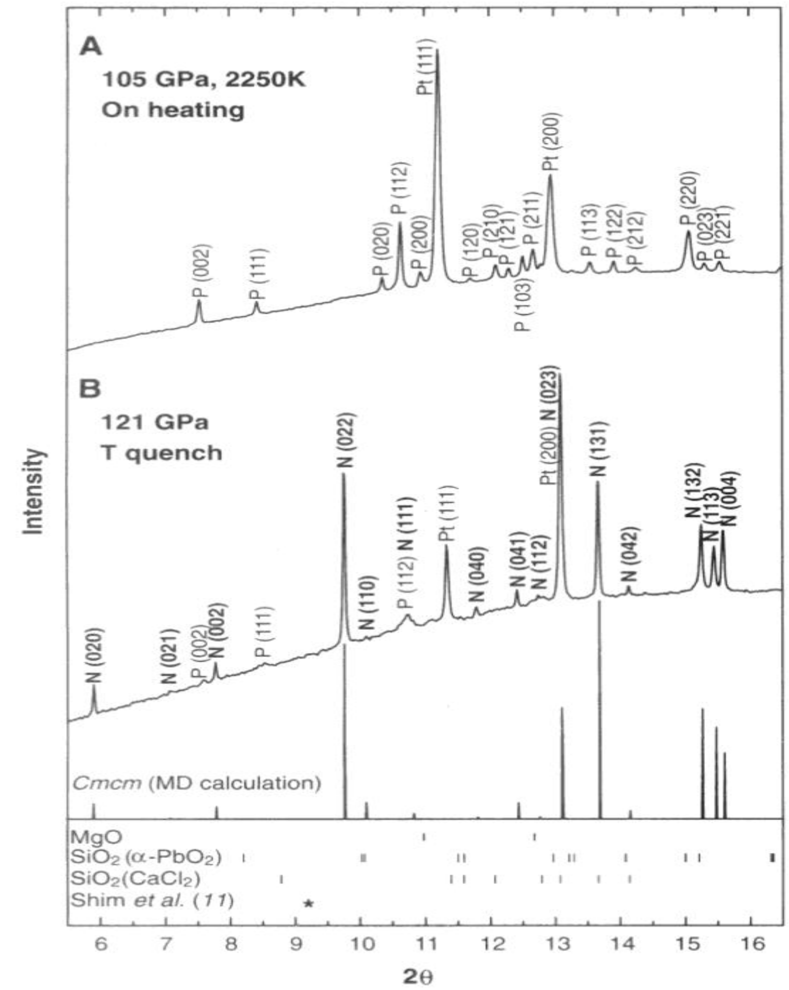
SPring-8

BL10-XU

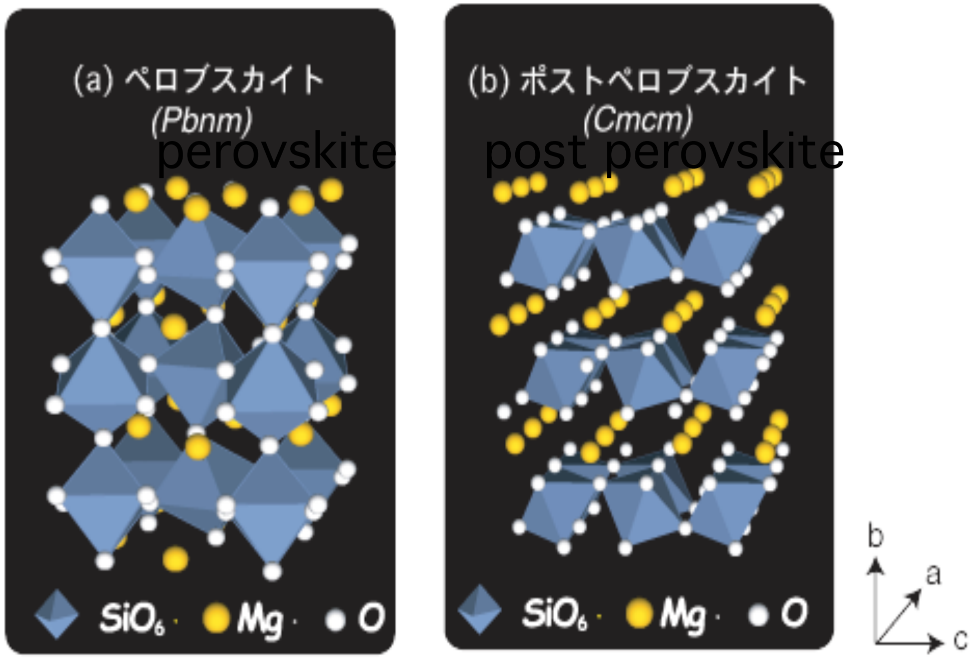


Finding of A New Phase in $MgSiO_3$

"Post-Perovskite Phase Transition in $MgSiO_3$"
Murakami et al., (2004)



Structures of Perovskite and Post-perovskite



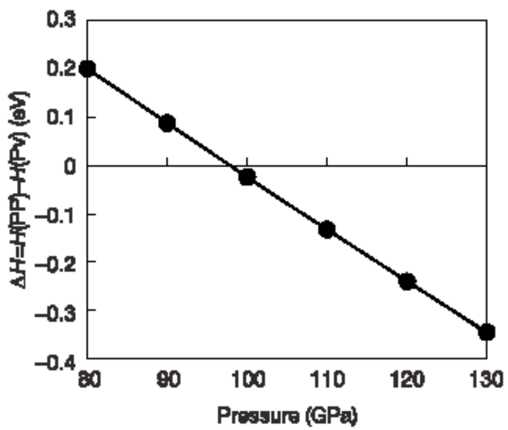
perovskite　　post perovskite

$CaIrO_3$, $AgTaS_3$, $UFeS_3$, $LaYbS_3$, $UScS_3$, $ThMnSe_3$, $UMnSe_3$, $CeYbSe_3$, ･･･

(high pressures ; $MgGeO_3$, $MnGeO_3$, ･･･)

Theoretical Calculations of Stability and Elasticity (I)

First principle calculation



ΔH=H(PP)-H(Pv)at 0K

The elasticity of the $MgSiO_3$ post-perovskite phase in the Earth's lower mantle,
T. Iitaka, et al., Nature, 430,442(2004)

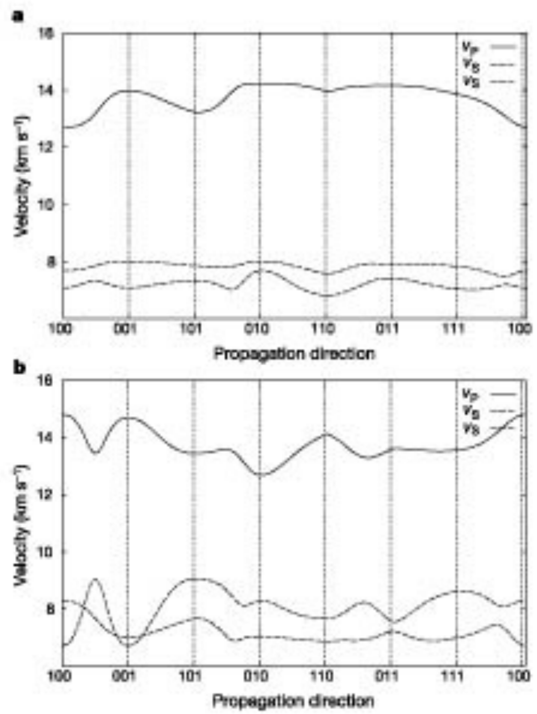


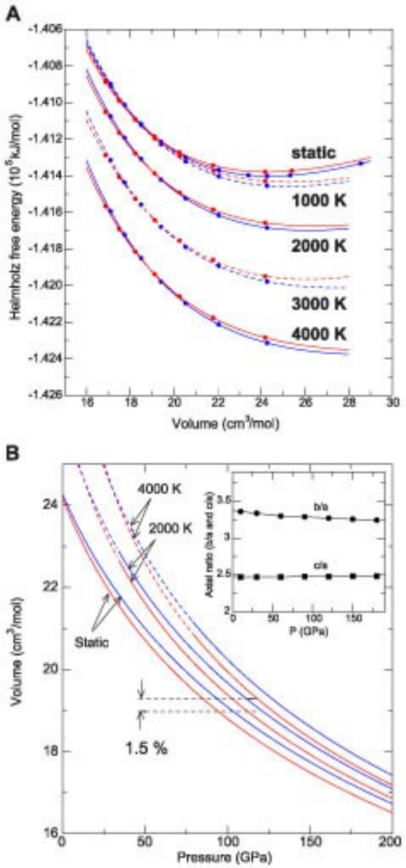
Figure 3 The variation of compressional (v_P) and shear (v_S) wave velocities as a function of propagation direction. a, Perovskite phase at 100 GPa; b, post-perovskite phase at 100 GPa. The two dashed lines represent the two polarizations of the shear waves.

Pv

PP

elasticity

Theoretical Calculations of Stability and Elasticity (II)



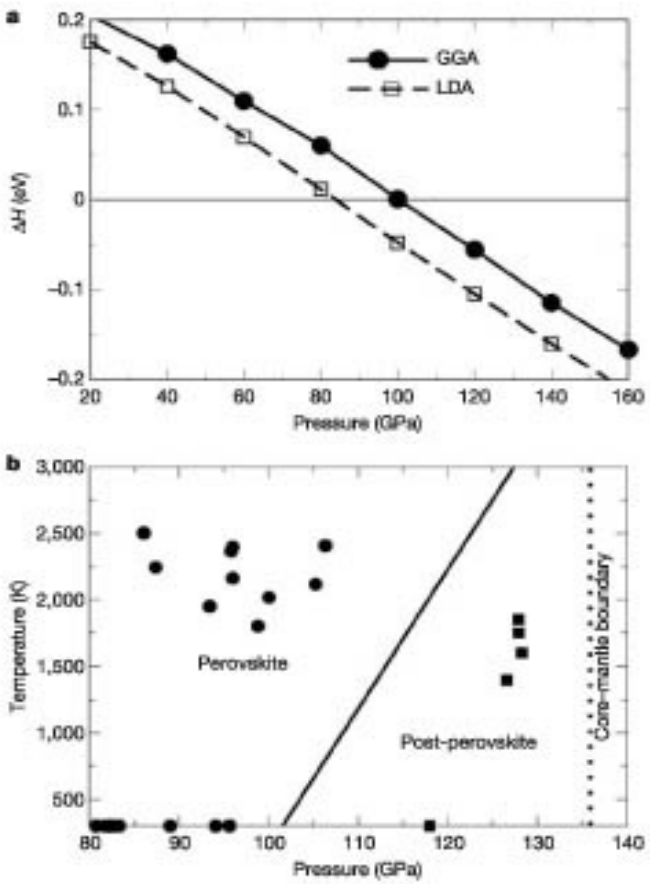
Observed unit cell

First principle calculation

Post perovskite structure

Theoretical and experimental evidence for a post-perovskite phase of $MgSiO_3$ in Earth's D" layer,
Tsuchiya et al., Earth Planet. Sci. Lett., 224, 241(2004)

Theoretical Calculations of Stability and Elasticity (III)



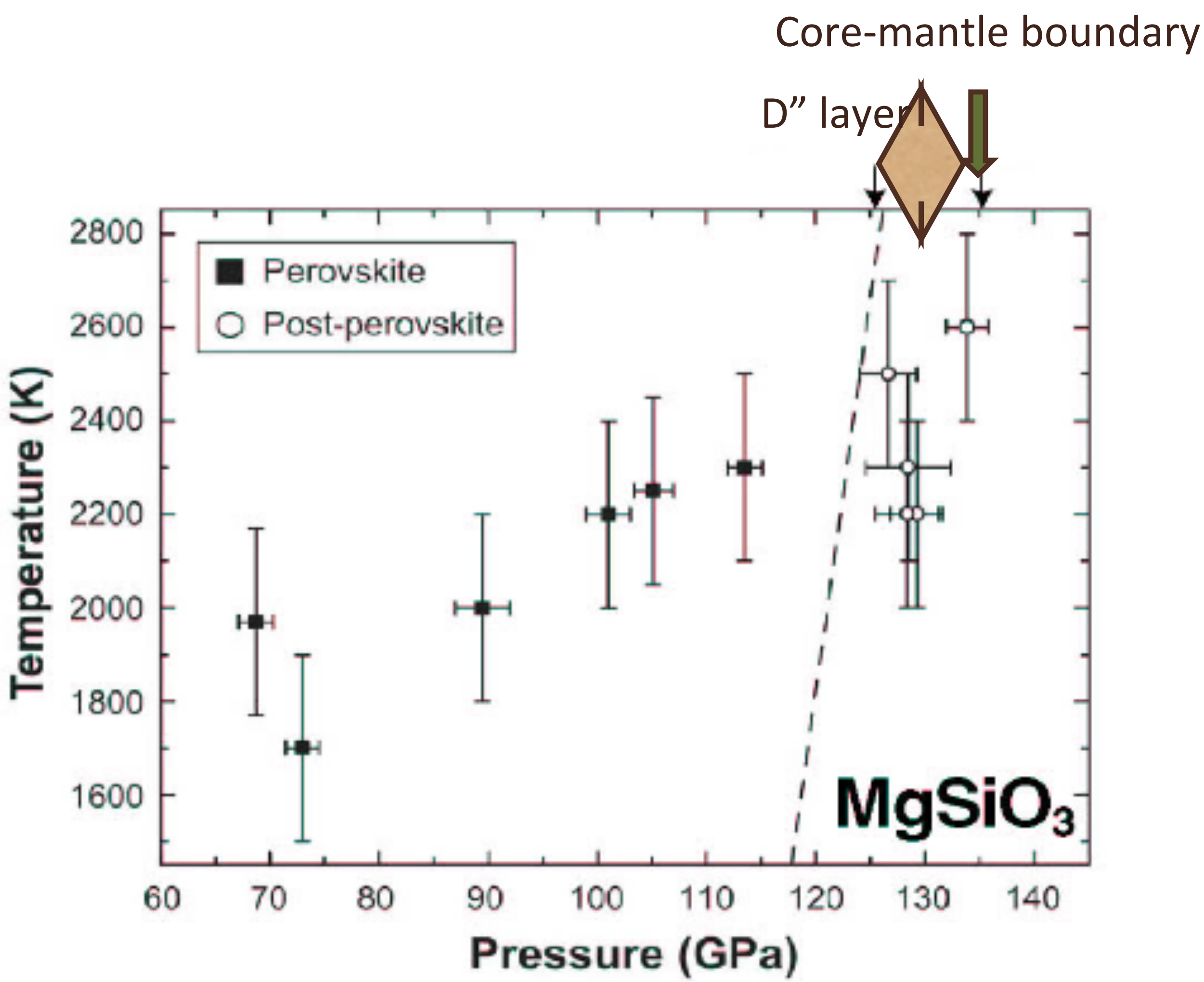
$CaIrO_3$-type Cmcm structure

ab initio simulations based on density functional theory

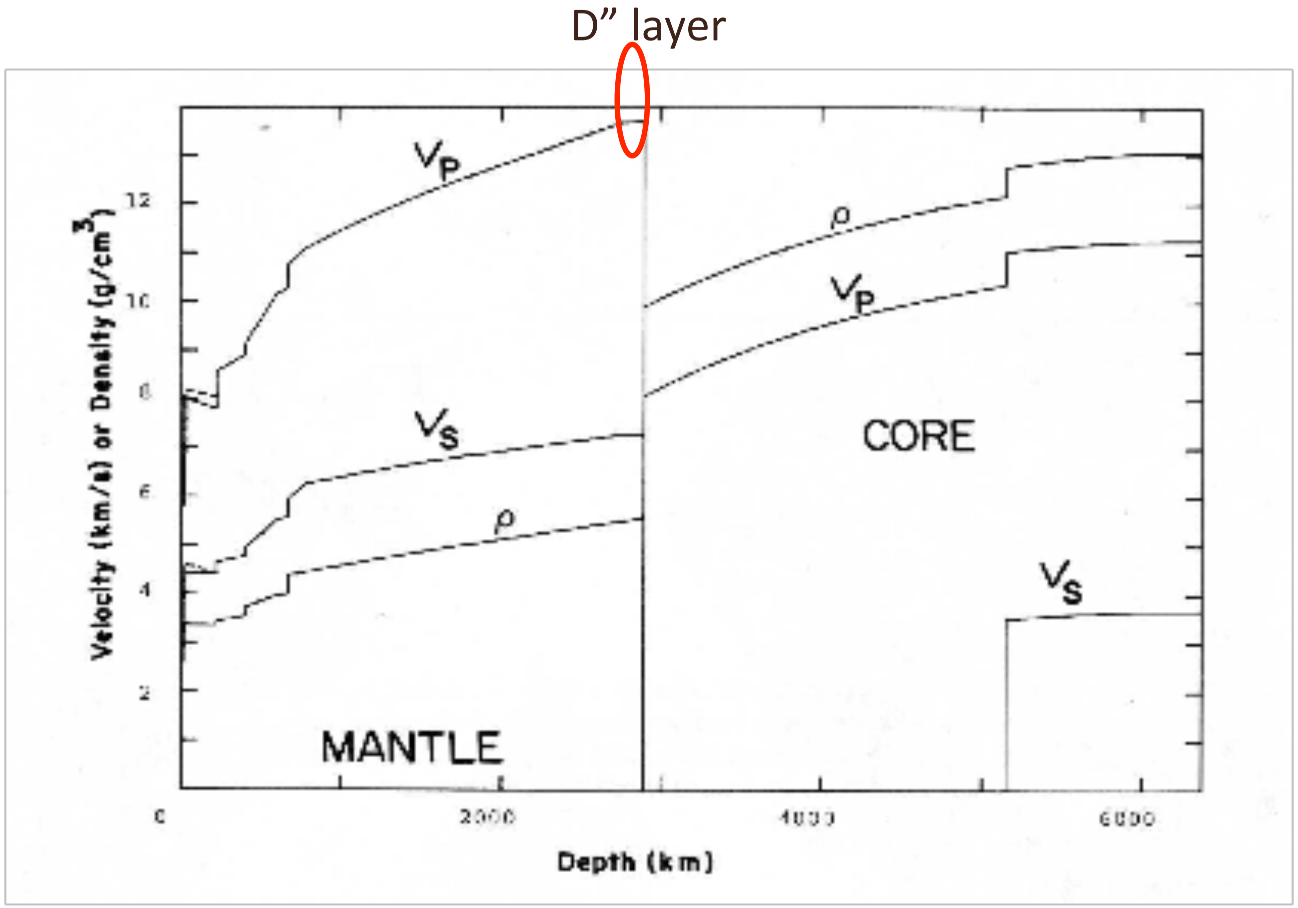
Theoretical and experimental evidence for a post- perovskite phase of $MgSiO_3$ in Earth's D" layer,

Oganov and Ono, Nature, (2004)

Stability Field of the New Phase



Seismic Discontinuities in the Mantle

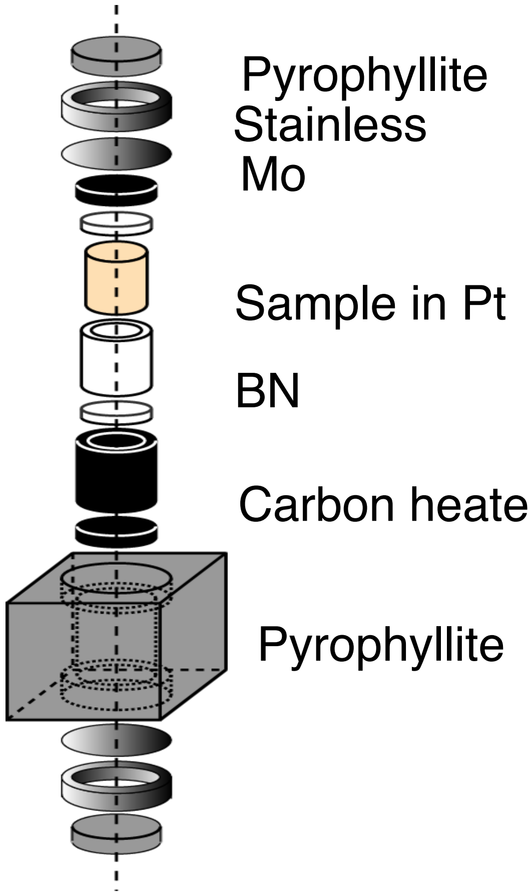


Property of Post-Perovskite Structure

Using $CaIrO_3$ as model material

- $MgSiO_3$
  formed only above 120 GPa
  unquenchable to ambient condition
- $CaIrO_3$
  formed much easily
  keep its structure at ambient condition
  TEM observation
  rheological property

High pressure synthesis of $CaIrO_3$



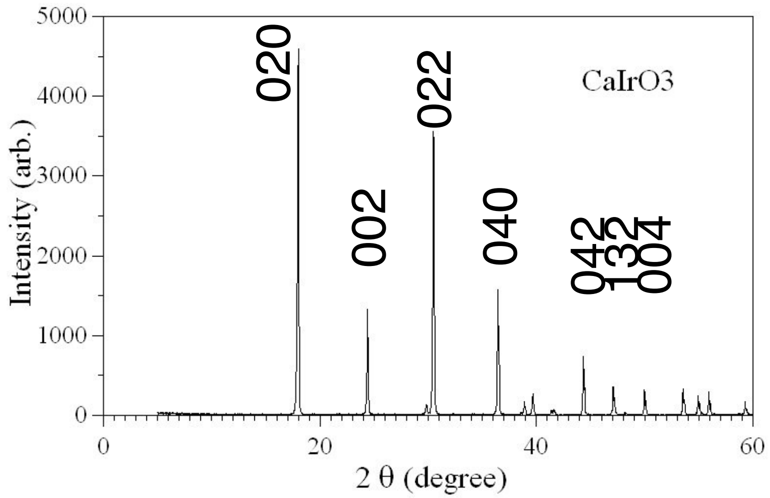
700 ton cubic press

$CaO + IrO_2$

4 GPa 1200 ºC 30 min.	1.5 GPa 1200 ºC 30 min.
post Pv $CaIrO_3$	Pv $CaIrO_3$

Synthesized post-perovskite type $CaIrO_3$

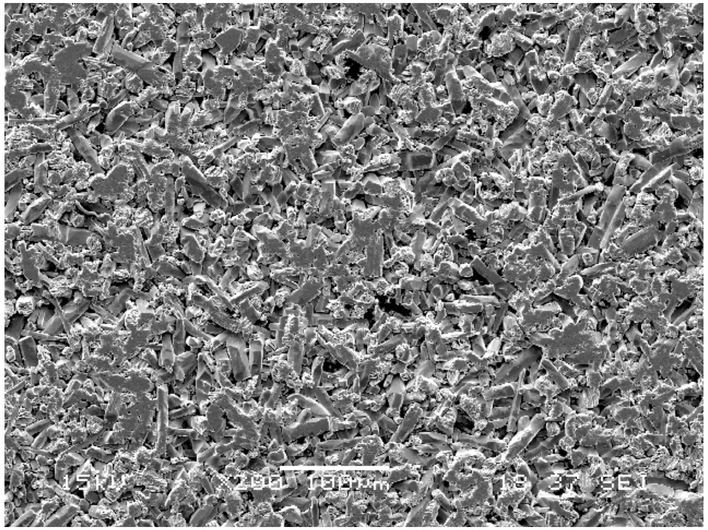
Powder X-ray diffraction



a=3.146Å
b=9.867Å
c=7.298Å
space group: Cmcm

SEM observation

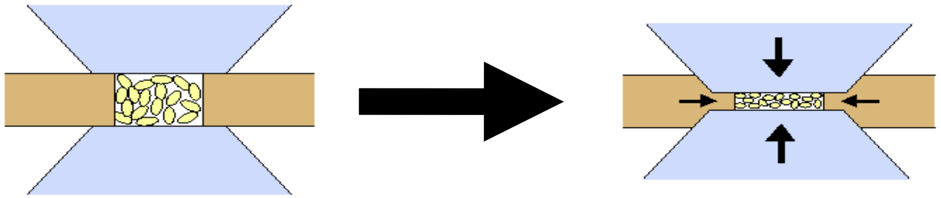
Needle like morphology



100μm

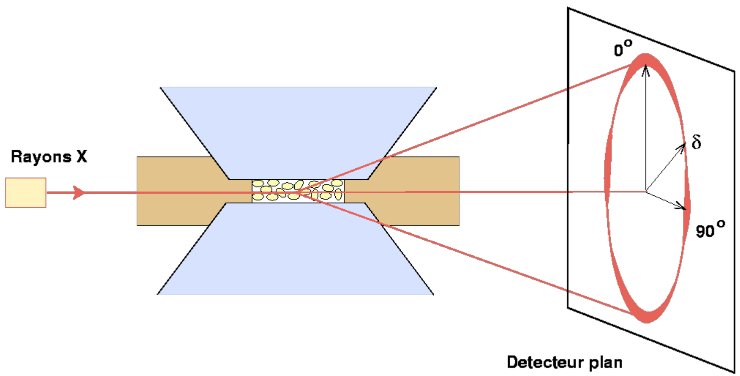
Radial diffraction technique

Large plastic deformation under uniaxial stress field



$200\mu m ø$ x $200\mu m h$ — $300\mu m ø$ x $50\mu m h$

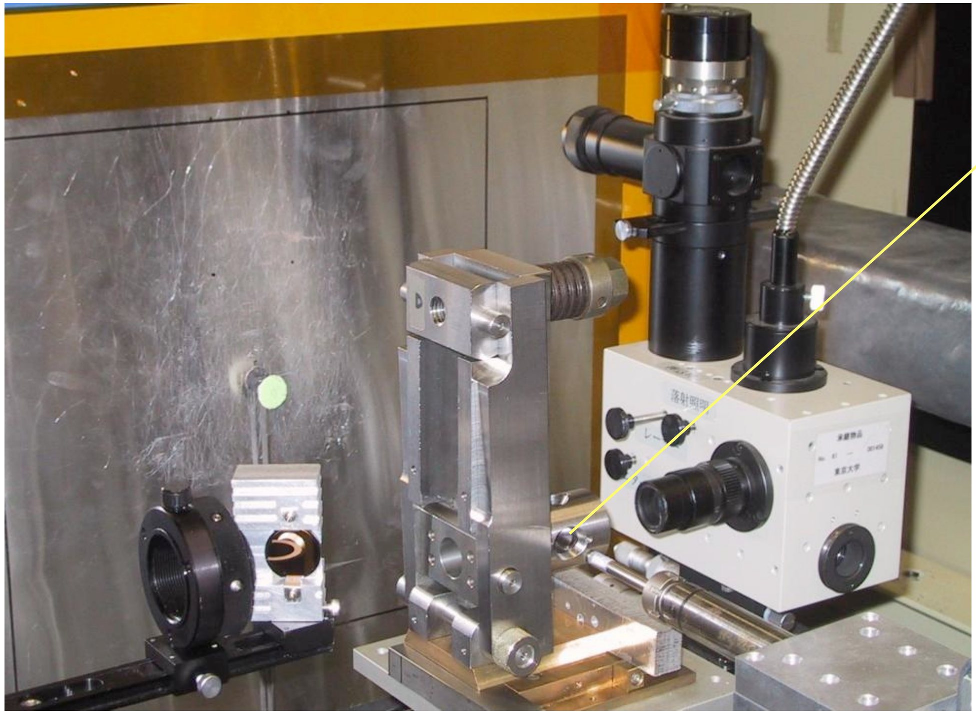
random orientation — preferred orientation



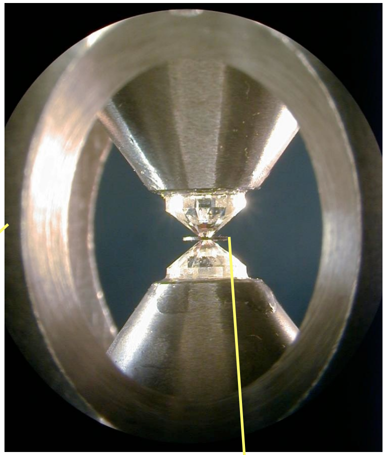
X-ray ⊥ compression axis

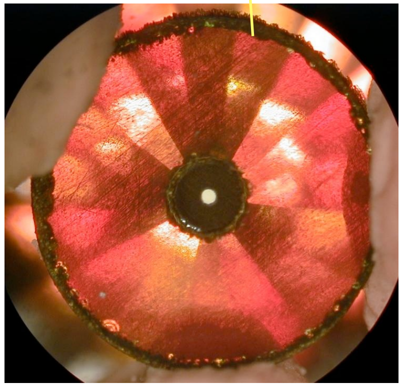
Radial diffraction experiment

Photon Factory BL13A



DAC with large side opening



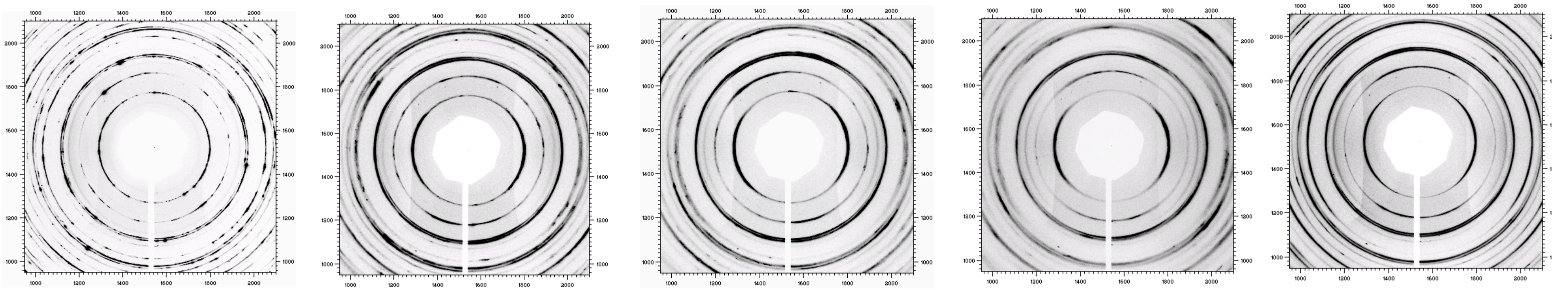


X-ray transparent gasket

Diffractions of post-perovskite phase

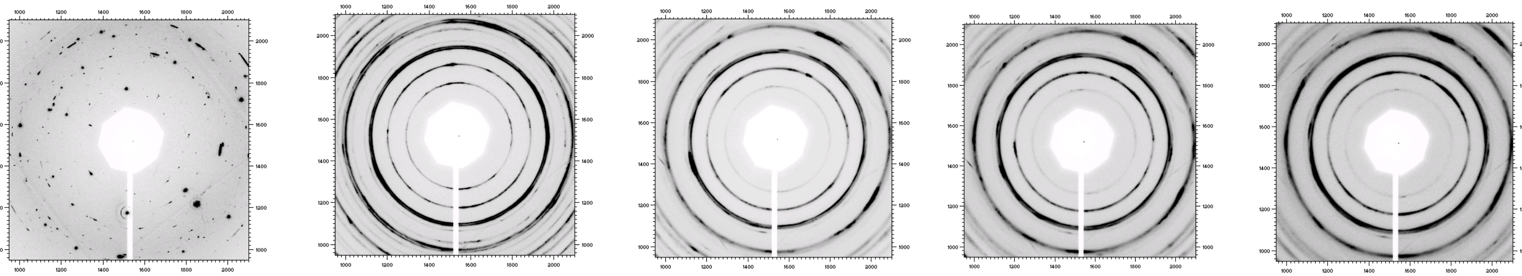
Radial diffraction

compression



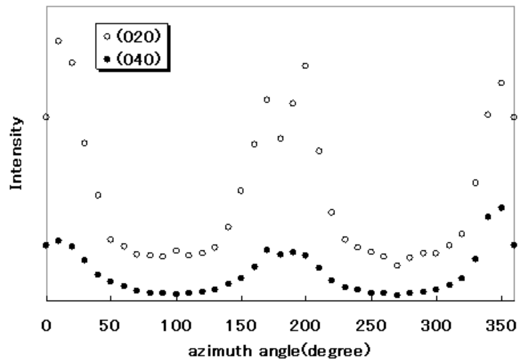
0.5GPa → 2.5GPa → 4.0GPa → 6.5GPa → 0GPa

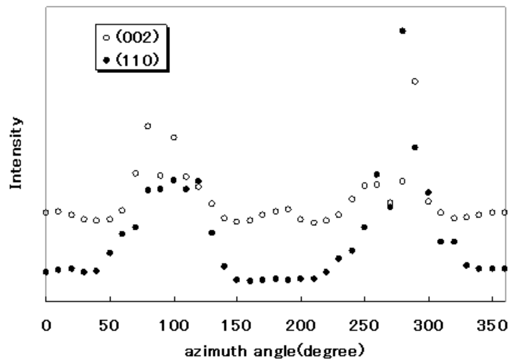
Axial diffraction

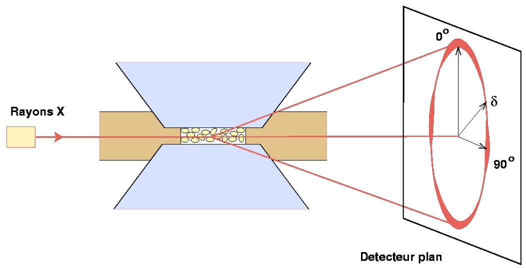


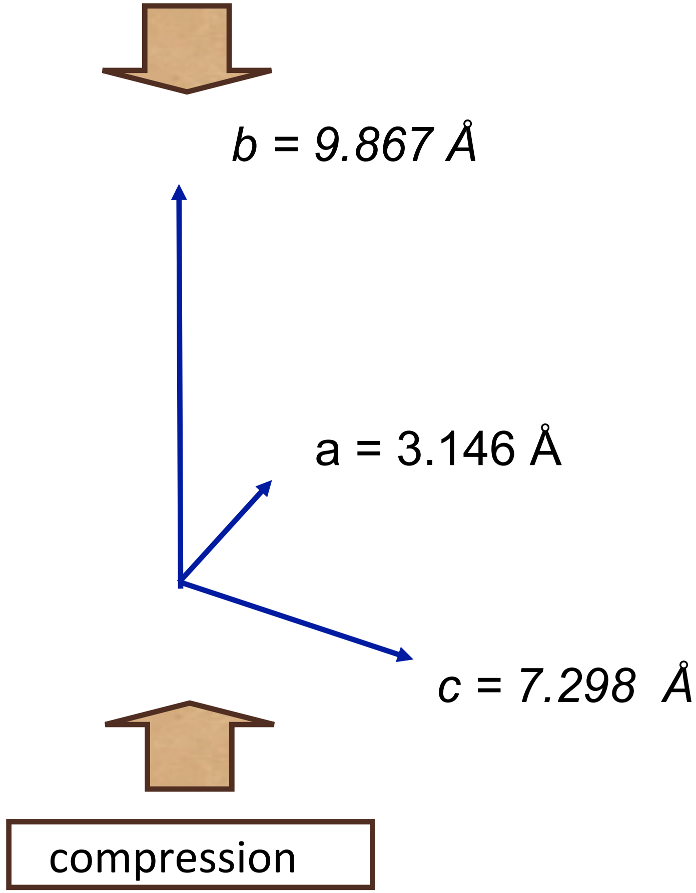
0.0GPa → 1.0GPa → 2.0GPa → 4.5GPa → 6.4GPa

Lattice preferred orientation in pPv

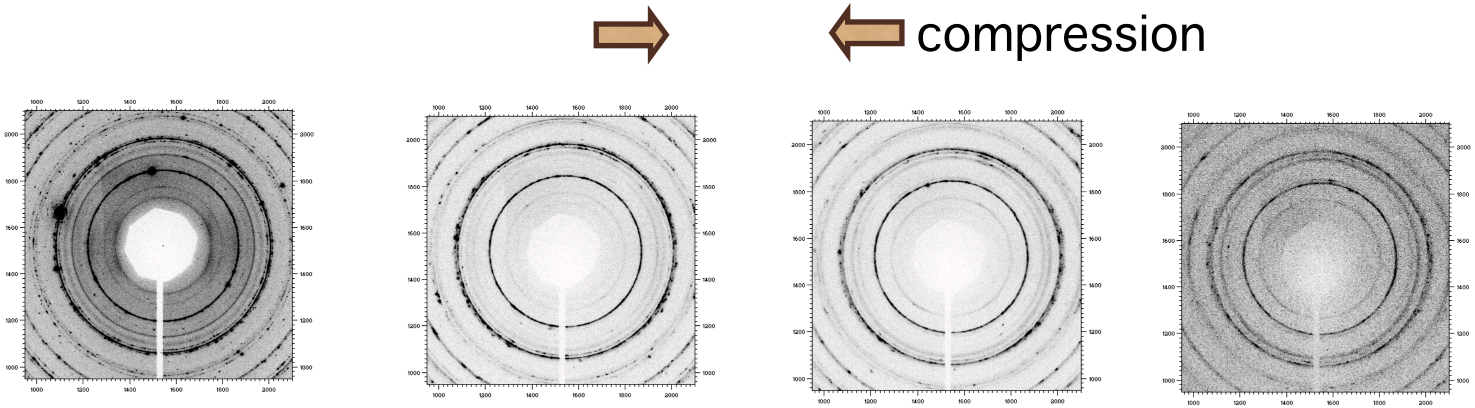






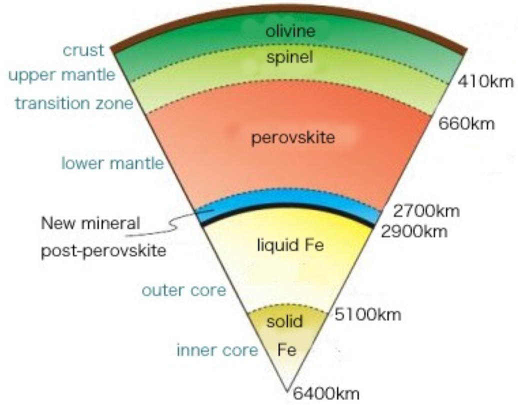


Radial diffraction of perovskite phase



0GPa 1.6GPa 3.5GPa 6.5GPa

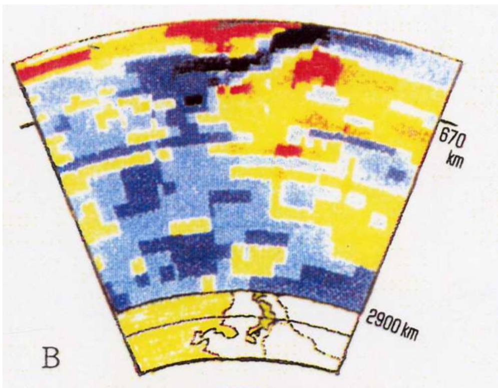
Current view of the Earth
- three dimensional dynamic model -

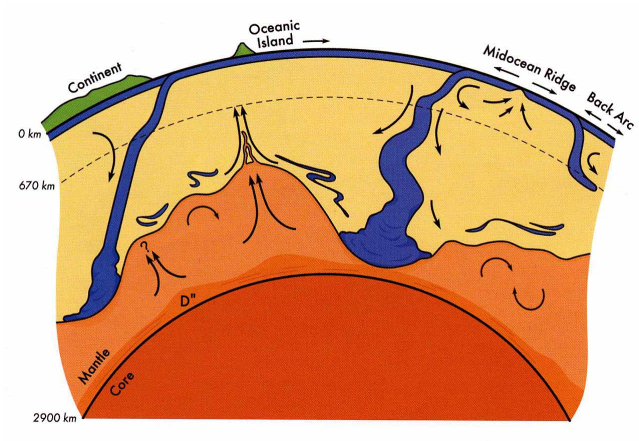


seismology

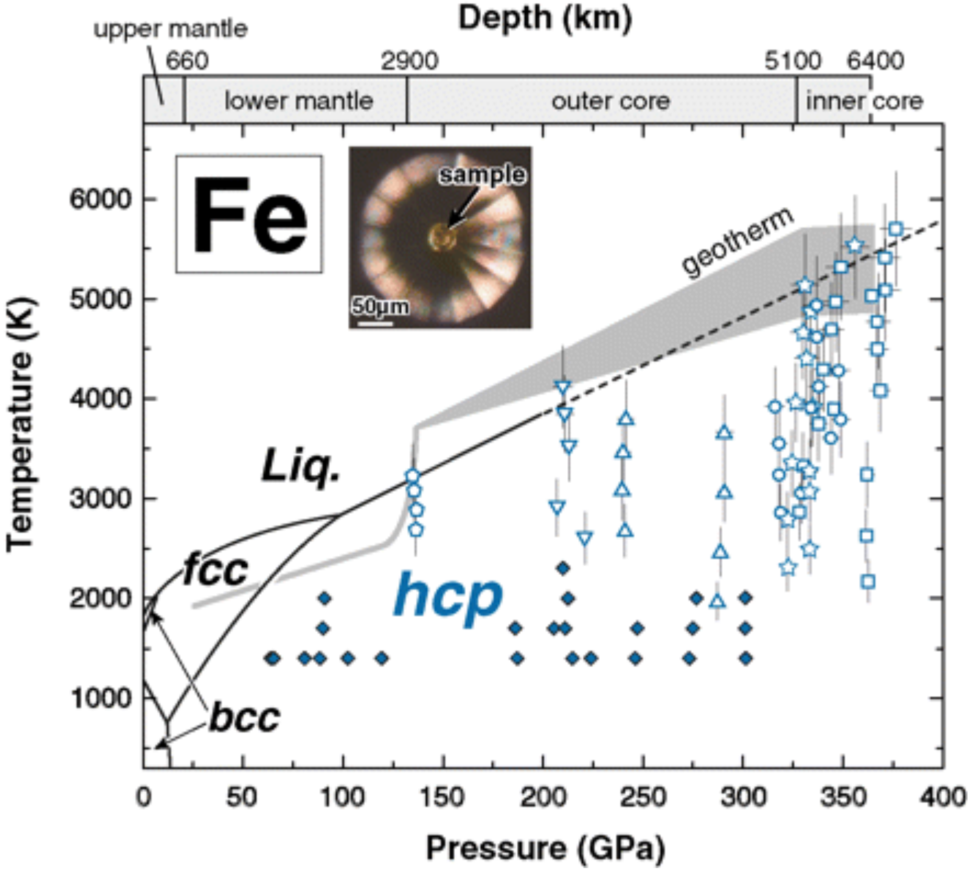
high P-T experiment

computer simulation

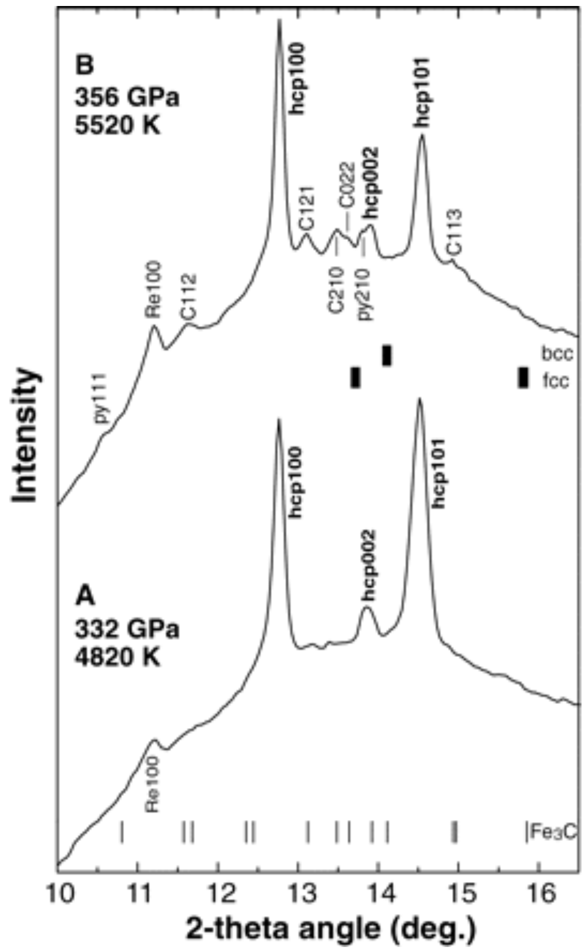




High P-T *in situ* experiments at the condition of the Earth's center

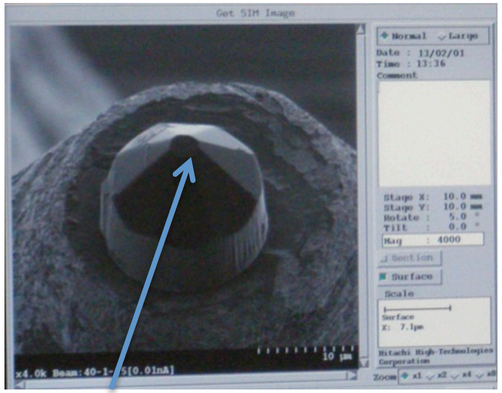


Tateno et al., *Science* (2010)

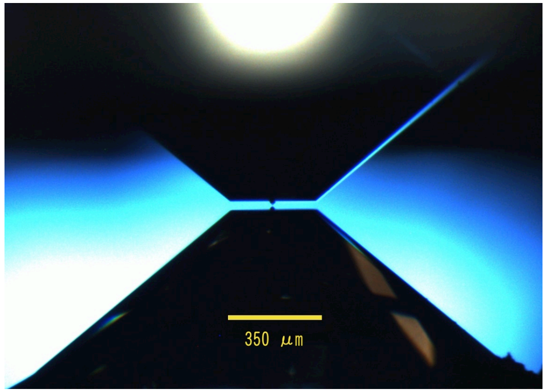


Beyond the center of the Earth

Micro diamond anvil fabricated by Focused Ion Beam (FIB) method

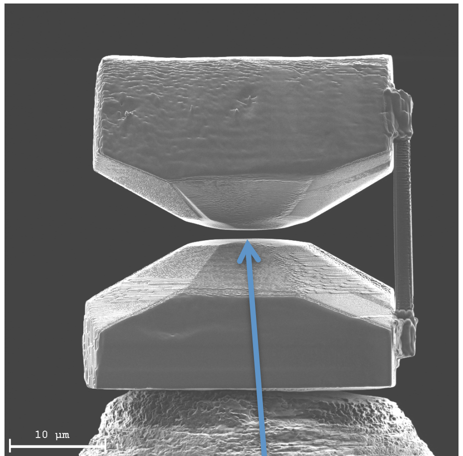


Culet diameter : 3 µm

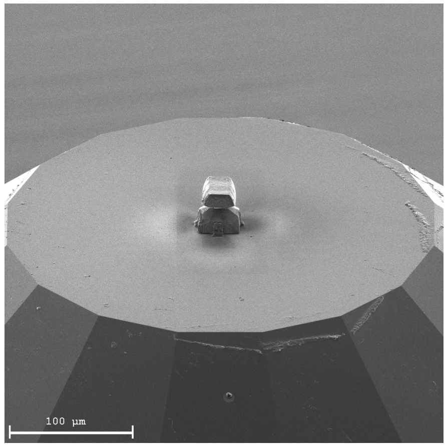


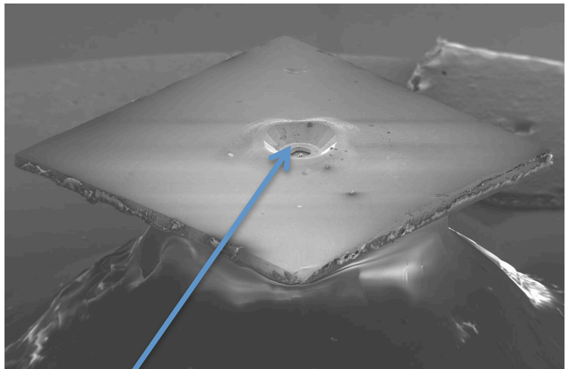
Micro anvils placed on top of normal anvils (350 µm culet)

“Micro paired-anvil”



Put sample here

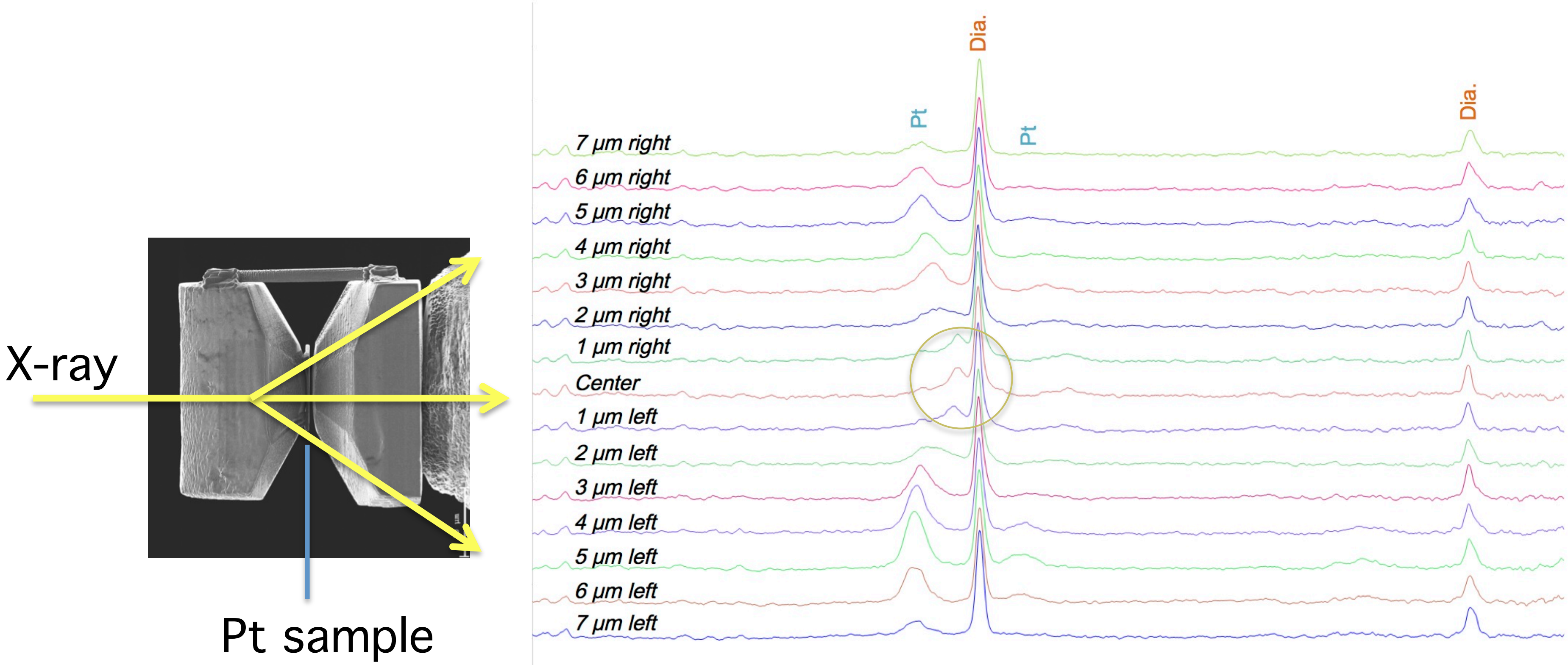




Gasket hole was filled with liquid

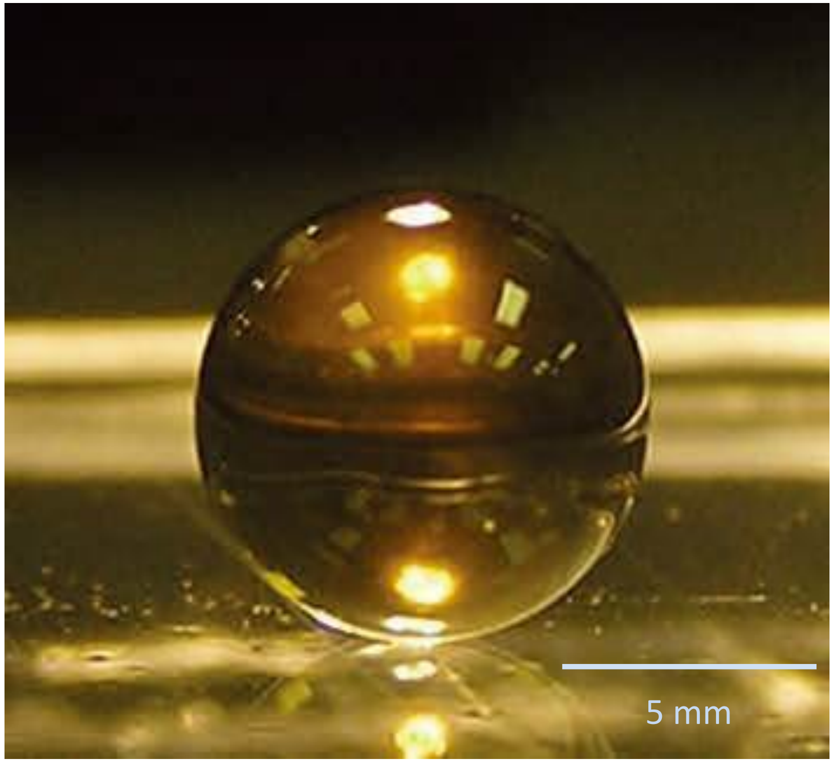
Sakai, Yagi, et al., *Rev. Sci. Instrum.* **86**, 033905 (2015)

Diffractions obtained by "1 µm" beam at BL-10



Pressure of 426 GPa was achieved by this technique just recently.

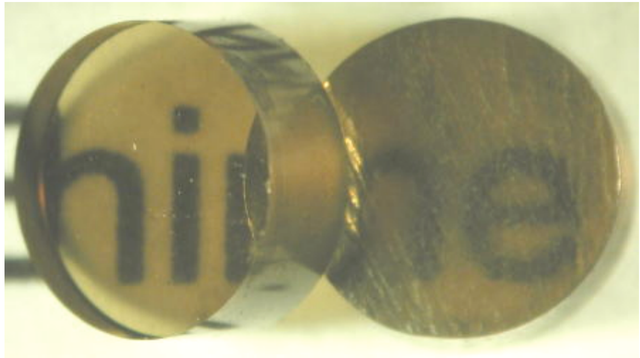
Application of high pressure techniques to the synthesis of new materials



nano-polycrystalline diamond synthesized at 15 GPa

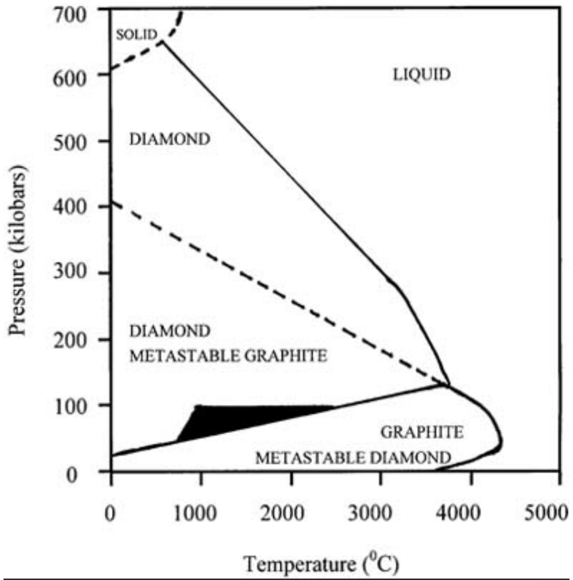
Irifune et al., (2013)

Synthesis of nano polycrystalline diamond

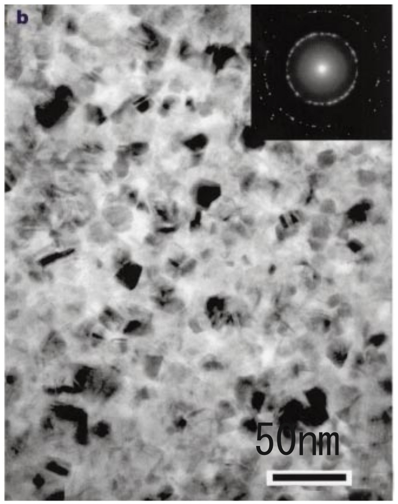


"Hime dia" synthesized at 15GPa,2000K

6000 ton multi anvil press
(Ehime University)



Phase diagram of carbon



TEM image

Synthesis of nano polycrystalline stishovite

SiO_2 phase diagram

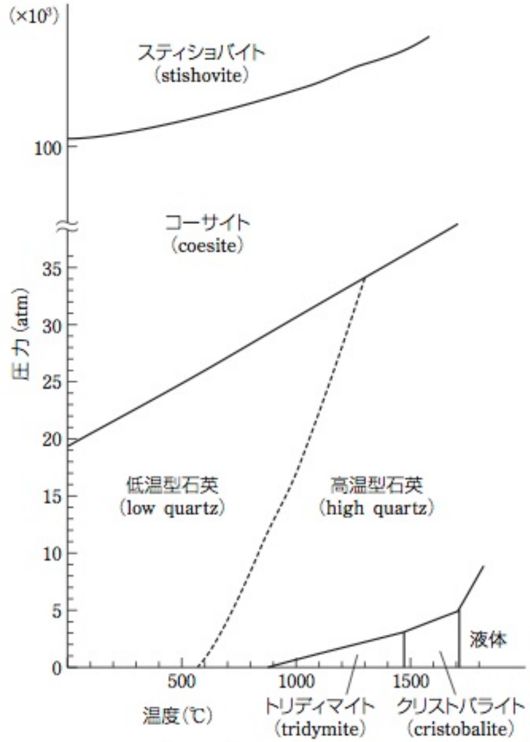
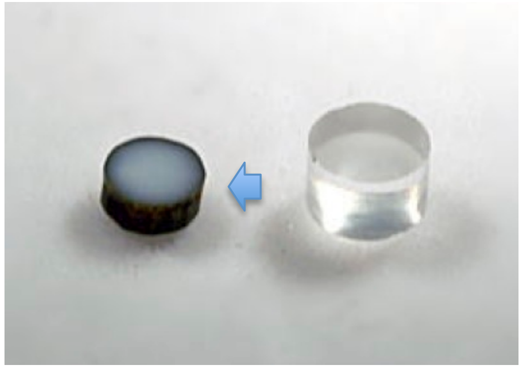
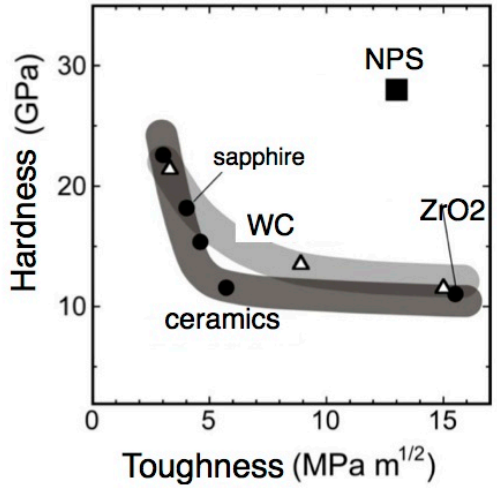
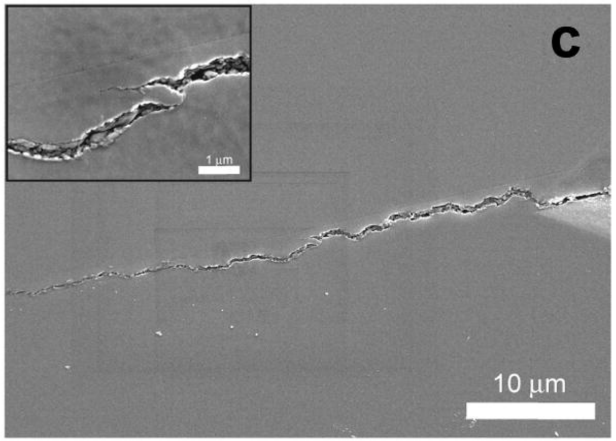


図3　SiO_2の相図(状態図)



NPS　starting glass



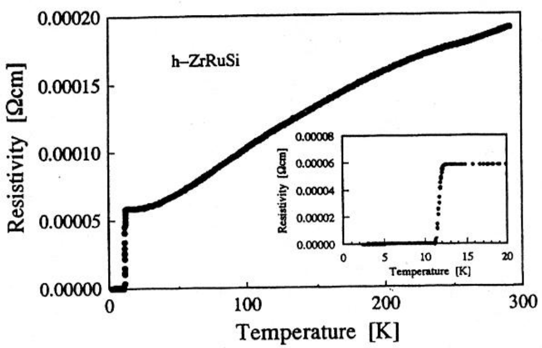


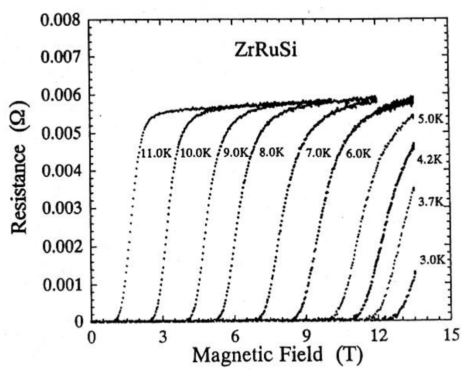
SEM observation of the crack

New super conductors synthesized under pressure

Tc > 10 K

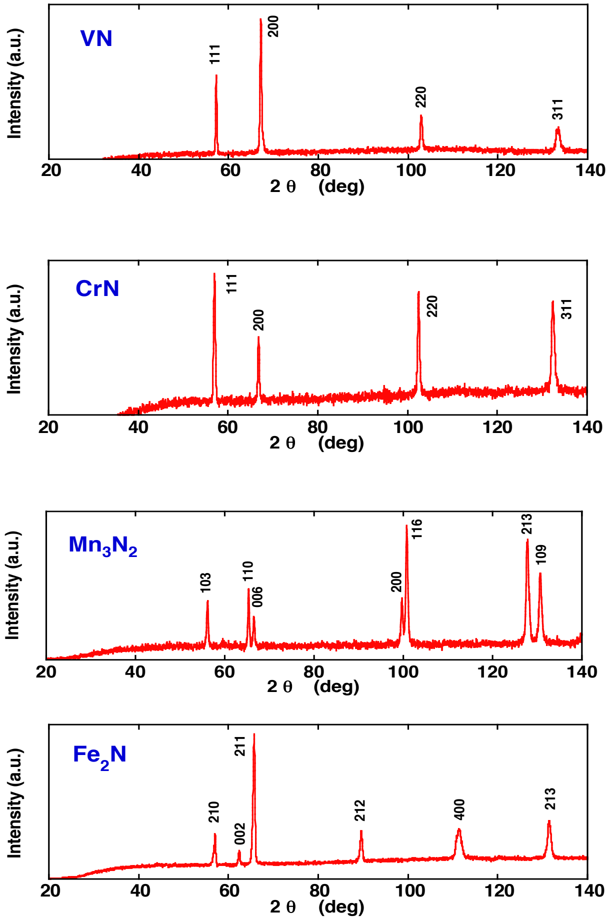
material	Tc	structure
• ZrRuSi	12.2	Fe_2P-type
• ZrRuCe	10.5	TiFeSi-type
• $ZrRu_4P_2$	11	$ZrFe_4Si_2$-type
• $LaRu_4As_{12}$	10.3	skutterudite
• ZrRhSi	10.5	Co_2P-type



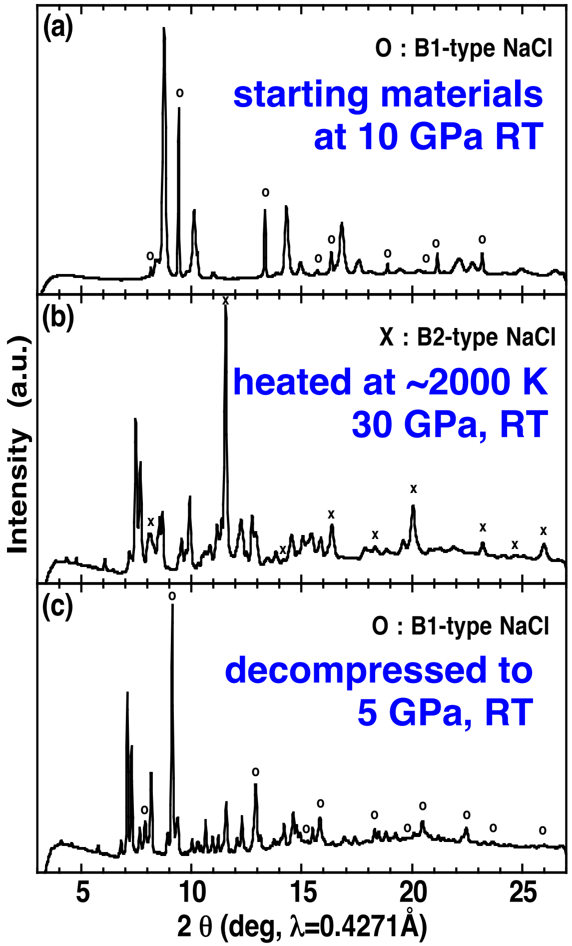


Synthesis of various nitrides

P～10 GPa, T～1800 K
transition metal nitride

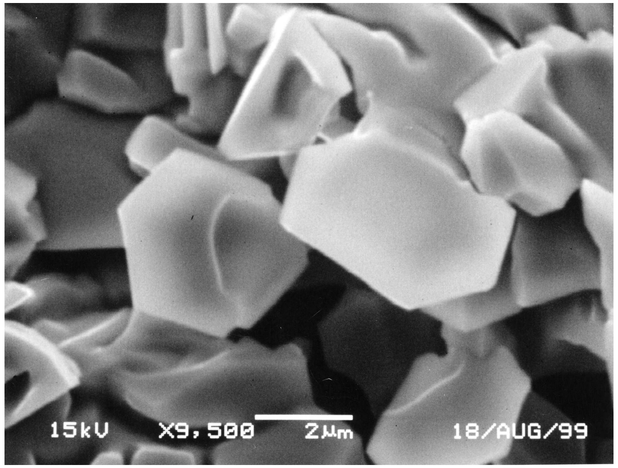


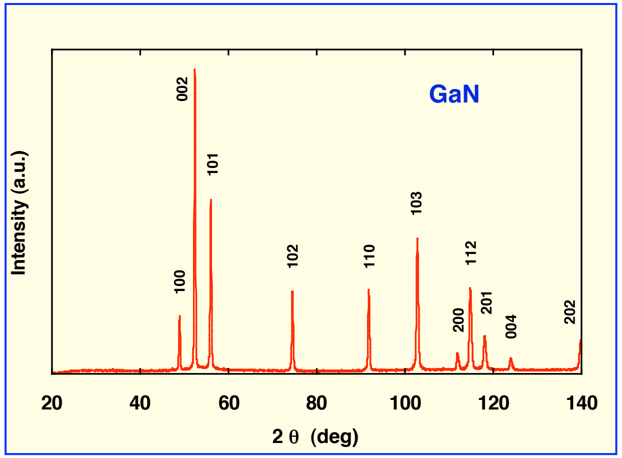
P～30 GPa, T～2000 K
La nitride



Synthesis of single crystals

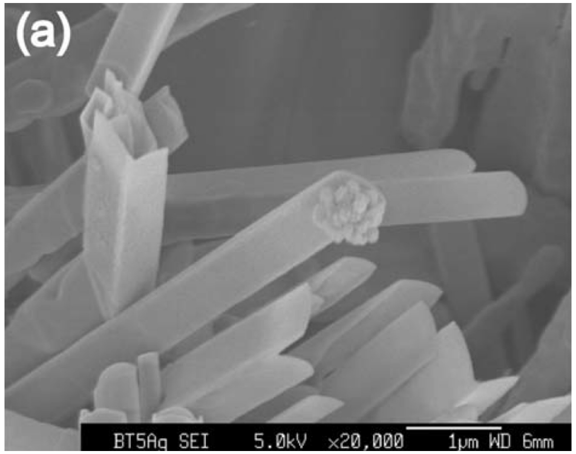
GaN

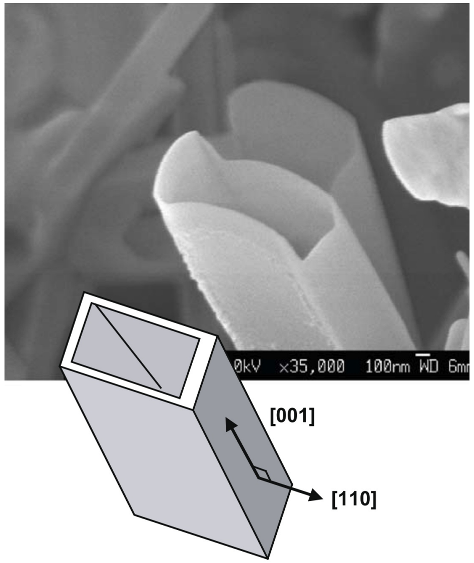




(Hasegawa & Yagi, 2003)

GeO_2





(Niwa et al., 2009)

Summary

- High-pressure minerals in the Earth's deep interior were clarified through high-pressure and high-temperature X-ray experiments.

- High P & T *in situ* X-ray diffraction study is now possible at the condition corresponding to the center of the Earth.

- Further efforts are made to extend the pressure ranges beyond the center of the Earth

- Experimental techniques developed for such studies are now applied to make new novel materials.