



TOHOKU
UNIVERSITY



Hydrous Phases in TZ and Top of Lower Mantle

Eiji OHTANI

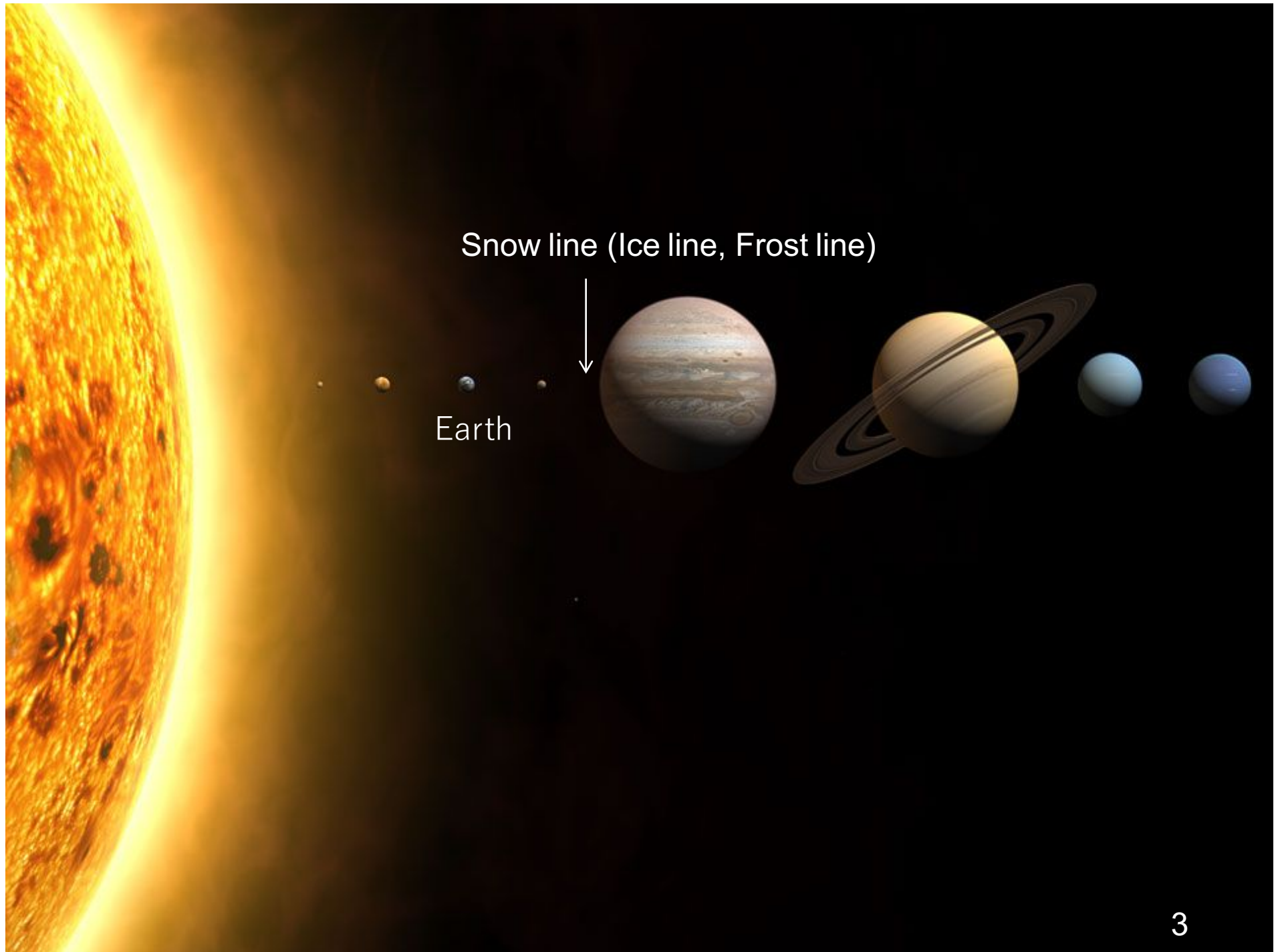
Department of Earth Science, Graduate School
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Nov 19th -20th, 2018 @ College de France

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Contents:

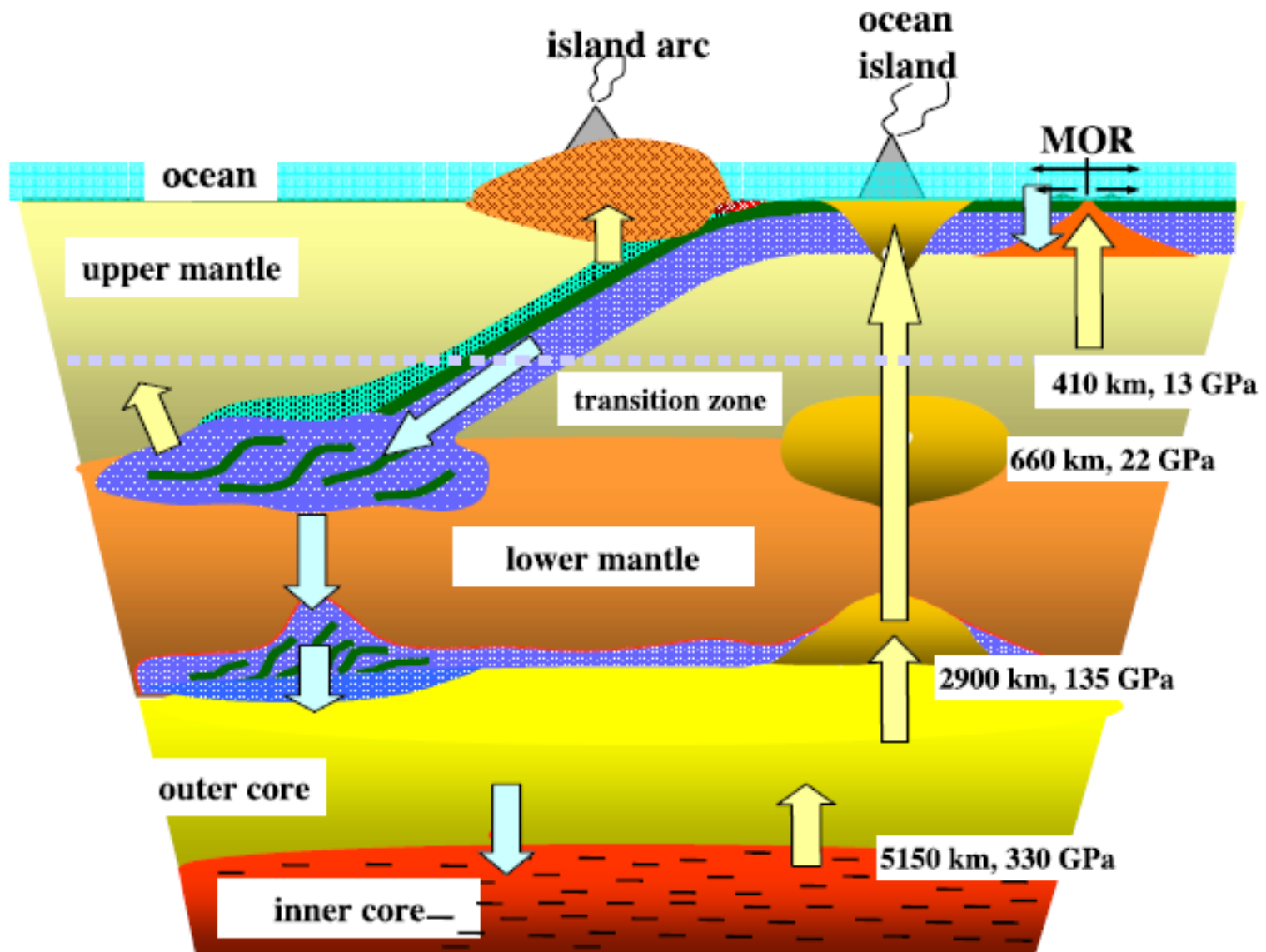
1. Dehydration in TZ and Top of the Lower mantle, and deep seismicity.
2. Metastable olivine wedge and water in the slabs: Effect of water in α - β transformation and deep seismicity.
3. Hydrogen transport into the lower mantle



Snow line (Ice line, Frost line)

Earth

Deep Volatile Cycle in global Earth



Ohtani (Elements, 2005)

Tomographic images of the subduction zones in the circum Pacific region.

King (2007)

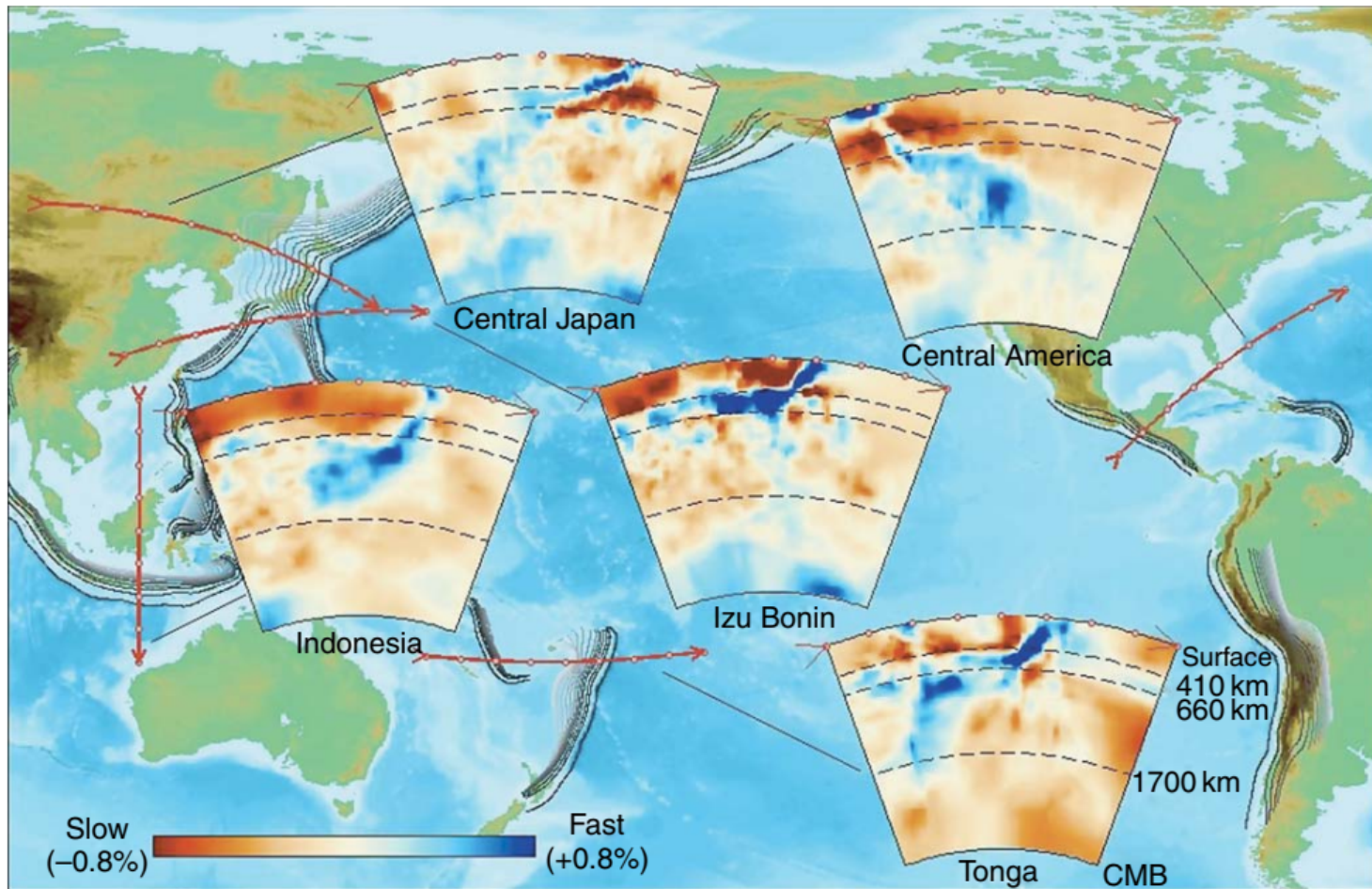


Figure 4 Summary of seismic tomography P-wave cross-sections through Pacific subduction zones. Reproduced from Albarède F and van der Hilst RD (2002) *Zoned mantle convection. Philosophical Transactions of the Royal Society of London A* 360: 2569–2592, with permission from Royal Society.

Tomography of the subducting Pacific slab and the 2015 Bonin deepest earthquake (Mw 7.9)

Zhao et al. (2017)

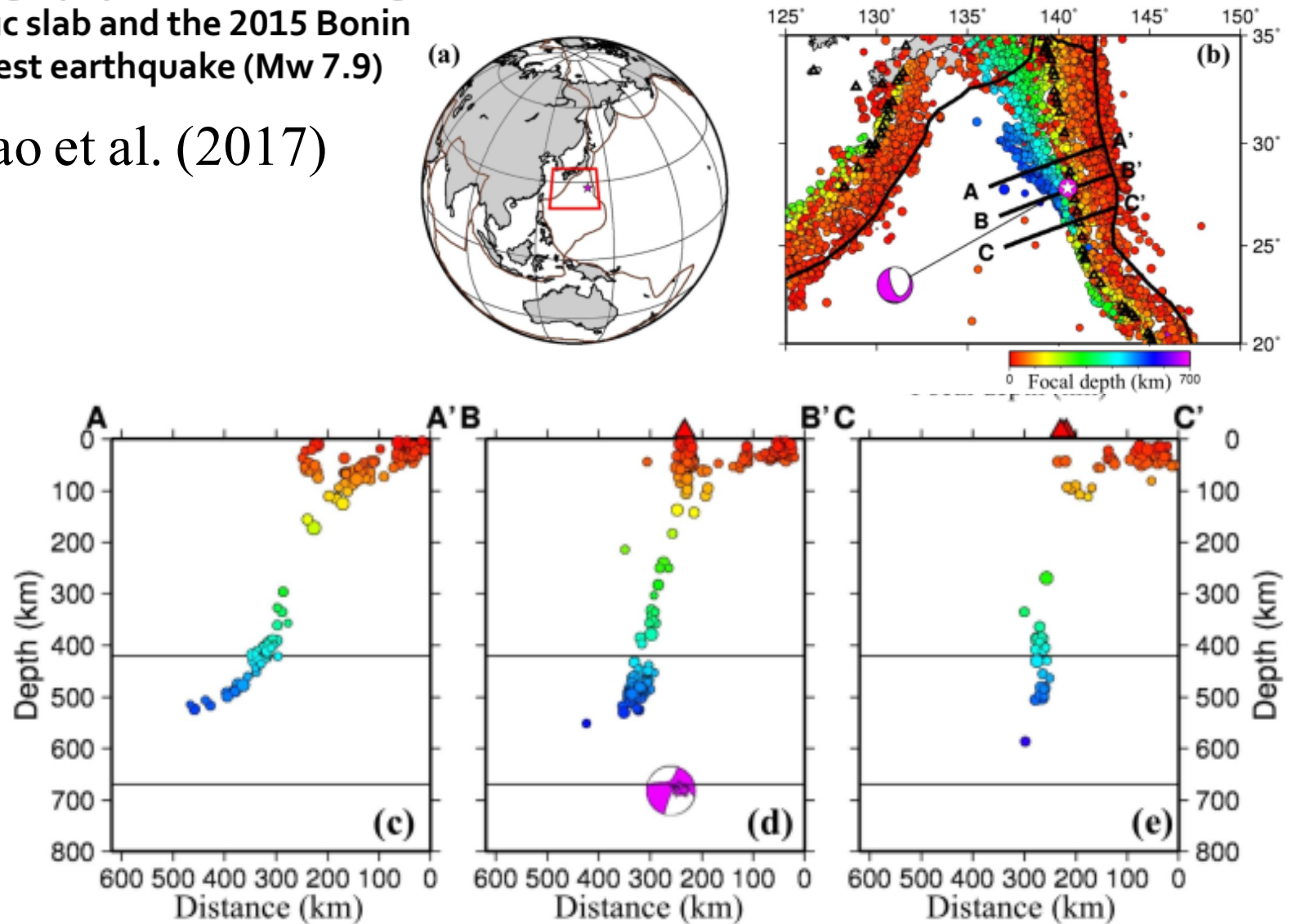


Figure 1. Seismicity of the study region. (a) The red star shows the epicenter of the 30 May 2015 Bonin deep earthquake (Mw 7.9). The red box shows the target area of the present study. The brown lines denote plate

King (2007)

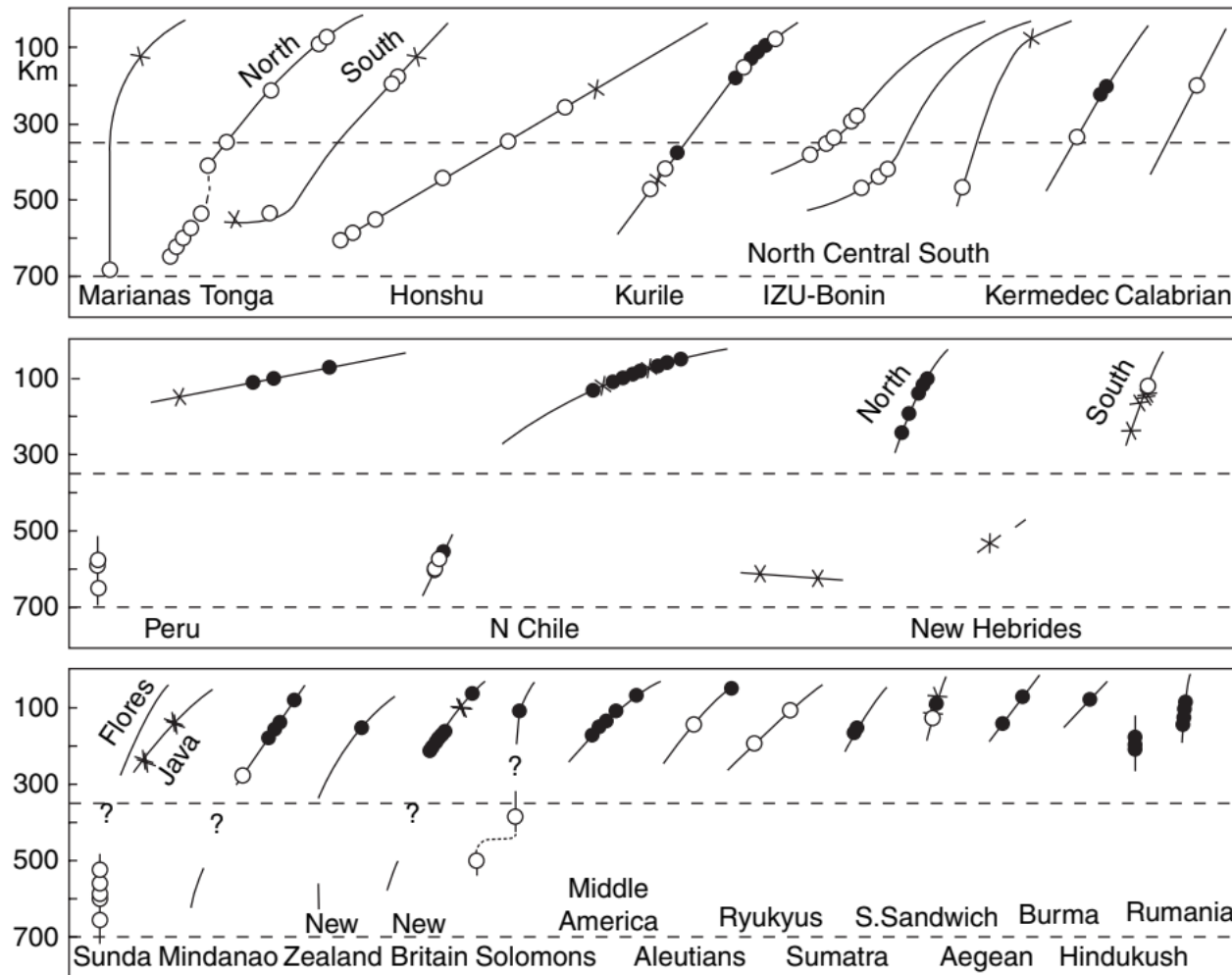
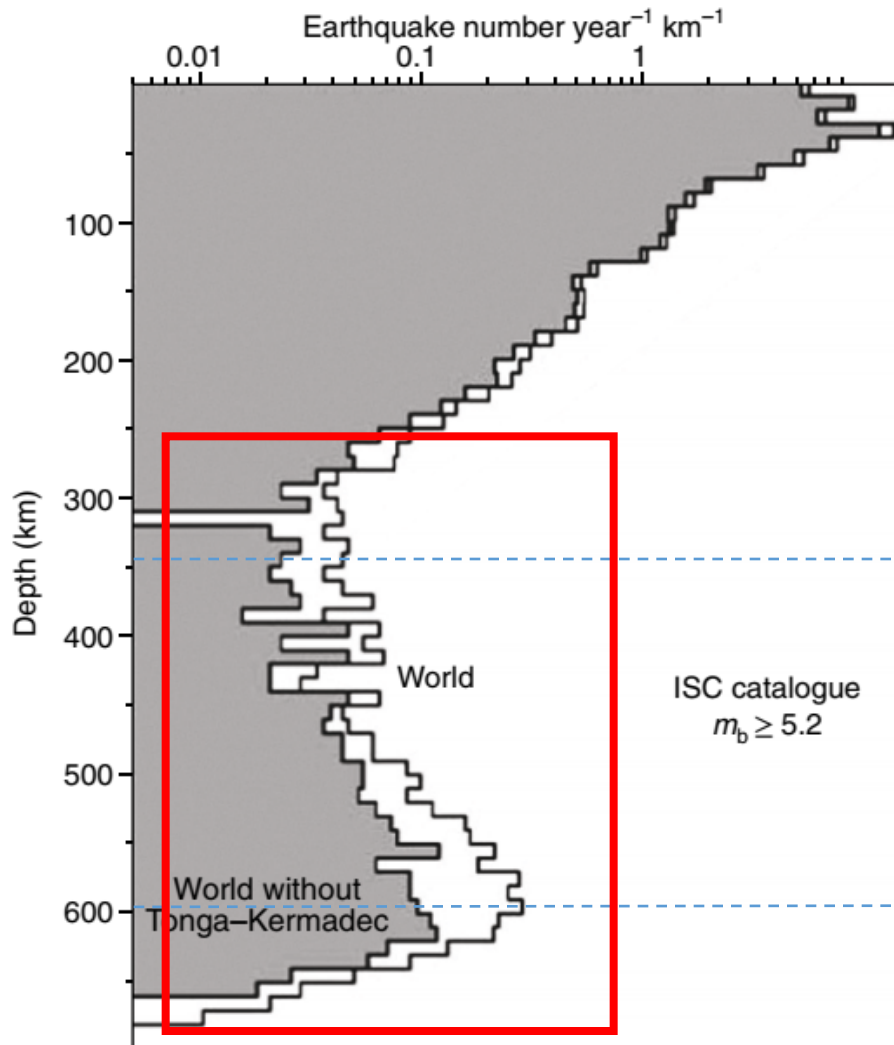


Figure 2 A global summary of down-dip compressive stresses calculated from focal mechanisms. The open circle is for down-dip compressive or P axis roughly parallel to the slab dip and the filled circles are down-dip T or tensional axis parallel to slab dip. The line represents the dip and length of the seismicity in the subduction zone. Reproduced from Isacks B and Molnar P (1971) Distribution of stresses in the descending lithosphere from a global survey of focal-mechanism solutions of mantle earthquakes. *Reviews of Geophysics and Space Physics* 9: 103–174. With permission from American Geophysical Union.

Deep Earthquakes are remarkable characteristics of slabs



Mechanism

Metastable phase transitions:
Metastable olivine wedge (dry?)

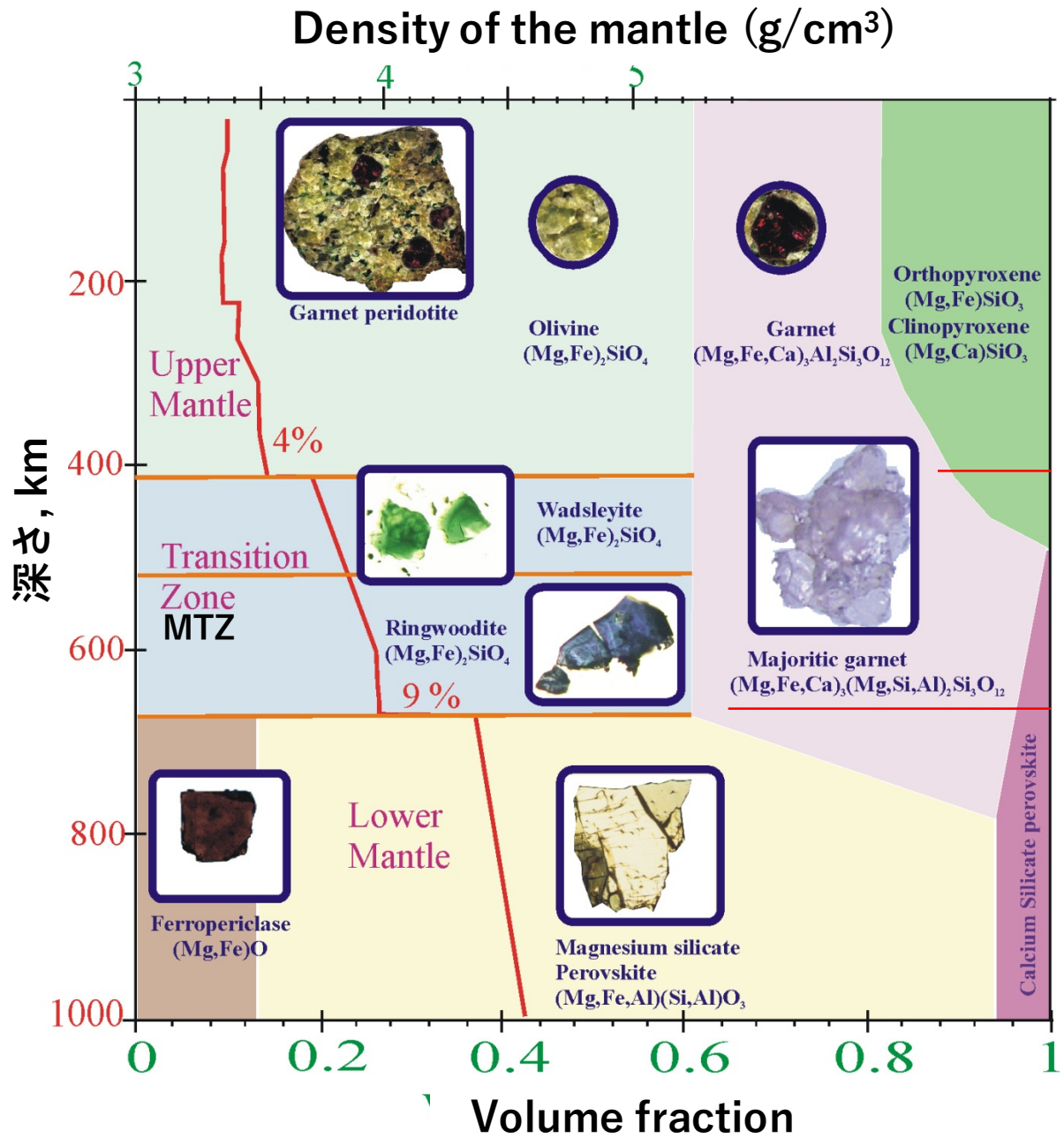
Dehydration of hydrous phases,
and fluid formation (wet?)

Other mechanisms: e.g.,
Existence of magnesite (MgCO_3)
and/or carbonate liquid (other
volatiles?)

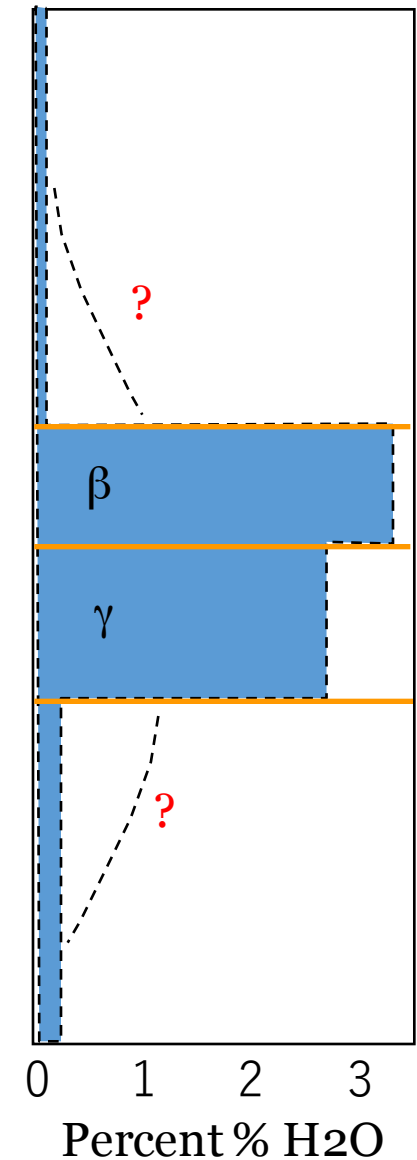
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Water exists in NAMs (Nominally Anhydrous Minerals)

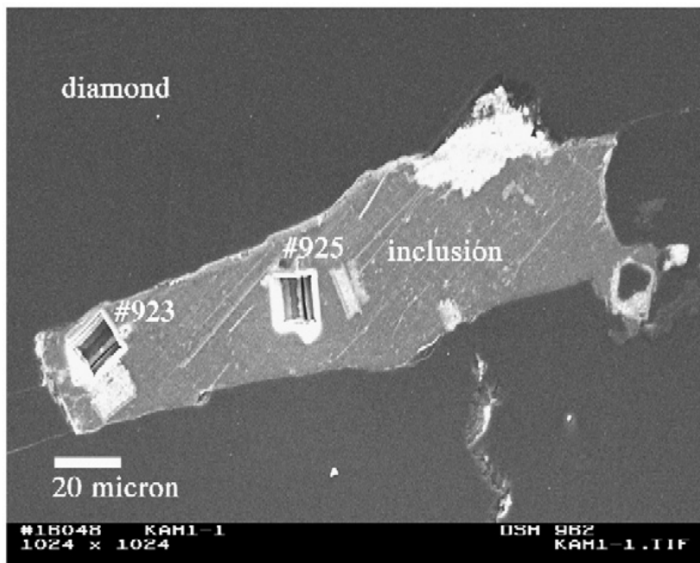


Water content



Transition zone: Some regions are wet.

Three hydrous minerals were reported as inclusions in kimberlitic diamond from Juina, Brazil



High pressure hydrous phases:
Phase Egg AlSiO_3OH and $\delta\text{-AlOOH}$ (Wirth et al., 2007; Kaminsky, 2017)

Hydrous ringwoodite
 Mg_2SiO_4 (with ~1 wt.% water) inclusion in diamond
JUc29 (Pearson et al., 2014)



Candidates of the hydrogen carriers in the mantle transition zone

Phase A: $\text{Mg}_7\text{Si}_4\text{O}_8(\text{OH})_6$

Wadsleyite Mg_2SiO_4

Ringwoodite Mg_2SiO_4

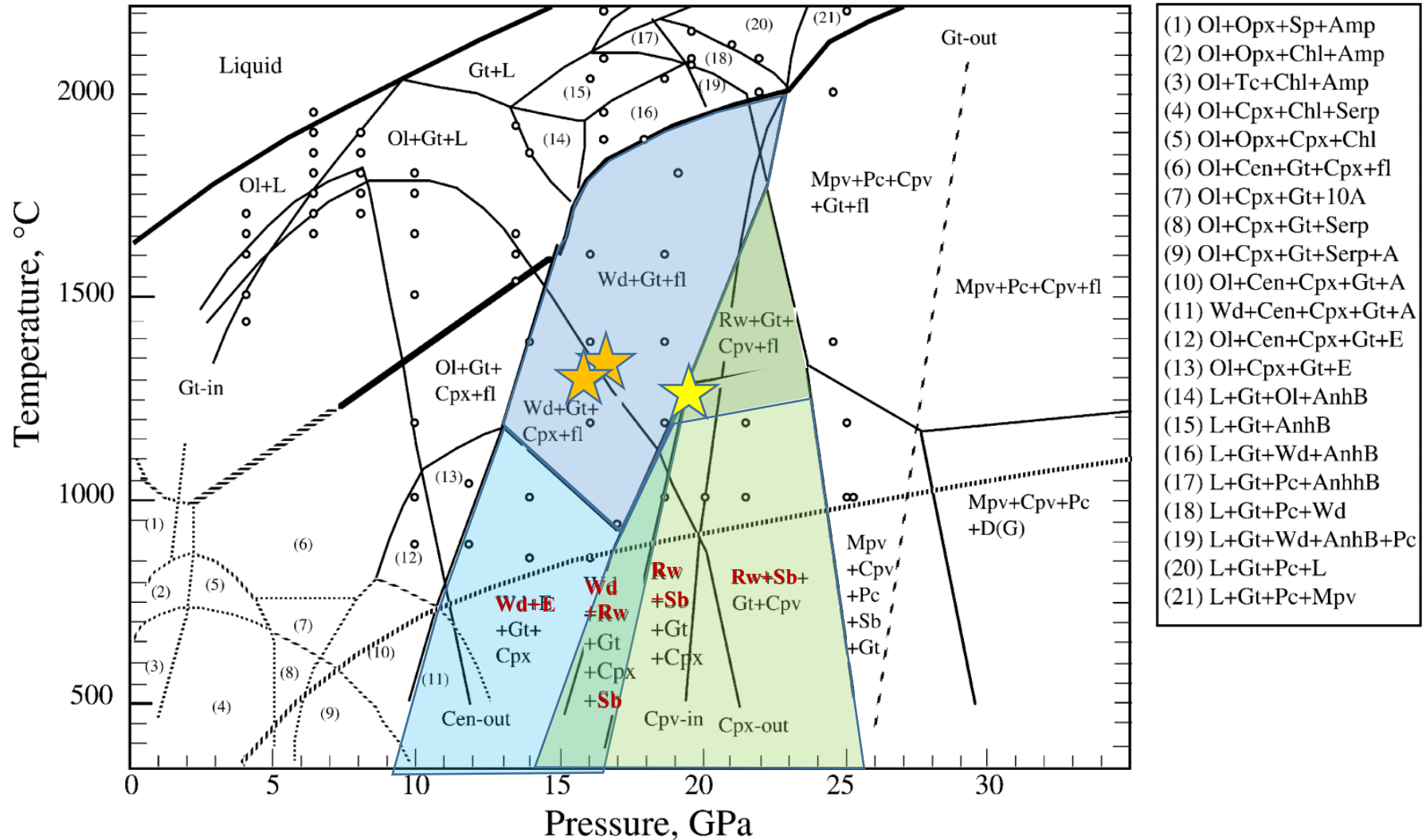
Phase E: $\text{Mg}_{2.3}\text{Si}_{1.25}\text{H}_{2.4}\text{O}_6$

Phase D: $\text{Mg}_{1.14}\text{Si}_{1.73}\text{H}_{2.81}\text{O}_6$

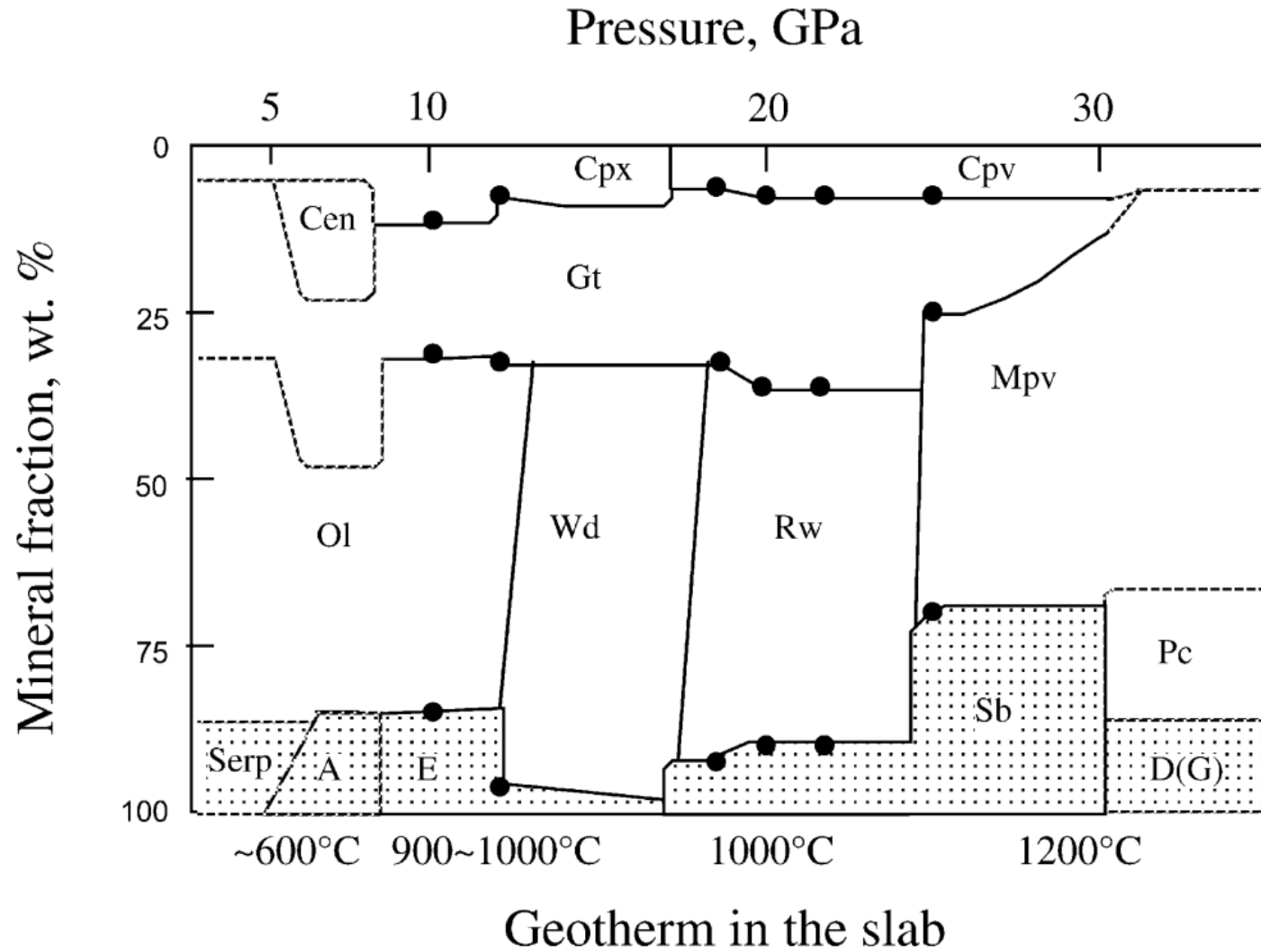
Superhydrous phase B: $\text{Mg}_{10}\text{Si}_3\text{O}_{14}(\text{OH})_2$

EGG: AlSiO_3OH

Partitioning of Hydrogen between Ol/Wd/Rg and hydrous phases



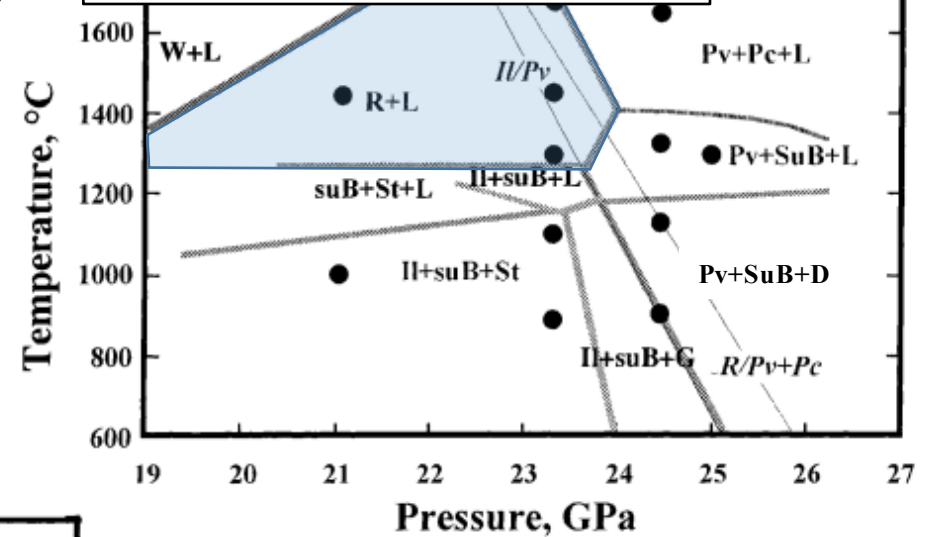
Hydrous phases coexist with Wd and Rg along the cold geotherm. High water contents in Wd and Rg were determined at higher temperature after dehydration of hydrous phases.



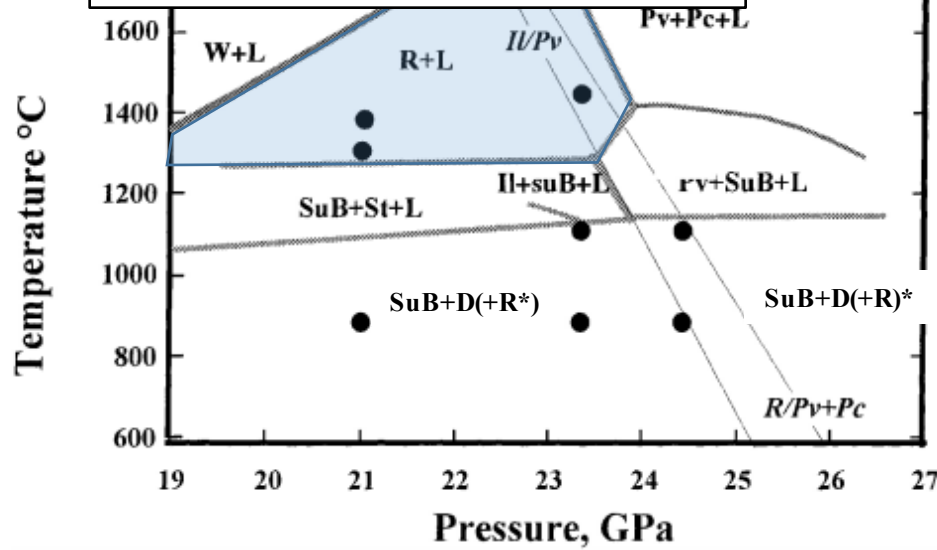
Ohtani et al. (2001)

Wadslyite and Ringwoodite are NOT stable under water saturated and low temperature conditions ($T < 1000$ °C)

Mg_2SiO_4 -5wt% H_2O



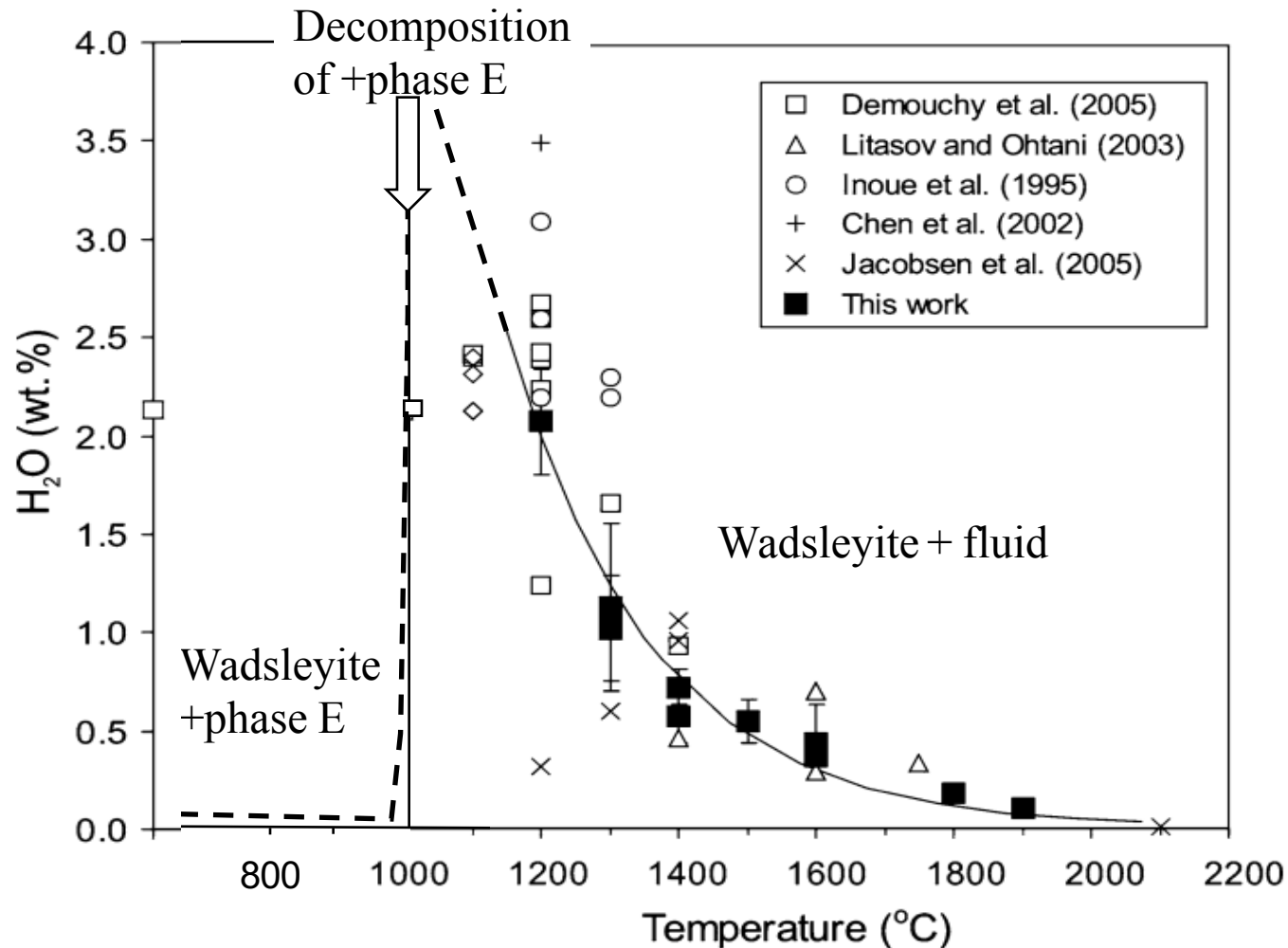
Mg_2SiO_4 -11wt% H_2O



Hydrogen can be absorbed by hydrous minerals, such as SuB, Phase D.

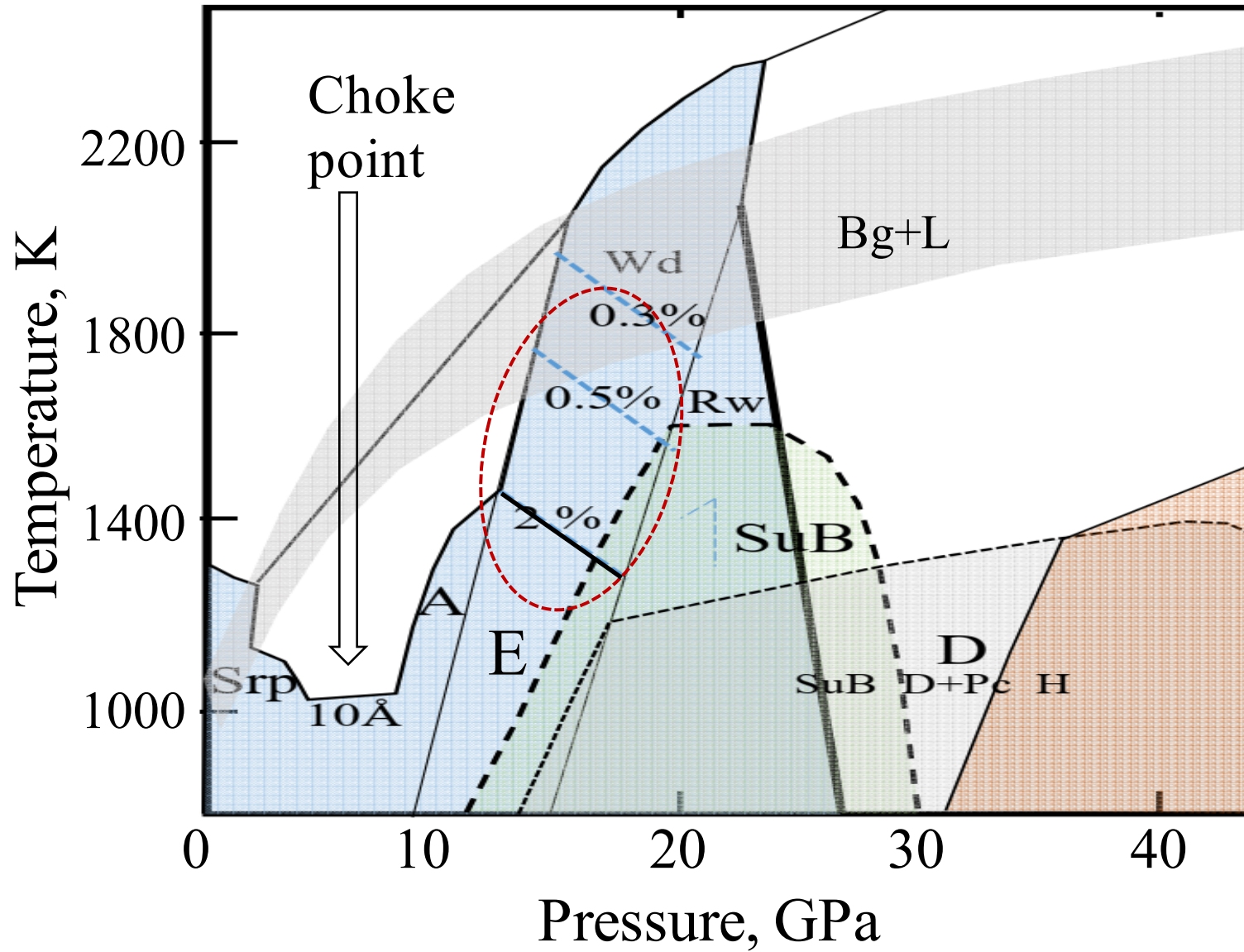
Hydrogen favors hydrous minerals compared to wadsleyite and ringwoodite.

Water content in wadsleyite at high temperature at 14-20 GPa (Litasov, Shatskiy, Ohtani, Katsura, 2011, modified)

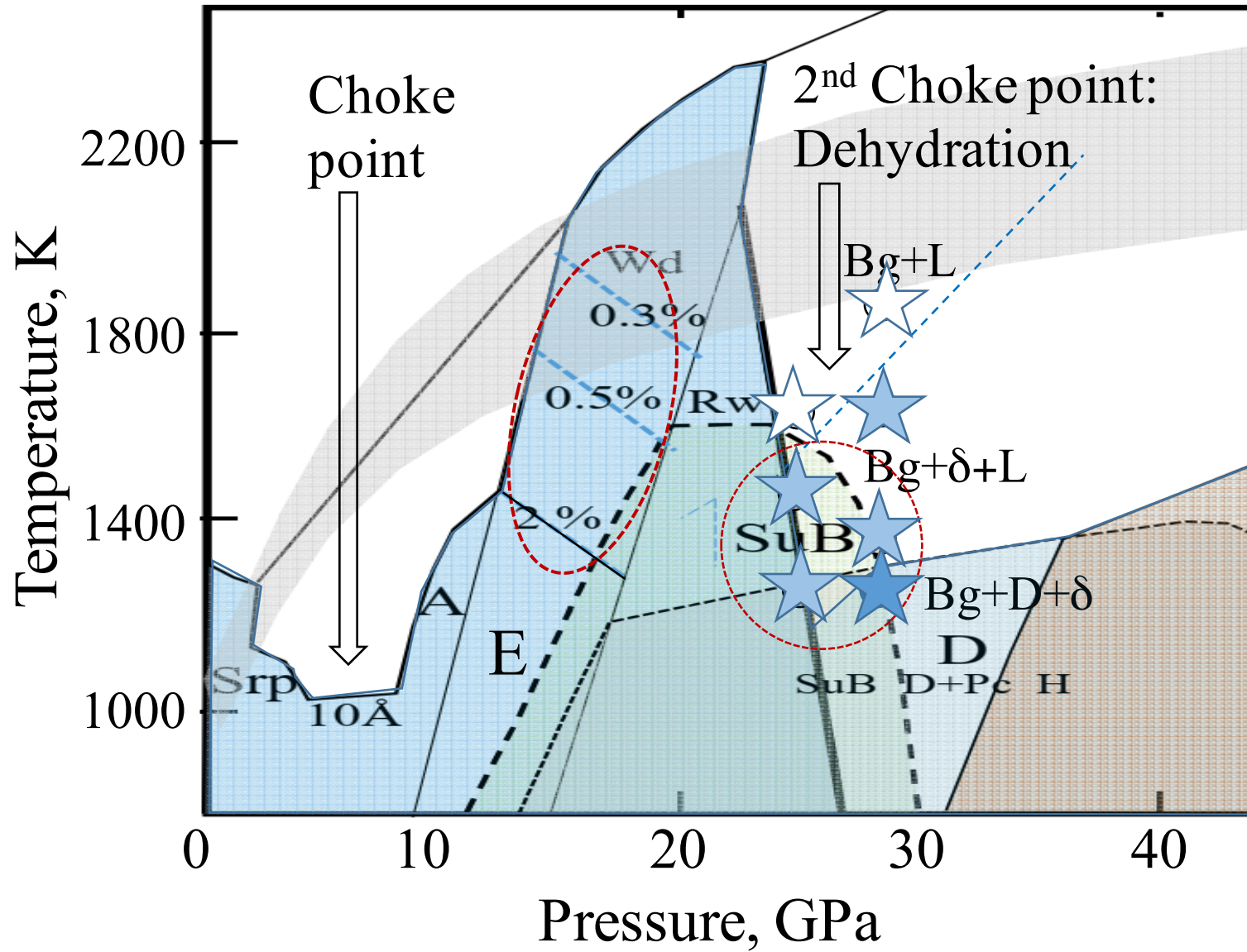


Dehydration of slabs due to decomposition of hydrous phases and decrease in H solubility in Wd/Rg with increasing temperature.

Dehydration sites in the mantle transition zone

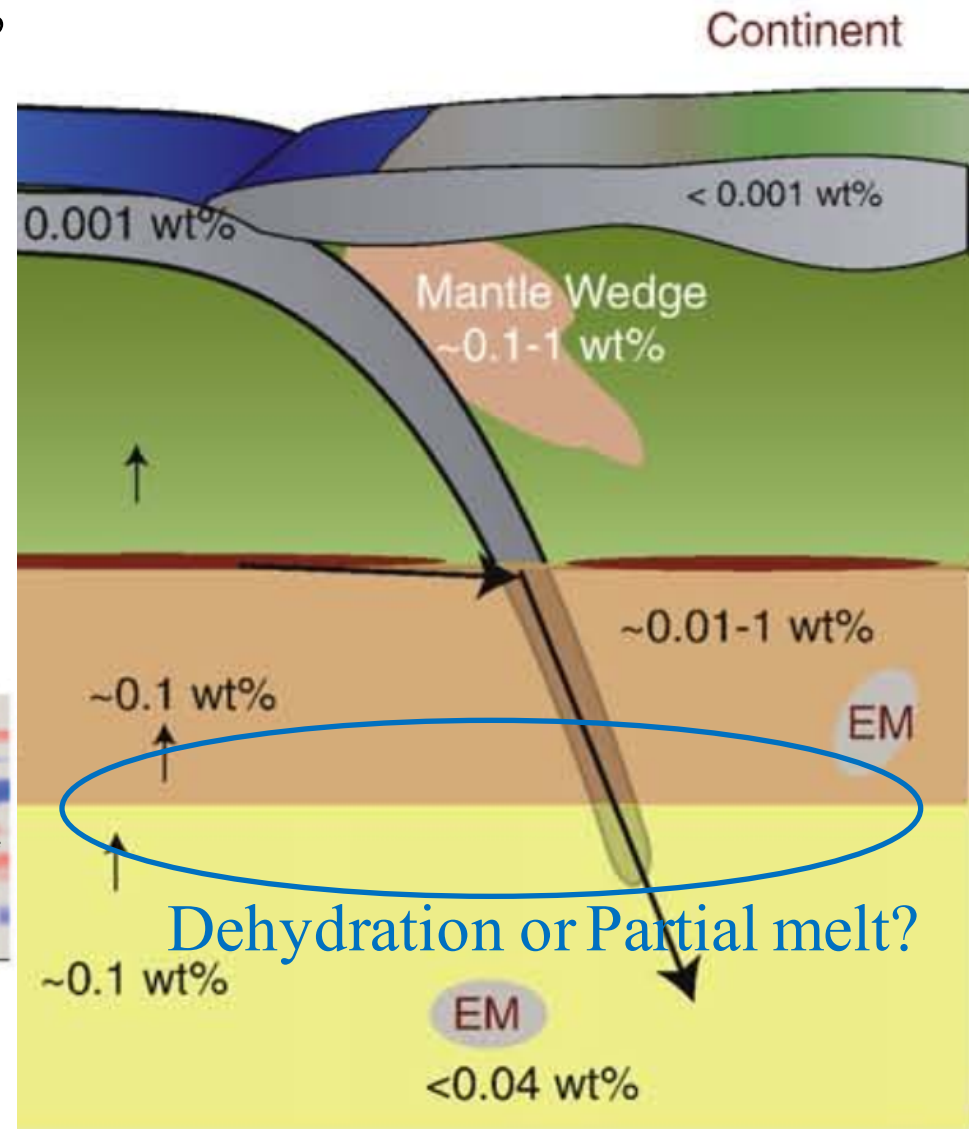
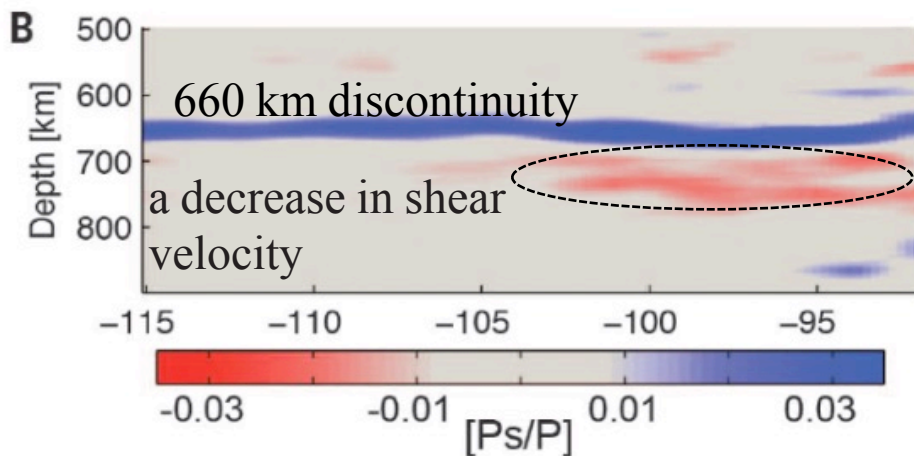
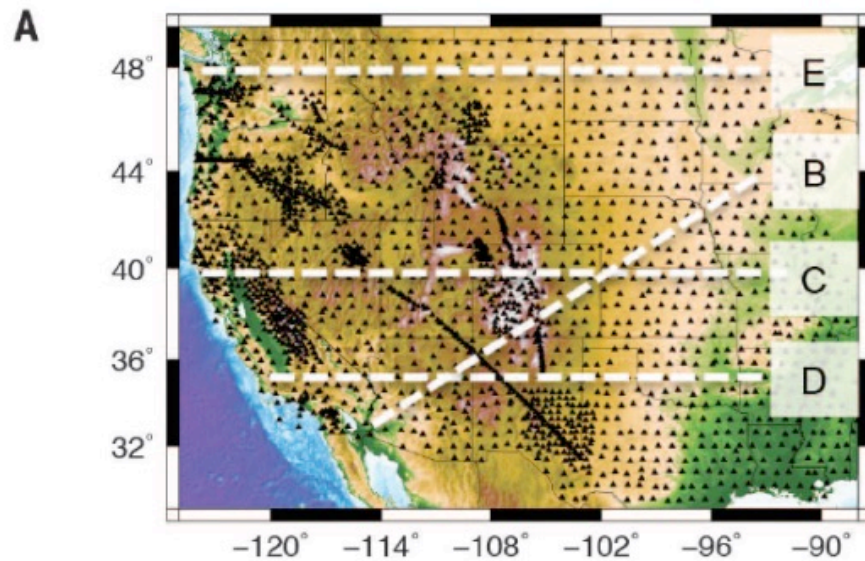


Dehydration sites in the mantle transition zone



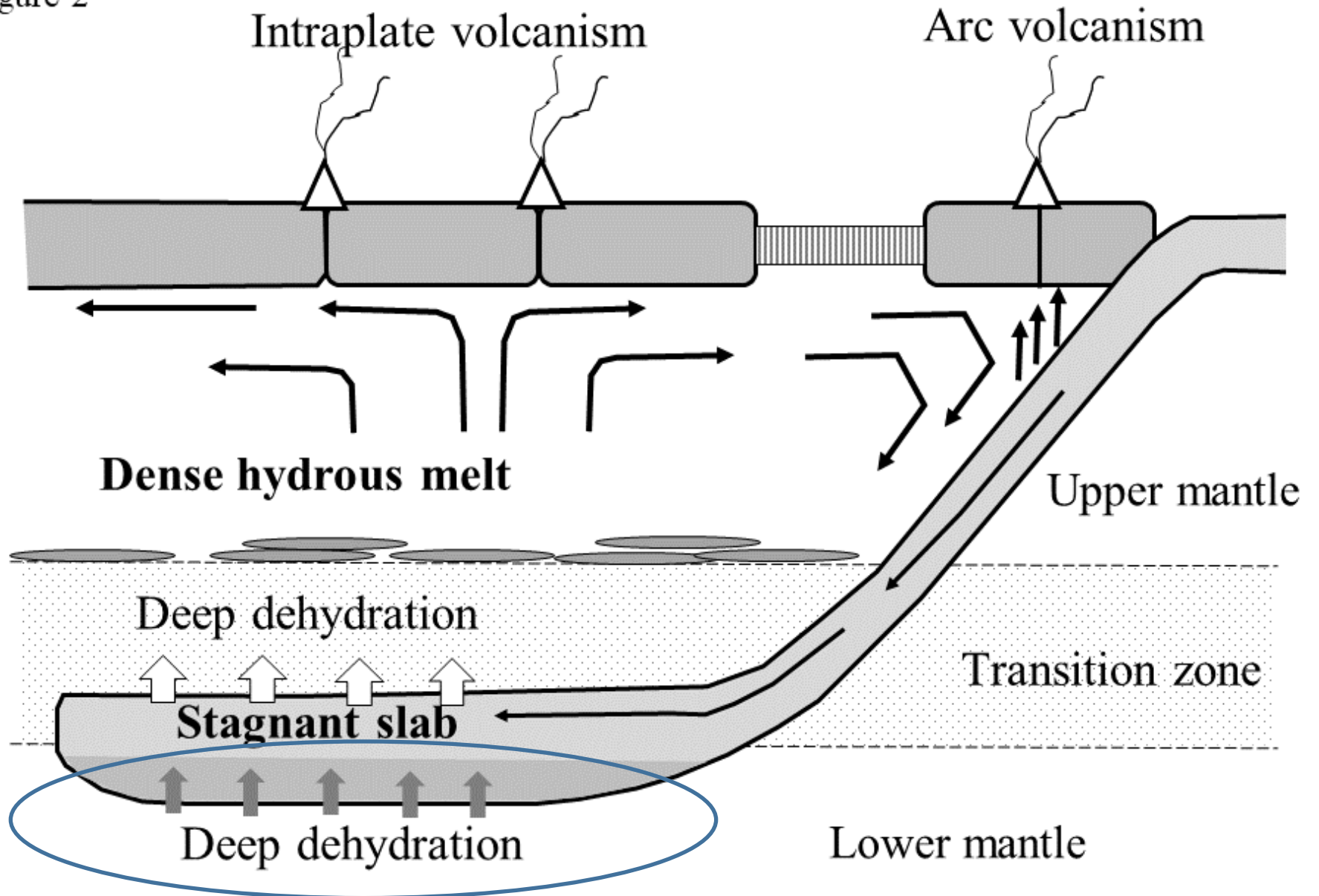
Anomalous low Vs and Q region at the top of the lower mantle,

Karato et al. (2014)

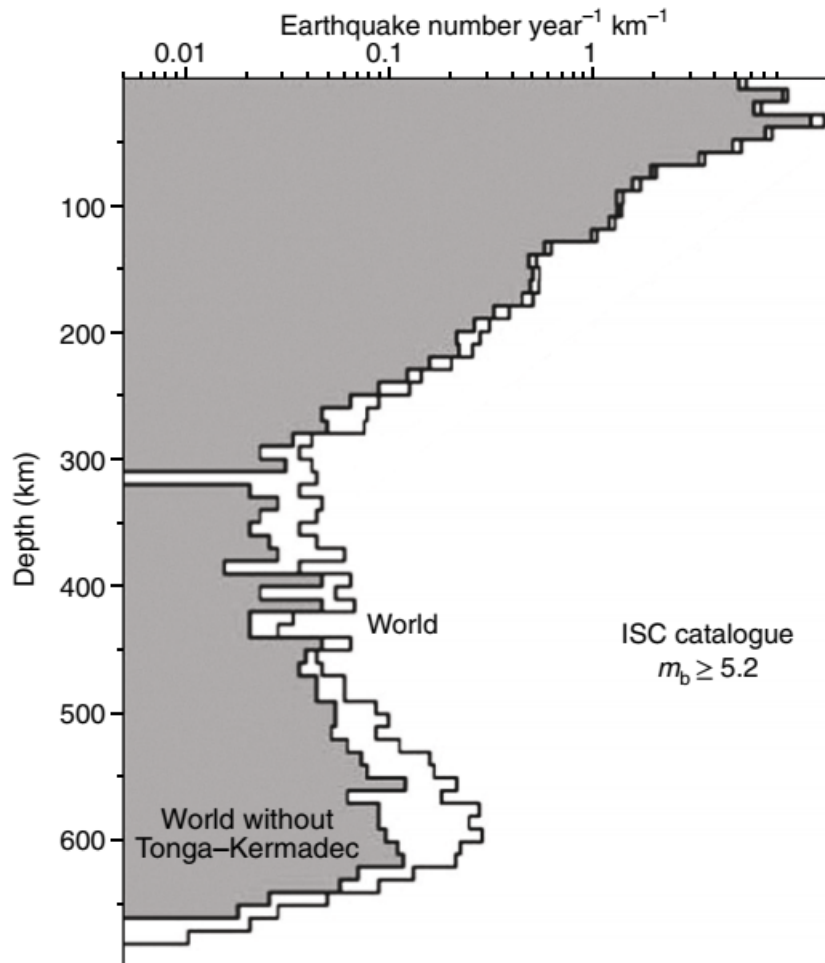


Schmandt et al. (2014)

Figure 2



Several dehydration sites exist in the transition zone:



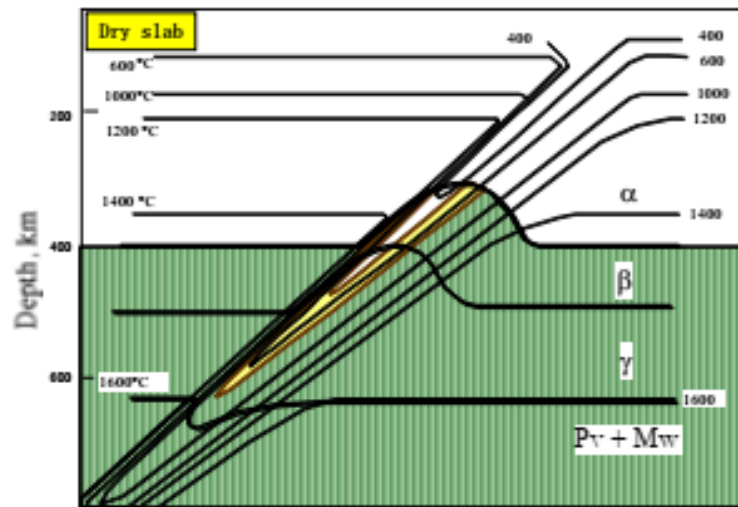
1. Dehydration of phase E, superhydrous phase B, phase D with increasing temperature.
 2. Decrease of water contents in Wd/Rg with increasing temperature.
 3. Decomposition of phase D and super B at the top of the lower mantle.
 4. Dehydration can trigger the deep mantle seismicity.
- $\Delta V(\text{dehydration}) < 0$

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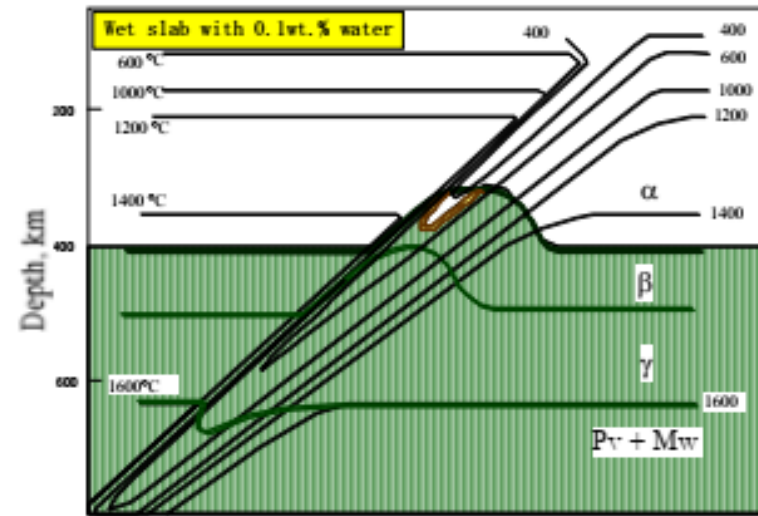
Effect of water on α - β transformation kinetics

Dry



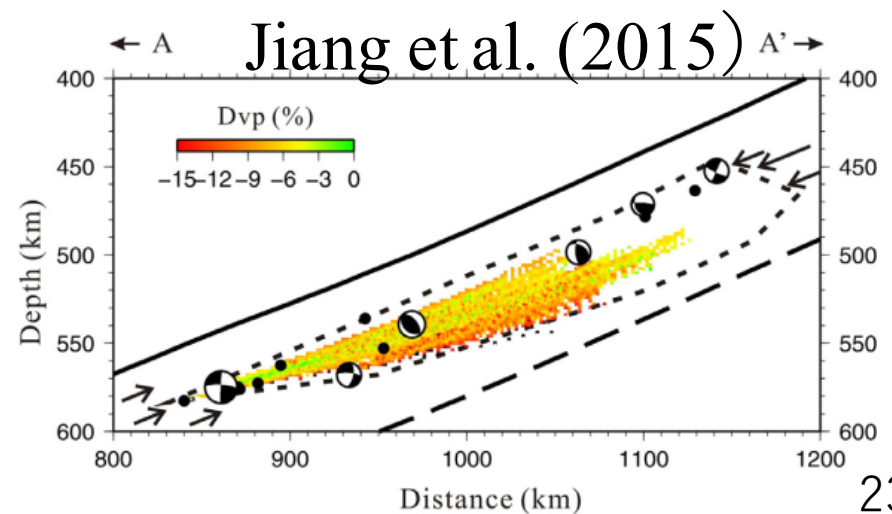
Dip angle of subduction $\theta=45^\circ$; Temperature gradient $0.7^\circ\text{C}/\text{km}$;
Subduction rate, $7\text{cm}/\text{year}$; Grain size 5mm

Wet



Dip angle of subduction $\theta=45^\circ$; Temperature gradient $0.7^\circ\text{C}/\text{km}$;
Subduction rate, $7\text{cm}/\text{year}$; Grain size 5mm

No metastable olivine wedge:
Tonga, (Koper and Wiens, 2000):
Metastable olivine wedge exists:
South-west Japan (Kawakatsu & Yoshioka, 2011):
Western Pacific slab (Jiang et al. 2015).



Effect of water in α - β transformation in olivine

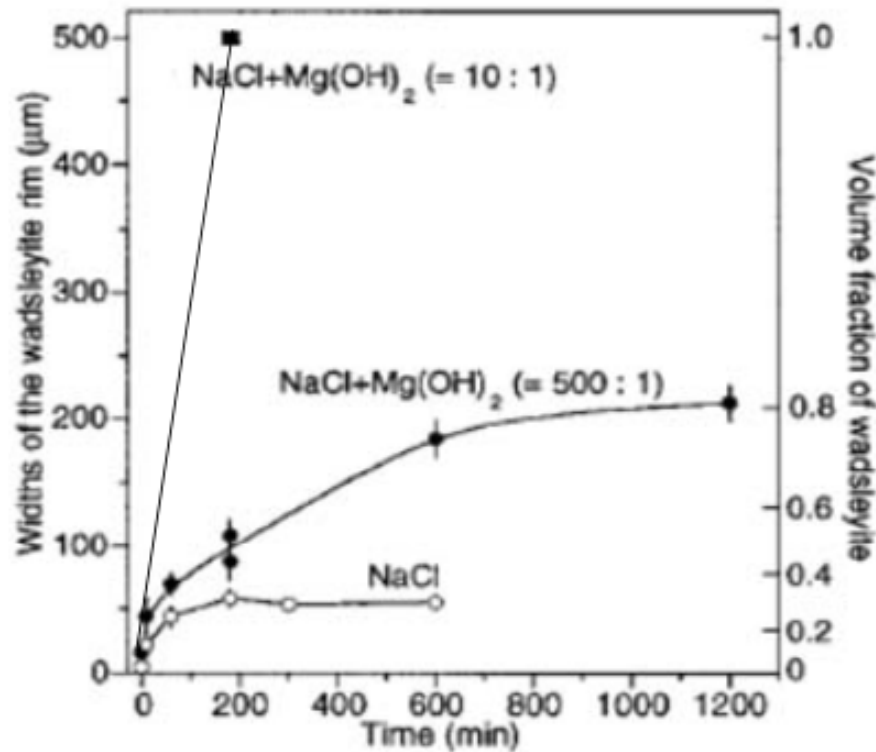
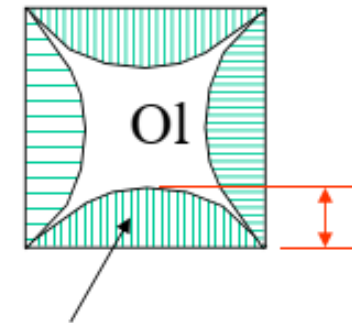
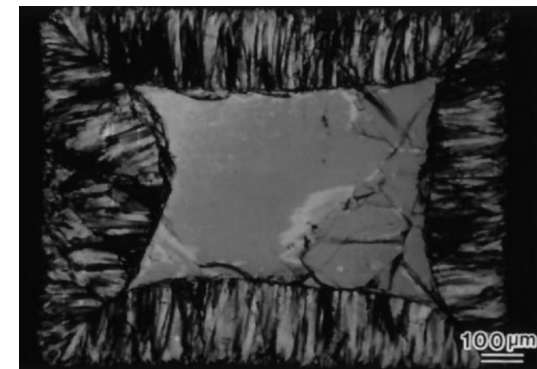


Fig. 2. Time dependence of the width and volume fraction of the wadsleyite rim in dry and wet runs at 13.5 GPa and 1030°C. The confining medium of the sample is also shown. The volume fraction of wadsleyite was estimated from widths of the wadsleyite rim. Time indicates the heating duration at the desired temperature.

Kubo, Ohtani et al.
(1998)

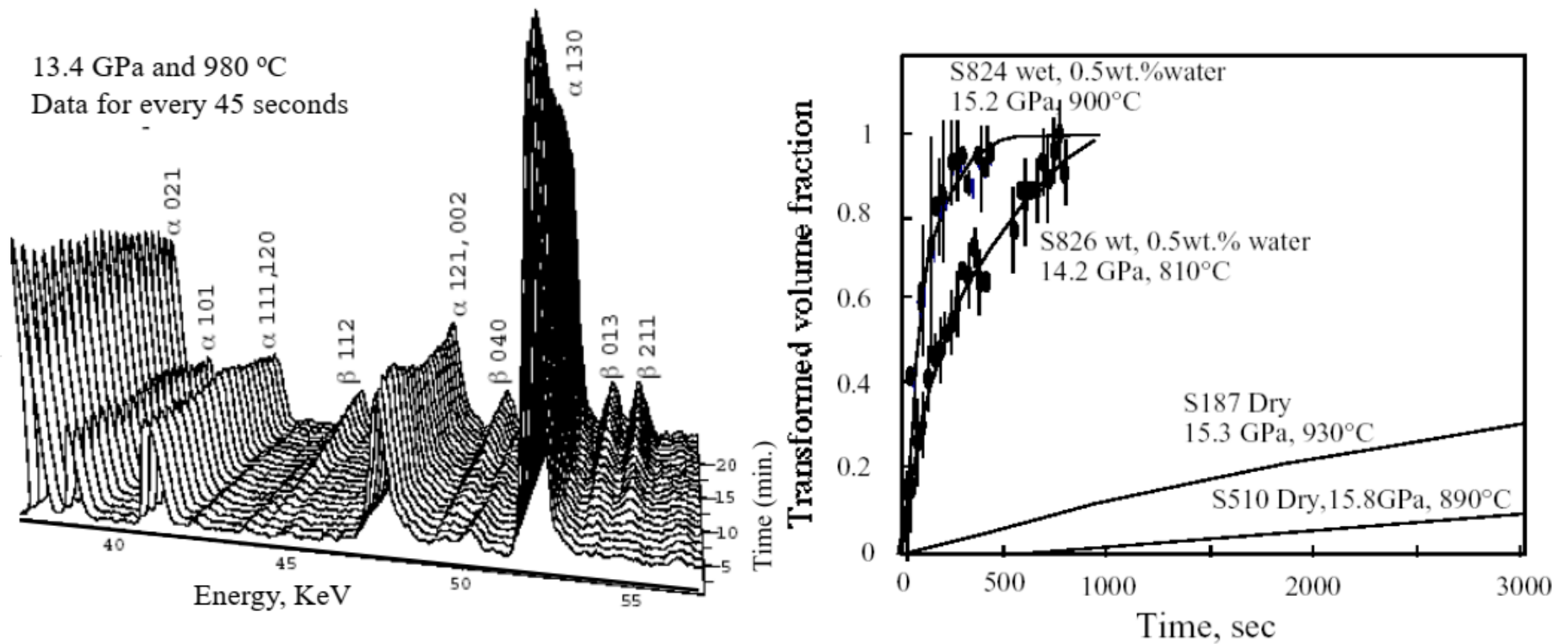


Wadsleyite rim



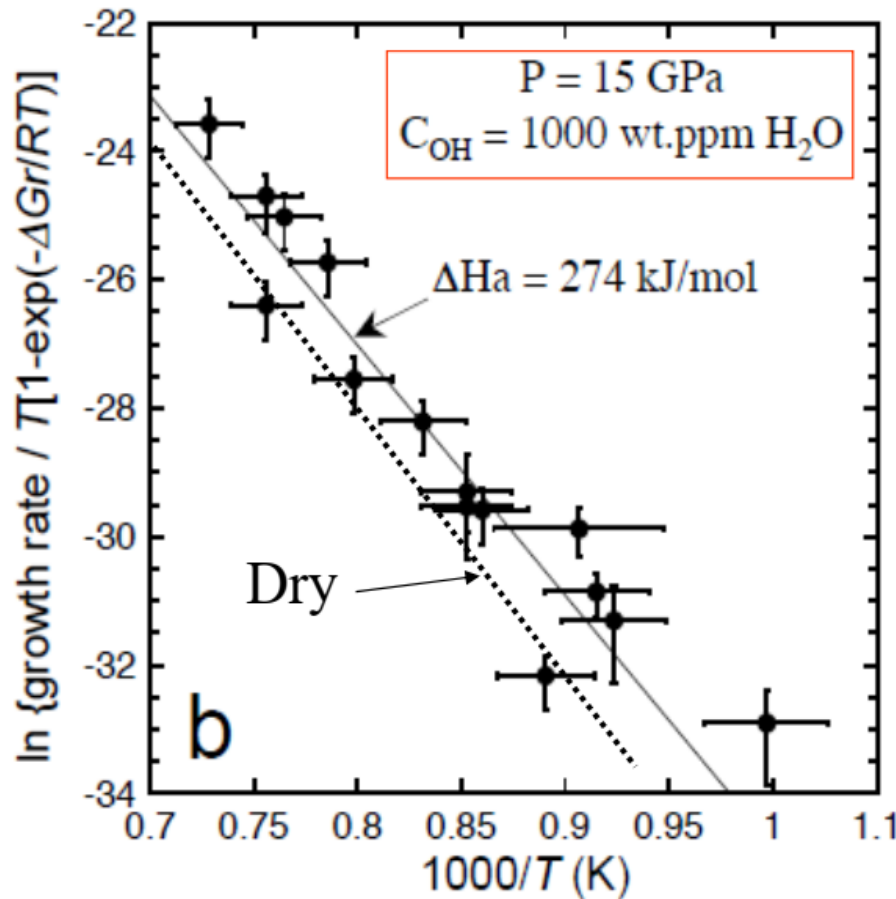
Hosoya, Kubo, Ohtani, Sano, Funakoshi (2005)

The reaction kinetics of α - β transformation in olivine
Kawai-type high-pressure apparatus “SPEED-1500”
installed in beamline BL04B1



Hosoya, Kubo, Ohtani, Sano, Funakoshi (2005)

The growth rates of wadsleyite as a function of temperature for the dry and wet experiments



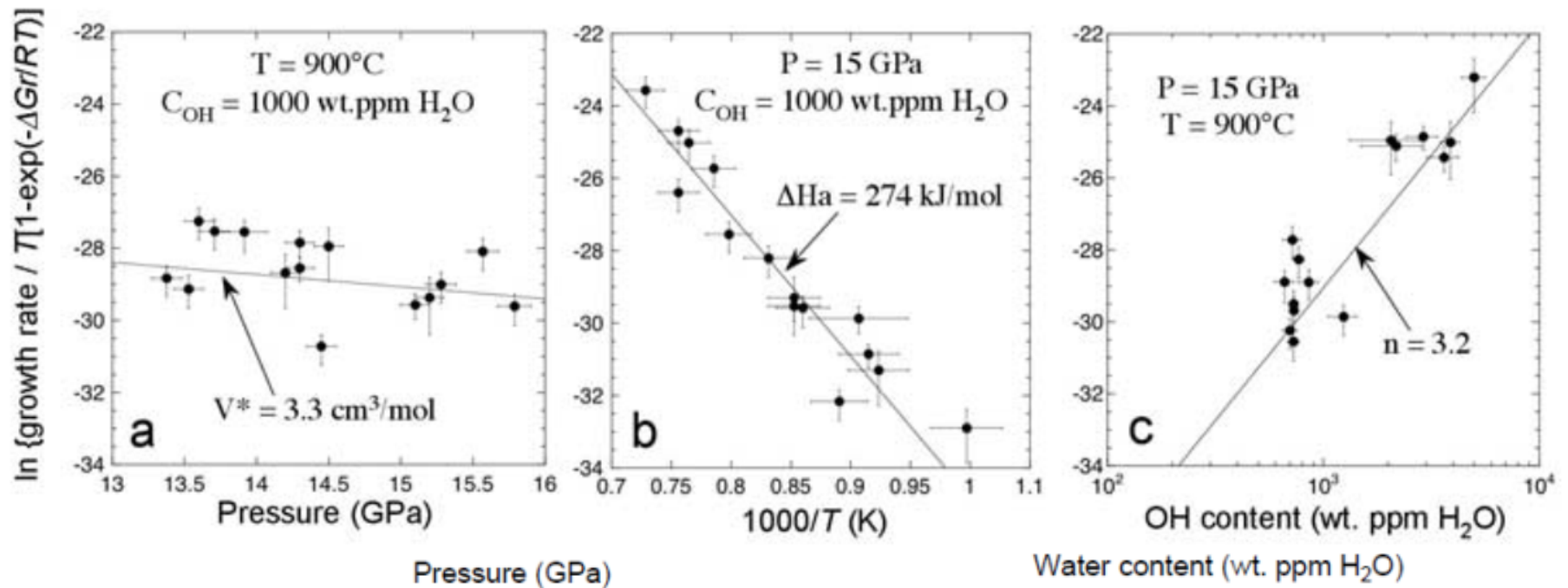
$$\dot{x} = ATC_{\text{OH}}^n \exp\left(-\frac{\Delta H_a + PV^*}{RT}\right) \left[1 - \exp\left(\frac{-\Delta G_r}{RT}\right)\right]$$

ΔH_a is the activation enthalpy for growth,

V^* is the activation volume for growth,

ΔG_r is the free energy change of the transformation

Hosoya, Kubo, Ohtani, Sano, Funakoshi (2005)



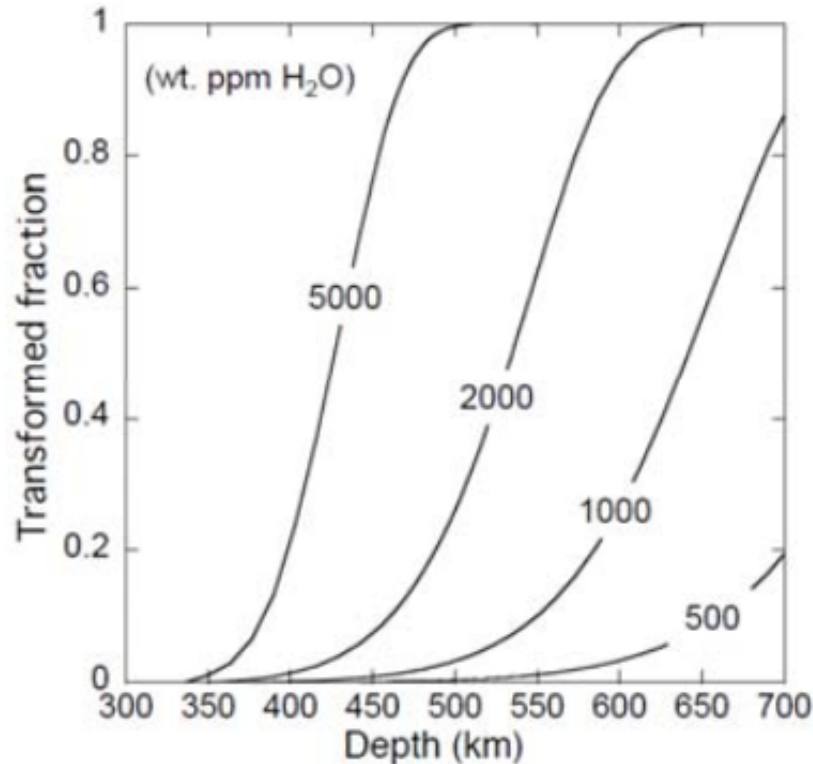
$$\dot{x} = AT C_{\text{OH}}^n \exp\left(-\frac{\Delta H_a + PV^*}{RT}\right) \left[1 - \exp\left(\frac{-\Delta G_r}{RT}\right)\right]$$

where ΔH_a is the activation enthalpy for growth, V^* is the activation volume for growth, and ΔG_r is the free energy change of the transformation

$\ln A = -18.0 \pm 3.8 \text{ ms}^{-1} \text{ wt.ppmH}_2\text{O}^{-3.2}$, $n = 3.2 \pm 0.6$, $\Delta H_a = 274 \pm 87 \text{ kJ/mol}$, and $V^* = 3.3 \pm 3.8 \text{ cm}^3/\text{mol}$.

Hosoya, Kubo, Ohtani, Sano, Funakoshi (2005)

Effect of water on olivine-wadsleyite phase transition



Temperature at 660 km depths is 600°C.

Thermal gradient of 0.6°C/km.

Vertical speed of subduction, 12 cm/year.

The P-T-t (Pressure-Temperature-time) path of the cold slab with water contents. **The metastable olivine can survive at the depths greater than the 650 km in cold slabs with water less than 500 wt. ppm H₂O.**

Mechanism of deep earthquakes

1. **Water contents in olivine/wadsleyite/ringwoodite are low** when coexisting with hydrous phases, i.e., Hydrogen favors Hydrous phases compared to Ol/Wd/Rg.

2. **Dehydration occurs due to warming up of the slabs**, which also can trigger the deep mantle seismicity. $\Delta V(\text{dehydration}) < 0$

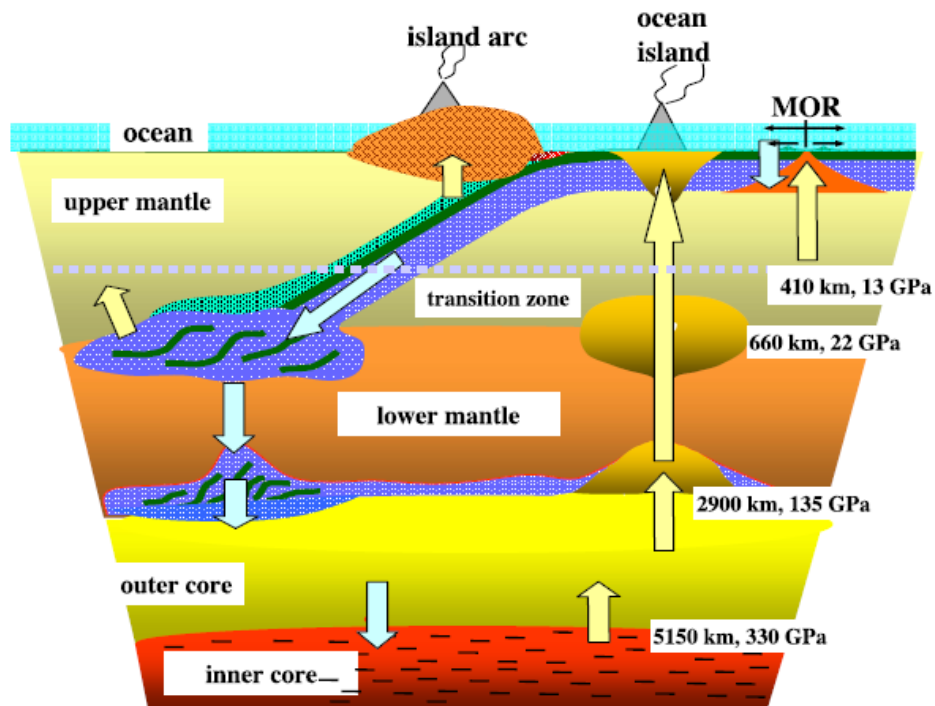
3. Sluggish α - β transformation can occur under the wet slab conditions, i.e., metastable olivine wedge exists even in the wet mantle transition zone, and the α - β transformation of metastable olivine can trigger the deep mantle seismicity. $\Delta V(\alpha-\beta) < 0$

Metastable olivine wedge is NOT the signature of dry subduction.

Contents:

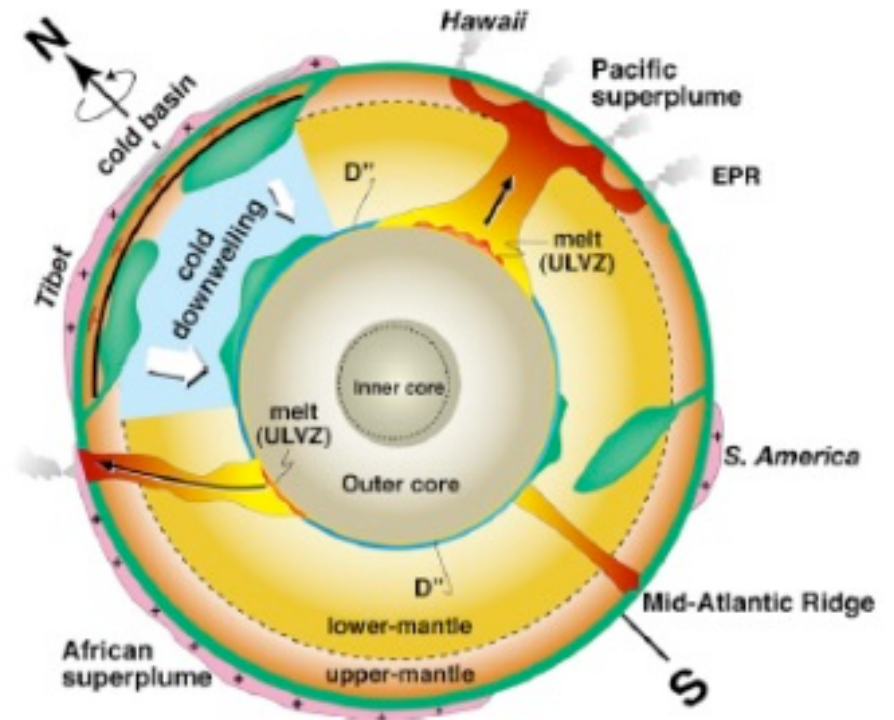
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Transport of water into CMB



Ohtani (Elements, 2005)

Superdownwelling/super continents



Maruyama et al. (GR 2007)

Candidates of the hydrogen carriers into the lower mantle

Phase D: $\text{Mg}_{1.14}\text{Si}_{1.73}\text{H}_{2.81}\text{O}_6$

Superhydrous phase B: $\text{Mg}_{10}\text{Si}_3\text{O}_{14}(\text{OH})_2$

Aluminous Phase D: $\text{Al}_2\text{SiO}_4(\text{OH})_2$

Phase δ : AlOOH Phase

Phase H: $\text{MgSiO}_2(\text{OH})_2$

Aluminous phase H: $\text{MgSiO}_2(\text{OH})_2\text{-AlOOH}$

Hydrous δ -phase (AlOOH)

Hydrous δ -phase H MgSiO₂(OH)₂ solid solution

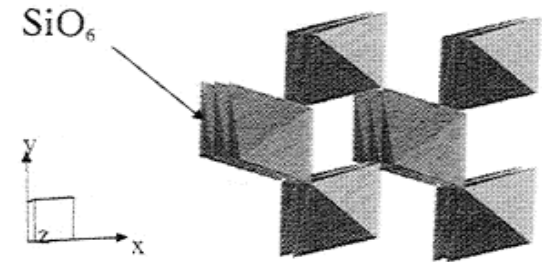
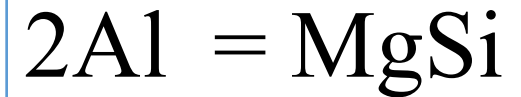
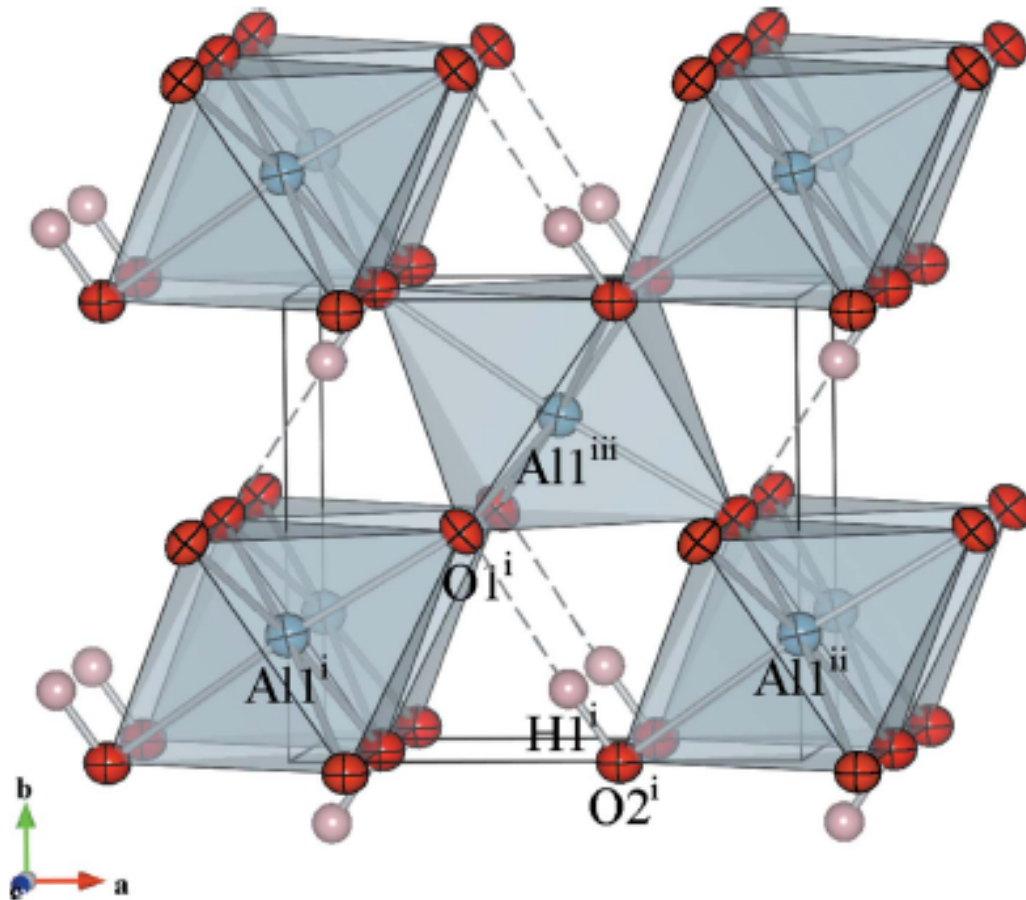


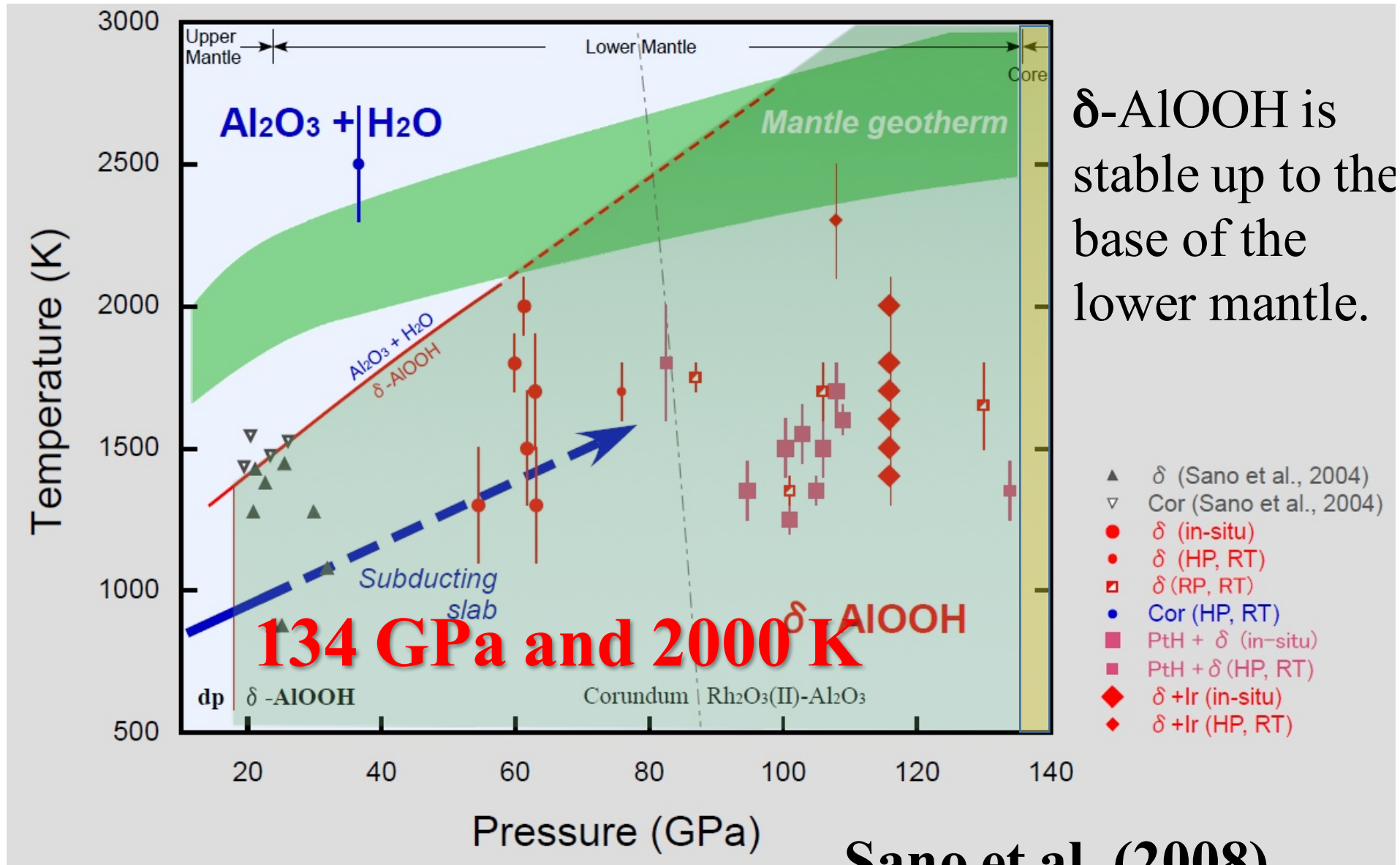
Figure 1. Structural similarity of δ -AlOOH and CaCl₂ type SiO₂. The positions of hydrogen atoms in δ -AlOOH are assumed to be the same as the other iso-structural compounds (e.g., Christensen *et al.*, 1976).

High pressure
polymorph of SiO₂:
CaCl₂ structure

Suzuki, Ohtani, Kamada (PCM 2000)

Bindi *et al.* (2014)

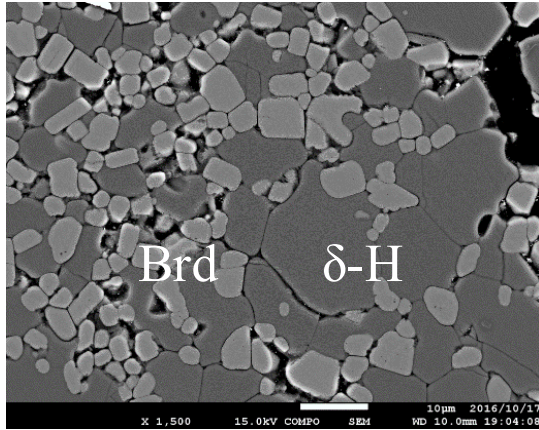
Phase δ -AlOOH



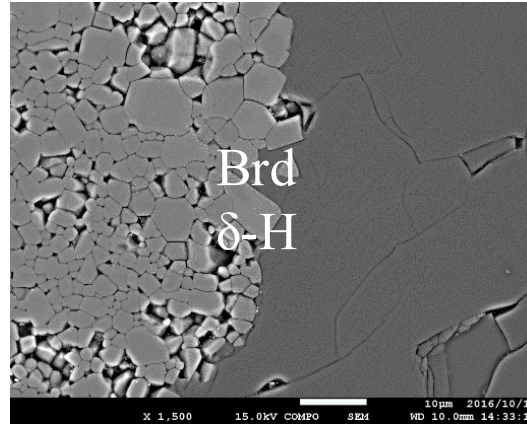
δ -AlOOH is stable up to the base of the lower mantle.

Sano et al. (2008)

δ -H solid solution coexists with **Al-depleted bridgmanite**



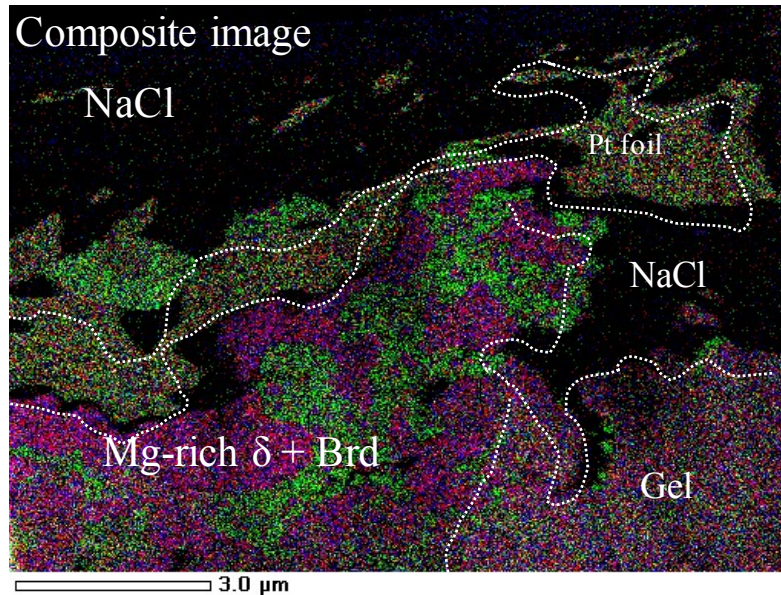
28 GPa, 1573K



28 GPa, 1373K

28 GPa, 1573 K
 δ -H: $H_{0.21}\delta_{0.57}S_{0.22}$
Brg: $M_{0.94}A_{0.06}$
 $K(Al_2O_3)=9.8$

28 GPa, 1373 K
 δ -H: $H_{0.59}\delta_{0.08}S_{0.33}$
Brg: $M_{0.98}A_{0.02}$
 $K(Al_2O_3)=5.1$



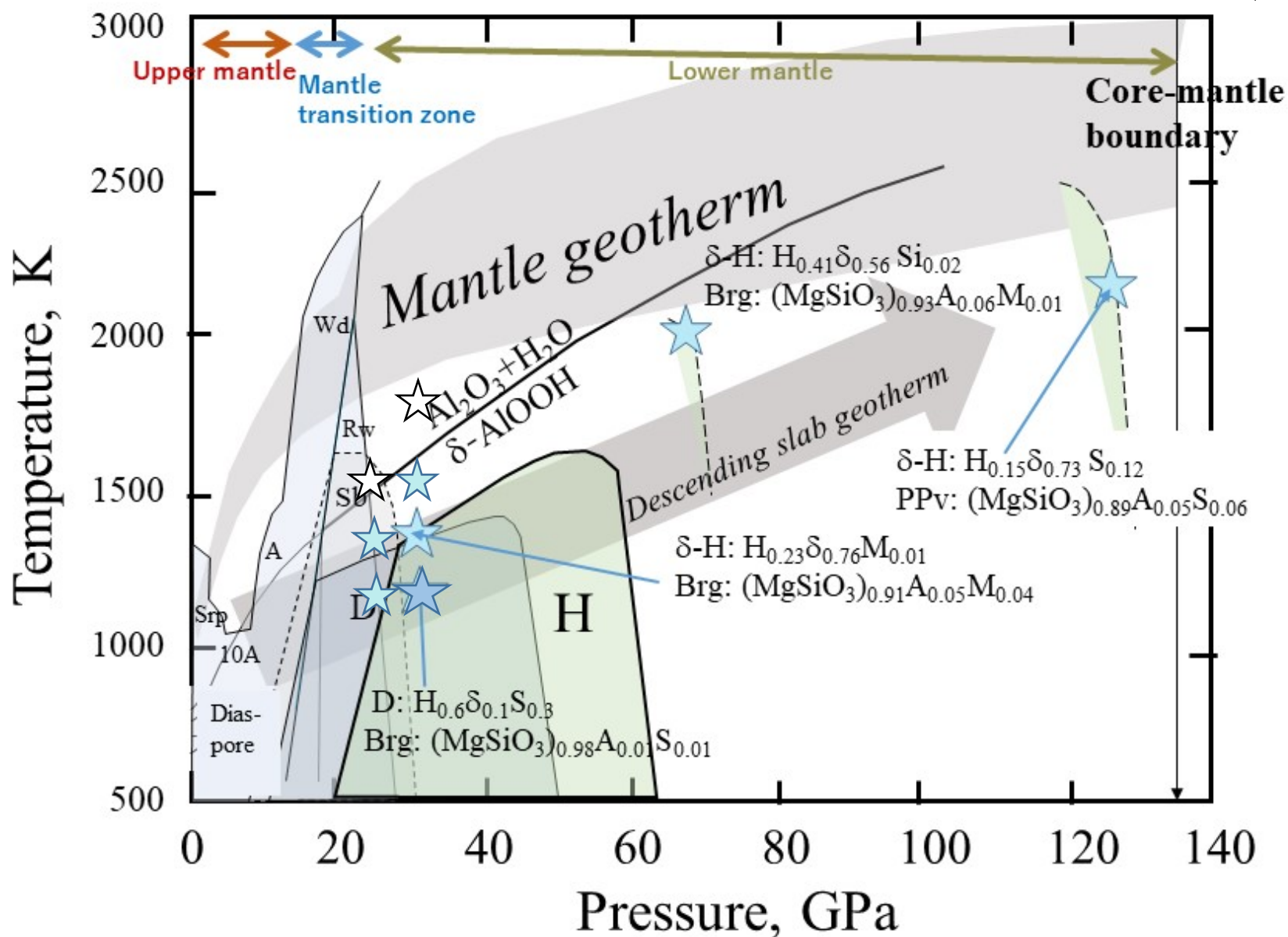
68 GPa, 2110 K

68GPa, 2110 K
 δ -H: $H_{0.43}\delta_{0.57}$
Brg: $M_{0.94}A_{0.06}$
 $K(Al_2O_3)=4.8$

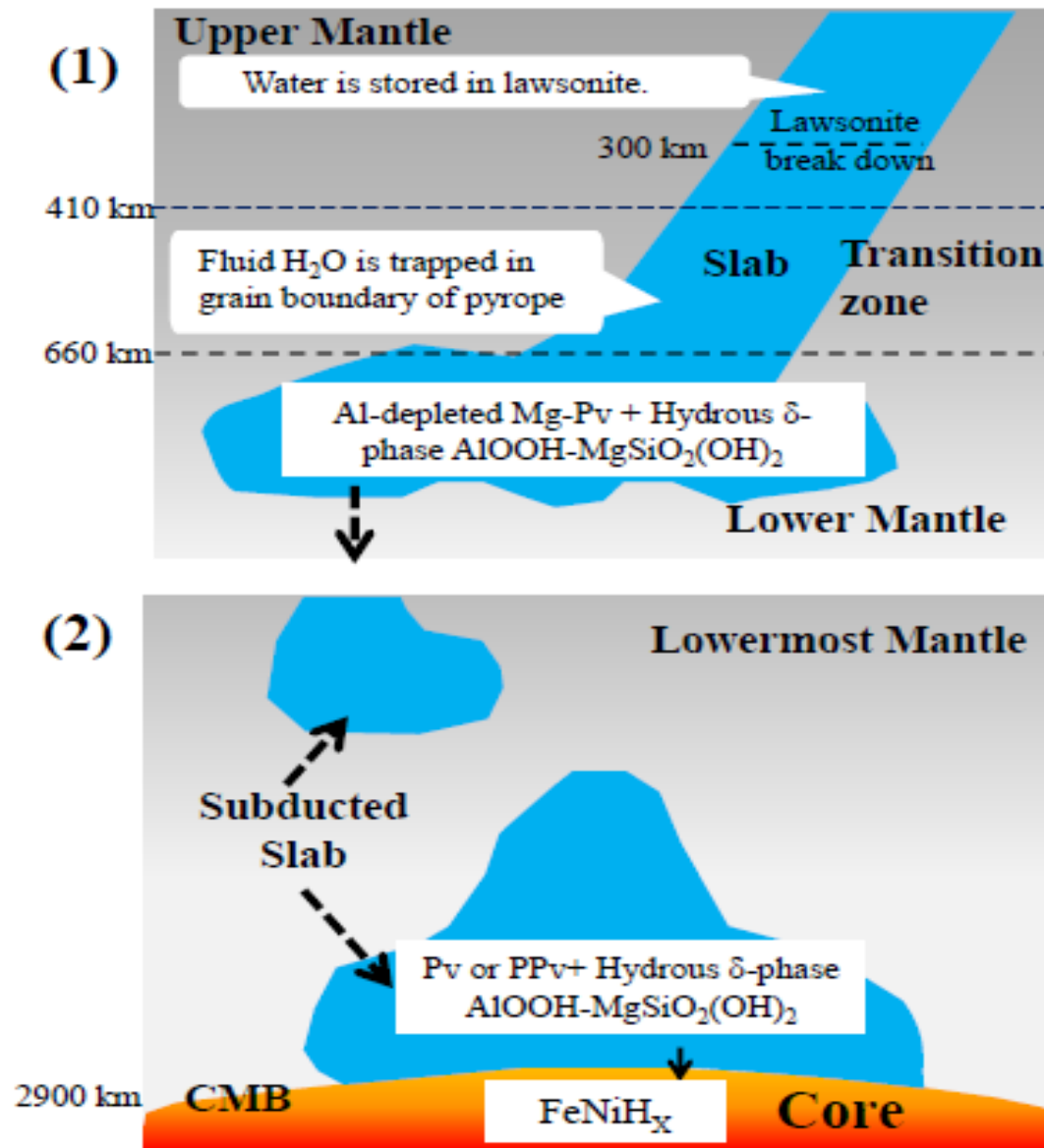
$H=MSi(OOH)_2$
 $\delta=2AlOOH$
 $S=SiO_2$
 $M=MSiO_3$
 $A=Al_2O_3$

Coexistence with post-perovskite
 120 GPa, 2000 K
 δ -H: $H_{0.23}\delta_{0.77}$
PPv: $M_{0.95}A_{0.05}$
 $K(Al_2O_3)=5.9$

δ -H solid solution coexists with **Al-depleted bridgmanite**
Ohtani et al. (2018)



Transport of water into CMB



Roles of hydrogen in the mantle

1. Mantle Transition zone (MTZ) is at least locally wet.
2. Metastable olivine wedge exists even under the wet upper mantle and transition zone, and it may trigger the deep earthquakes.
3. Dehydration in the mantle transition zone and the top of the lower mantle may cause deep earthquakes.
4. Wet lower mantle contains alumina-depleted bridgmanite/post-perovskite and hydrous δ -H solid solution.

Thank you for your attention!

