Chemical composition and hydrogen content inside Earth

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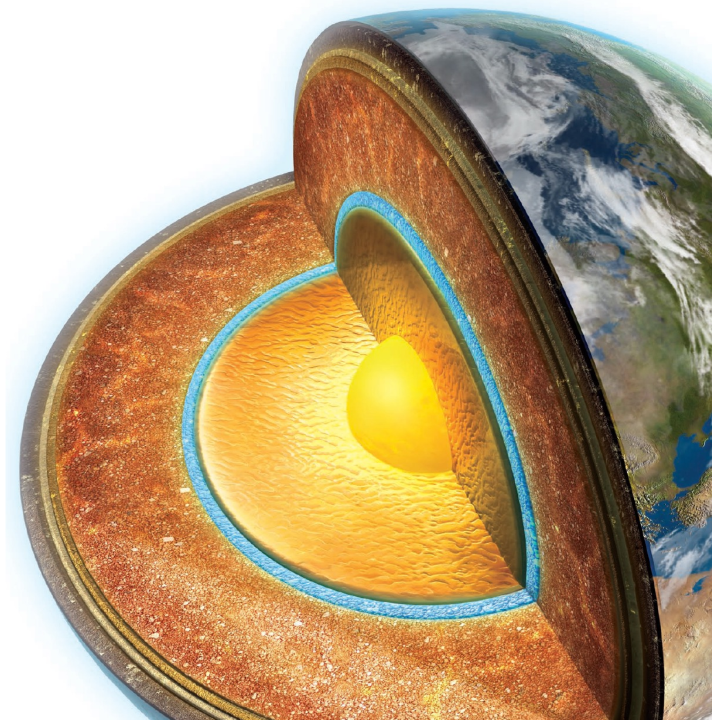


Contents

1. Mantle composition

– Is the **lower mantle** different in **composition** from the upper mantle?

– How much **H_2O** in the transition zone and the lower mantle?

2. Core composition

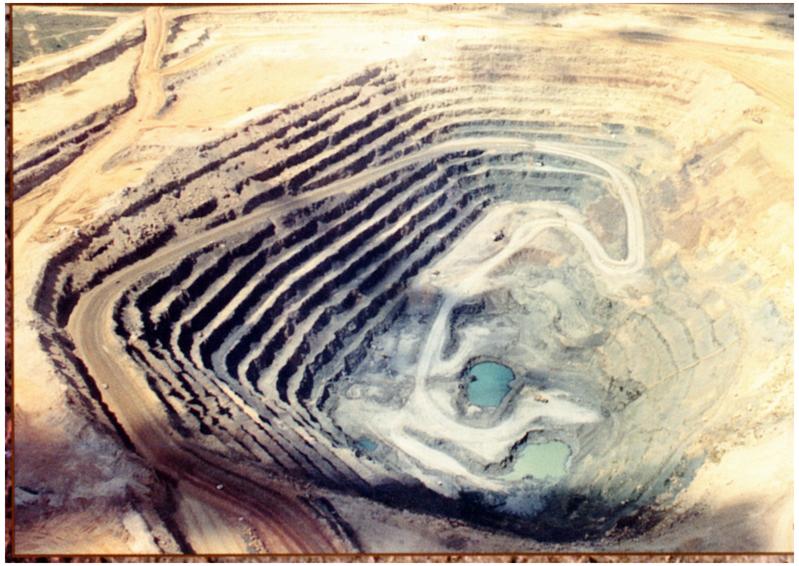
– What is the **light element** composition of the core?

– Is **hydrogen** major impurity element in the core?

1. Mantle composition

The upper mantle is known to be **pyrolitic** in composition.

But, we do not have rock samples from the deeper level; transition zone (410–660 km depth) and the lower mantle (>660 km depth).

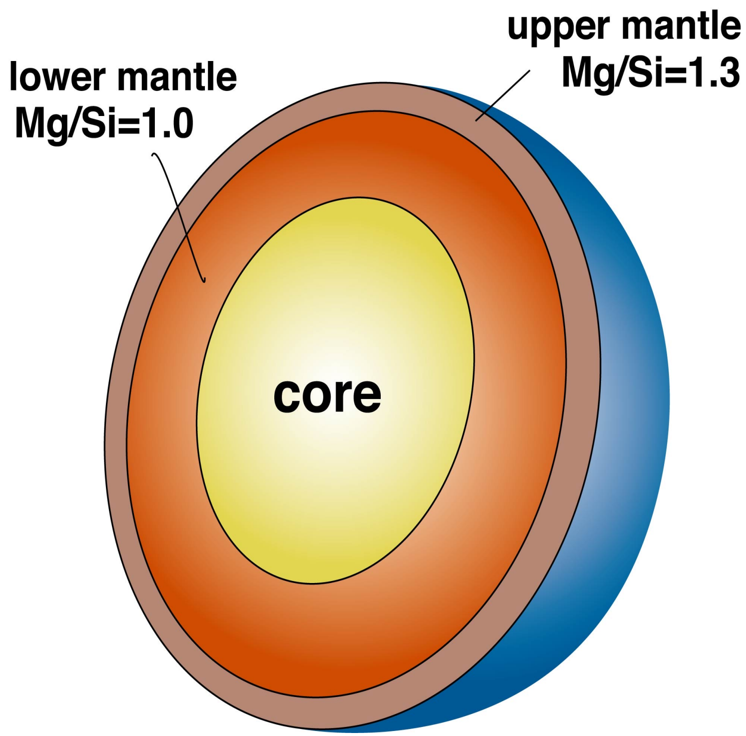


Is the lower mantle different in composition?

"Missing Si problem"

The upper mantle has the higher Mg/Si ratio (~1.3) than the solar composition (~1.1).

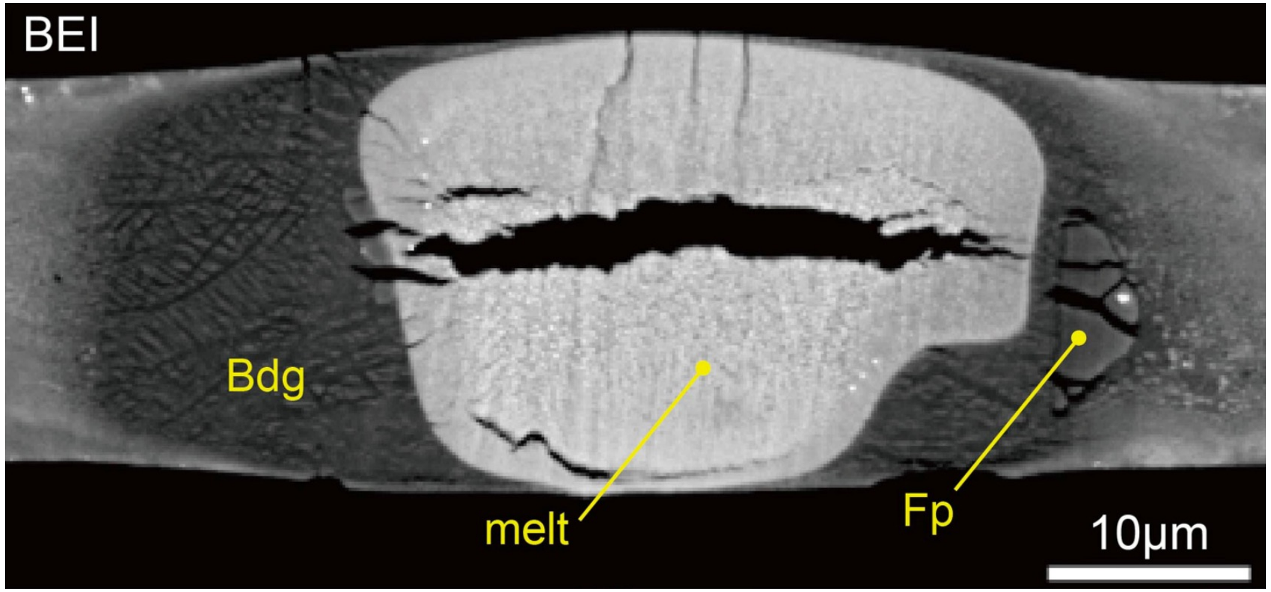
➡ **Is the lower mantle enriched in Si (Mg/Si ≈ 1.0)?**



Is the lower mantle different in composition?

Is the lower mantle enriched in Si (Mg/Si ≈ 1.0)?

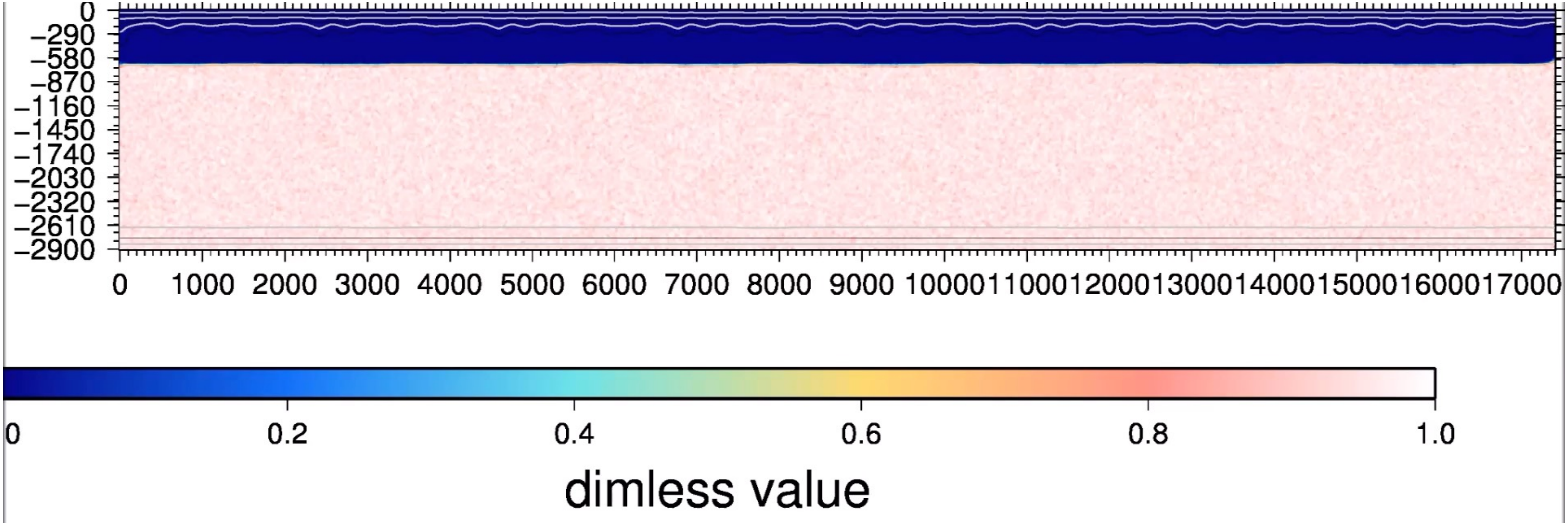
Possible. Deep magma ocean could have crystallized only $MgSiO_3$ bridgmanite until >60% crystallization under the lower-mantle pressure range.



A large part of the lower mantle could consist only of $MgSiO_3$ bridgmanite right after the solidification of a magma ocean.

Caracas et al. (2019 EPSL)

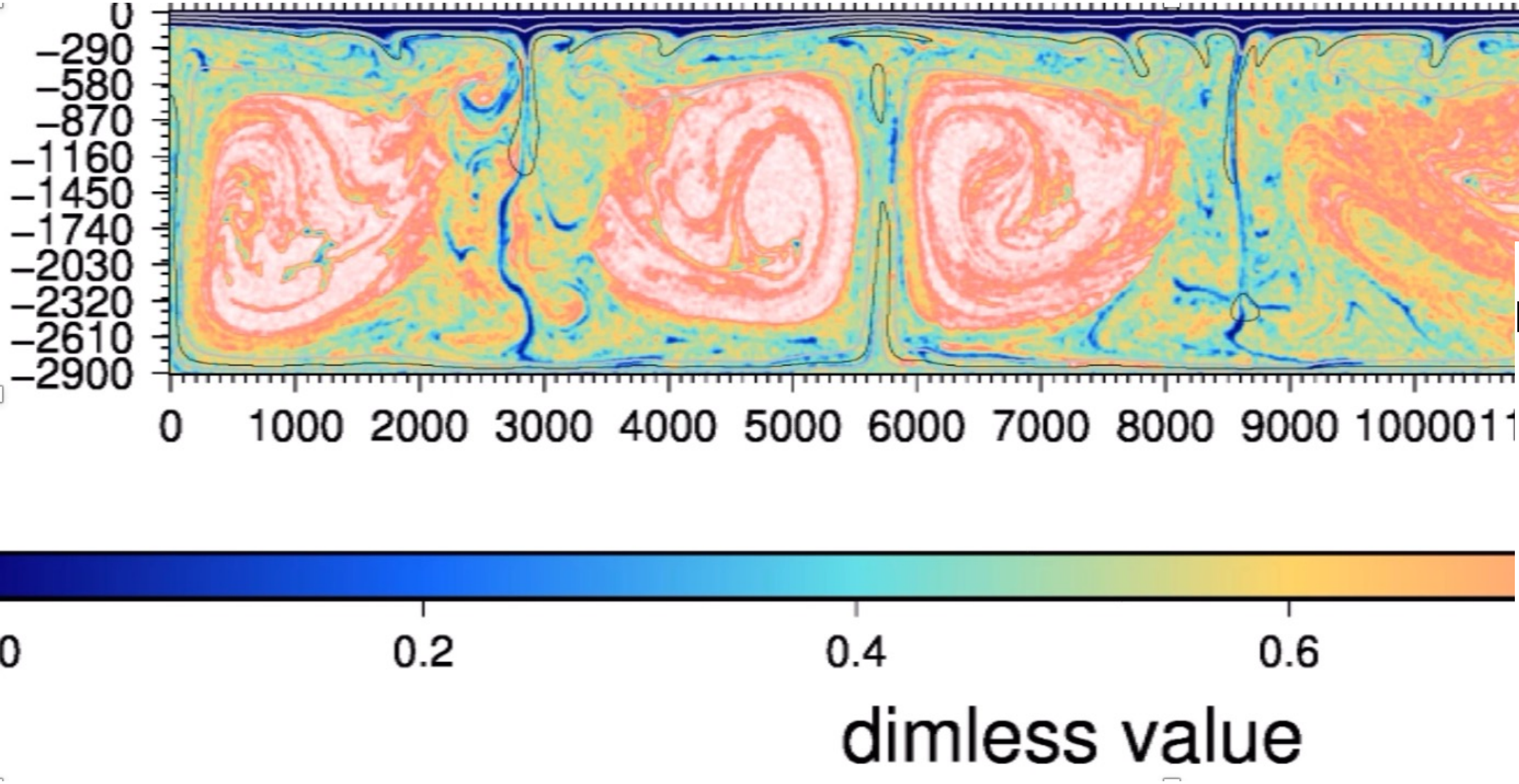
Is the lower mantle different in composition?

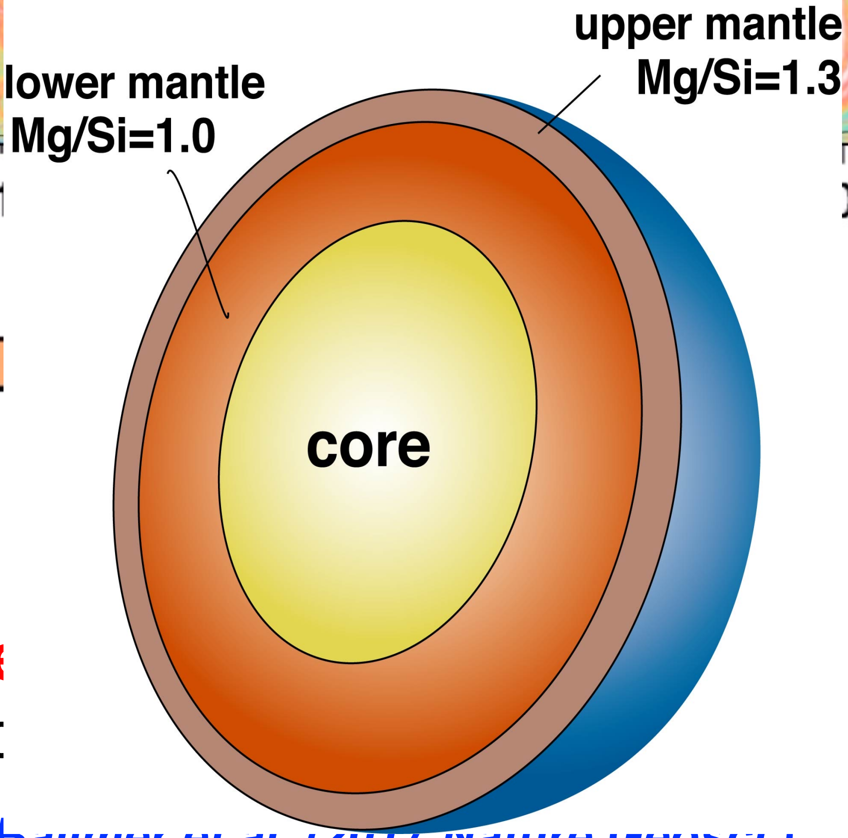


The **rigid** **bridgmanite-enriched ancient mantle structure (BEAMS)**, originally formed upon crystallization of a magma ocean, may be preserved until today.

Ballmer et al. (2017 Nature Geosci.)

Is the lower mantle different in composition?



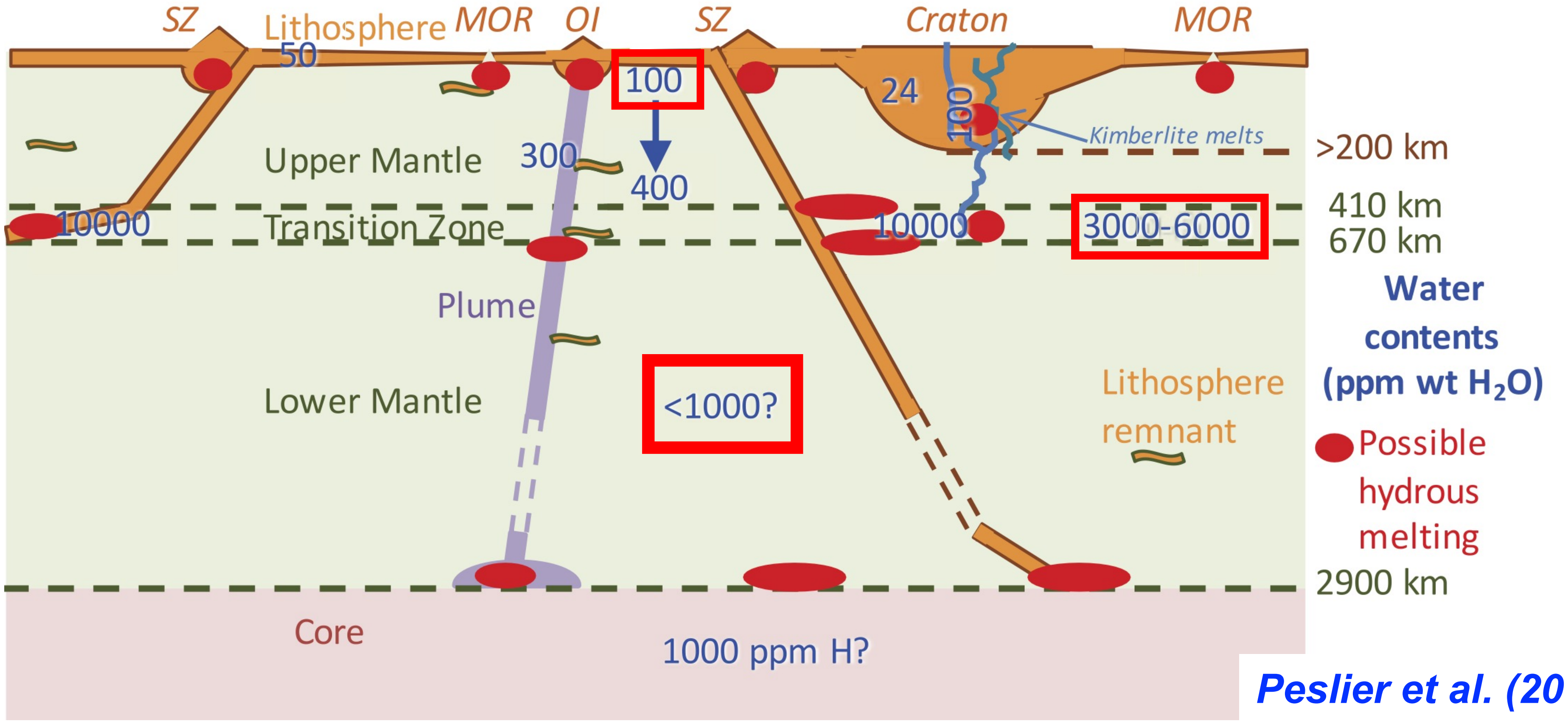


The **rigid** **bridgmanite-enriched ancient mantl**
originally formed upon crystallization of a magma oc
today.

Ballmer et al. (2017 Nature Geosci.)

How much H_2O in the deep mantle?

While the upper mantle includes 100–200 ppm H_2O, the transition zone and the lower mantle should contain more H_2O.

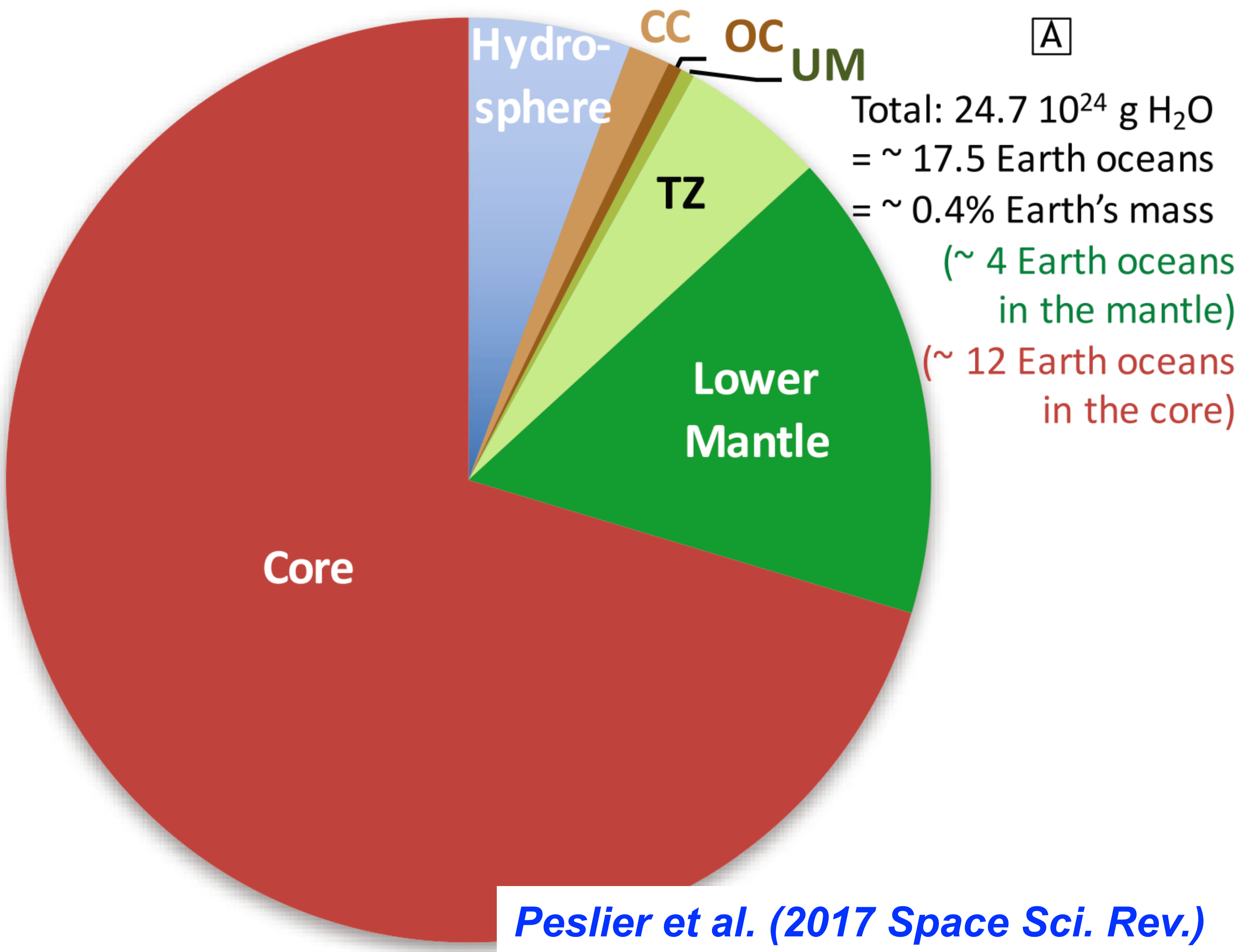


Peslier et al. (2017 Space Sci. Rev.)

How much H_2O in the deep mantle?

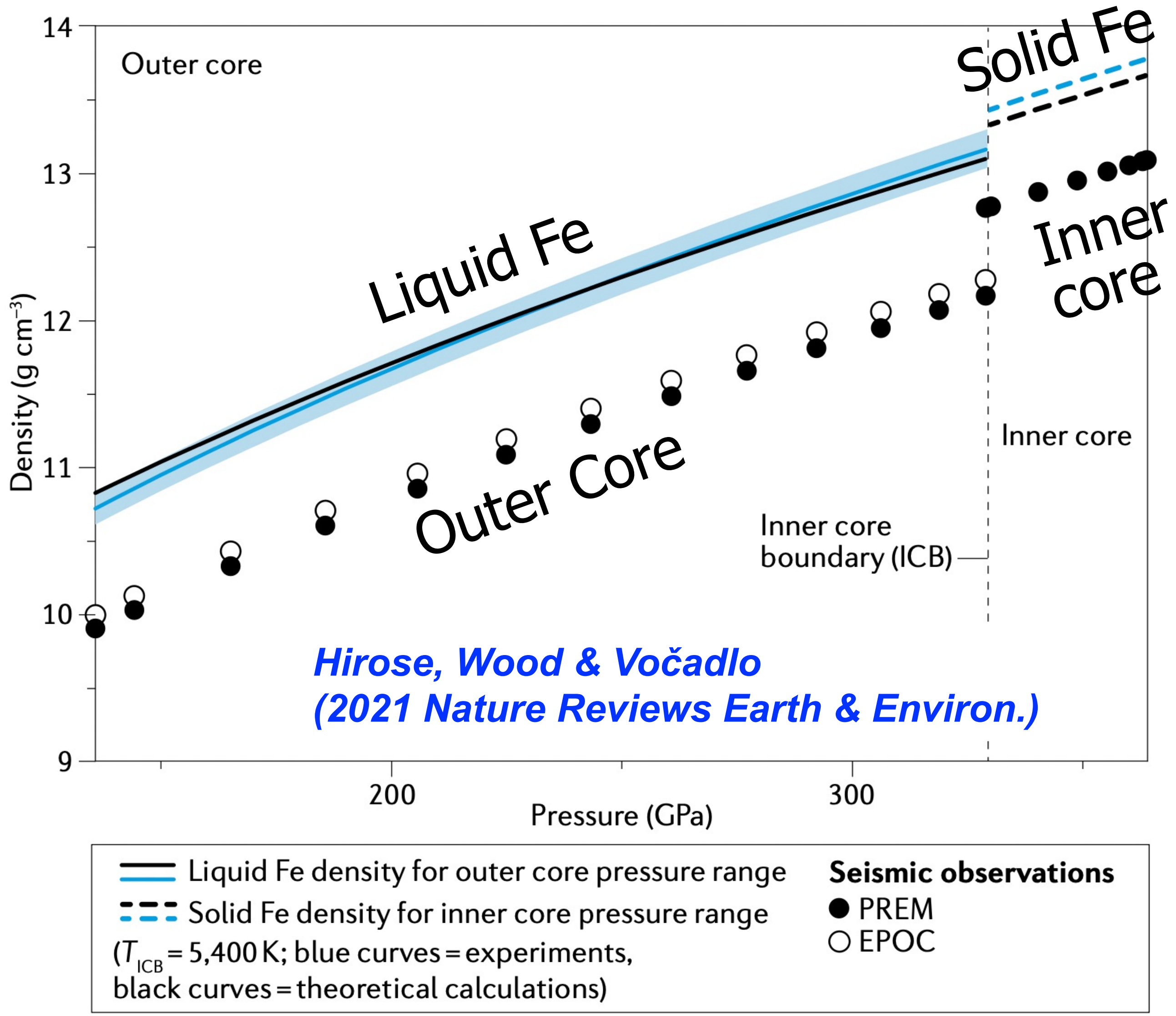
The deep mantle could be relatively enriched in H_2O.

But, the core is likely to be more important H reservoir.



Peslier et al. (2017 Space Sci. Rev.)

2. Core composition

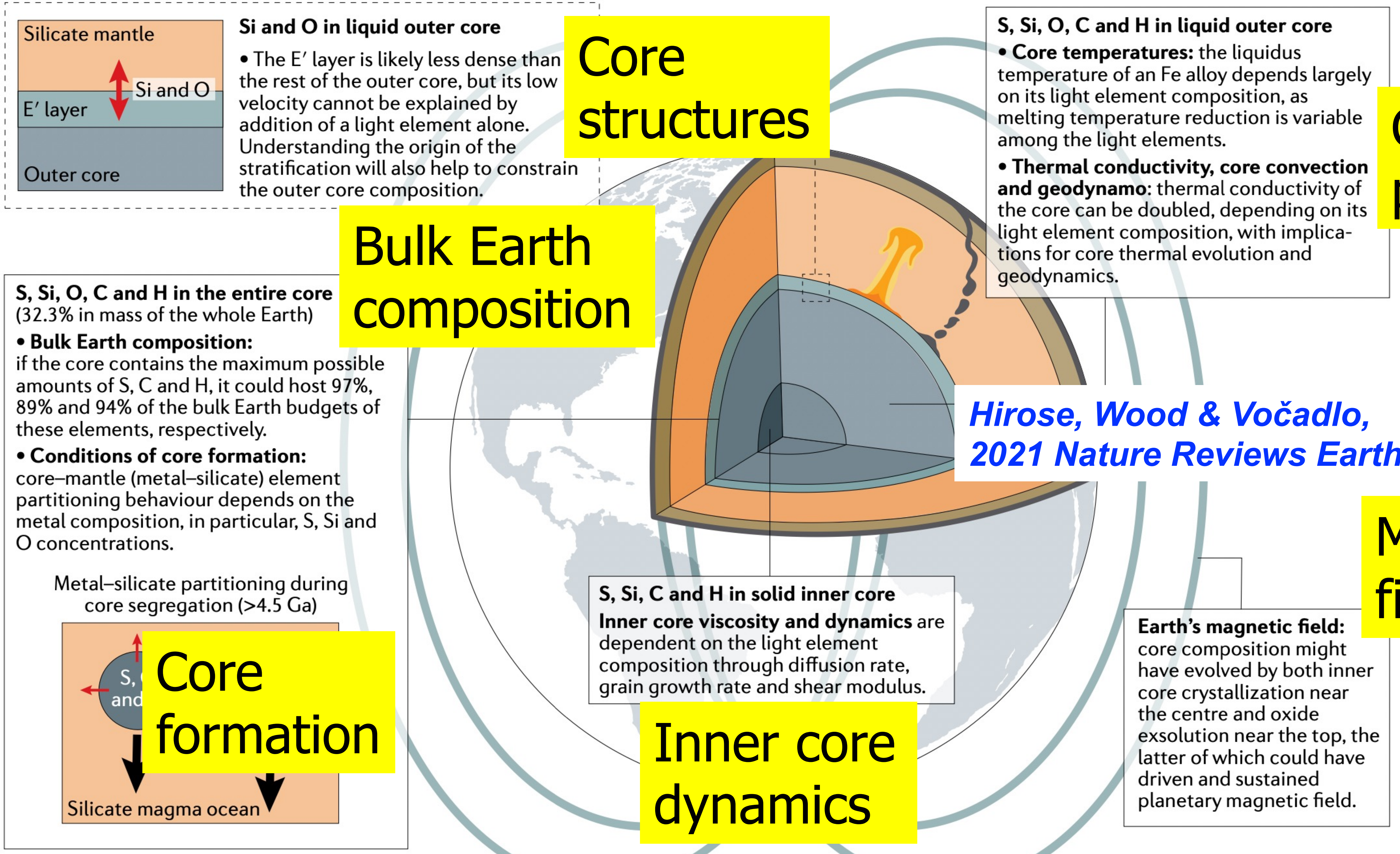


The core is not pure Fe nor Fe-Ni alloy.

The outer core includes **large amounts of light elements**; less dense than Fe by ~8%.

(the liquid outer core constitutes 95% of the entire core by volume)

Why do we explore the core composition?



Core structures

Bulk Earth composition

Core properties

Core formation

Inner core dynamics

Magnetic field

Hirose, Wood & Vočadlo, 2021 Nature Reviews Earth & Environ.

Why do we explore the core composition?

It gives 1) **core properties**; thermal conductivity, viscosity, melting temperature, etc.

Depending on the light element composition,

- core thermal conductivity can be doubled. Mechanism of core convection and geodynamo?
- estimates of core temperature based on melting temperatures of Fe alloys can change by >1000 K

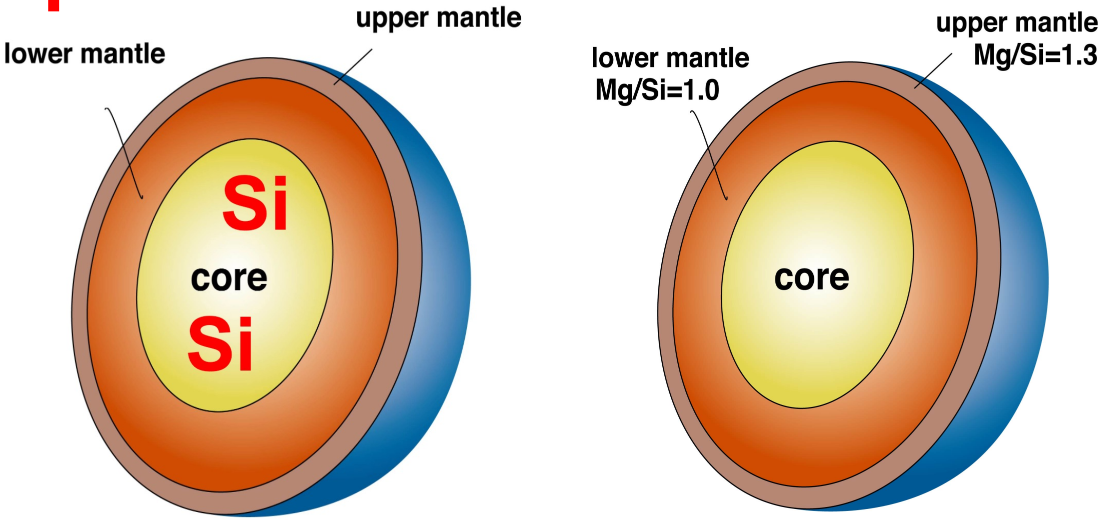
⬇

Present state and evolution of the core

The core composition also gives 2) the **bulk Earth composition** including the amount of **highly volatile elements (H, C, O)** & the **Mg/Si** ratio

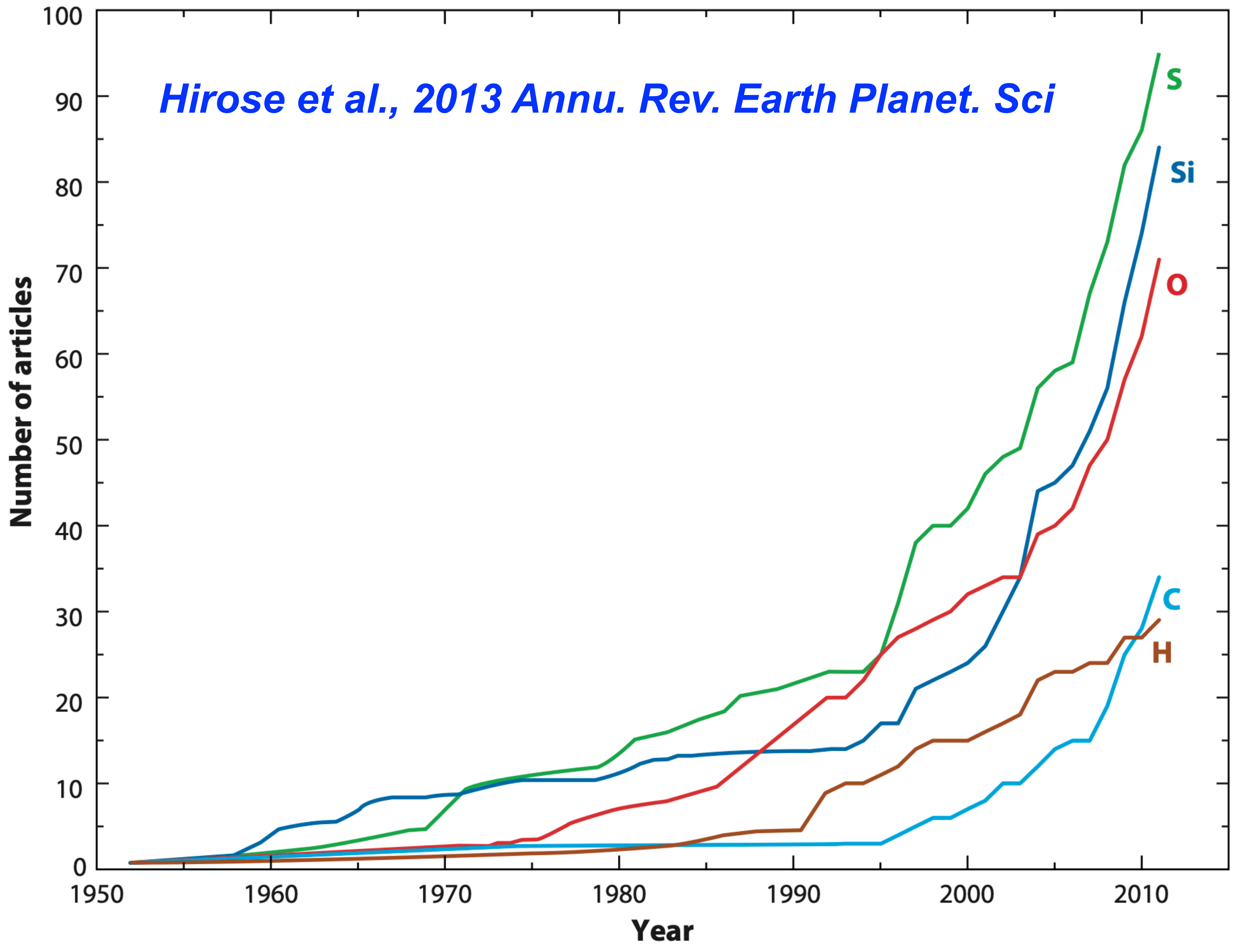
- When and how much water and organic materials were delivered to the Earth?
- Does Si in the core reconcile the bulk Earth Mg/Si ratio with the solar value?

"Missing Si problem"



Origin of the Earth

Core light elements unidentified for 70 years



Can we really reveal the core light elements?

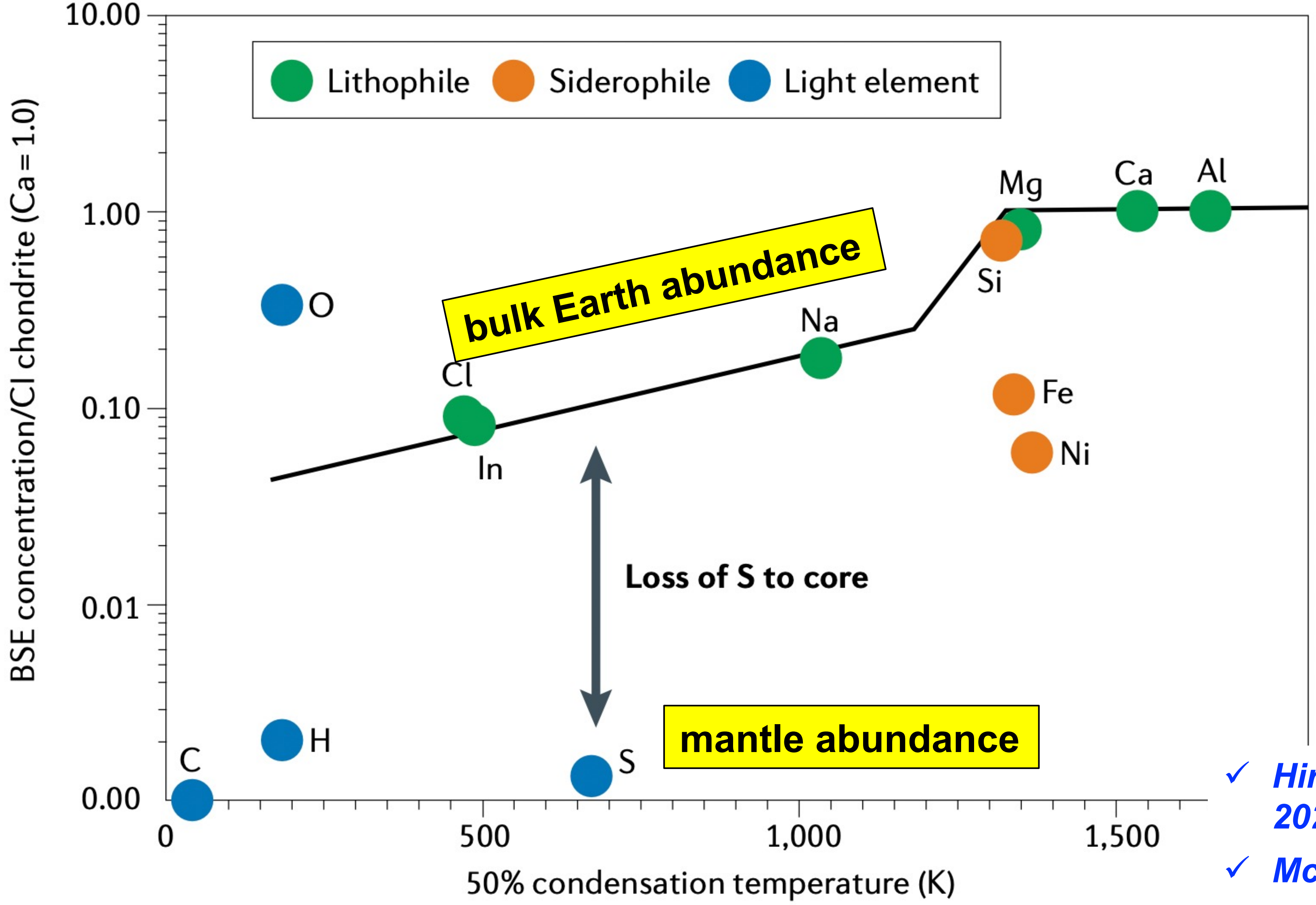
Five candidates:
S, Si, O, C, and H

Constraints on core light element composition

- **Cosmochemical and geochemical estimates:**
  — Calculated from 1) chondrite & mantle compositions
- **Seismological observations:**
  — Outer core 2) density & 3) V_P
  — Inner core 4) density, 5) V_P & 6) V_S
- **Phase relations:**
  — 7) Crystallization of solid Fe at the inner core boundary
  — 8) Si + O simultaneous solubility limit
- **Metal-silicate (core-mantle) partitioning:**
  — 9) Calculated from metal/silicate partition coefficients & BSE abundance
- **Neutrino observations:**
  — 10) Z/A ratio

Five candidates:
S, Si, O, C, and H

I. Cosmo-/geochemical constraints

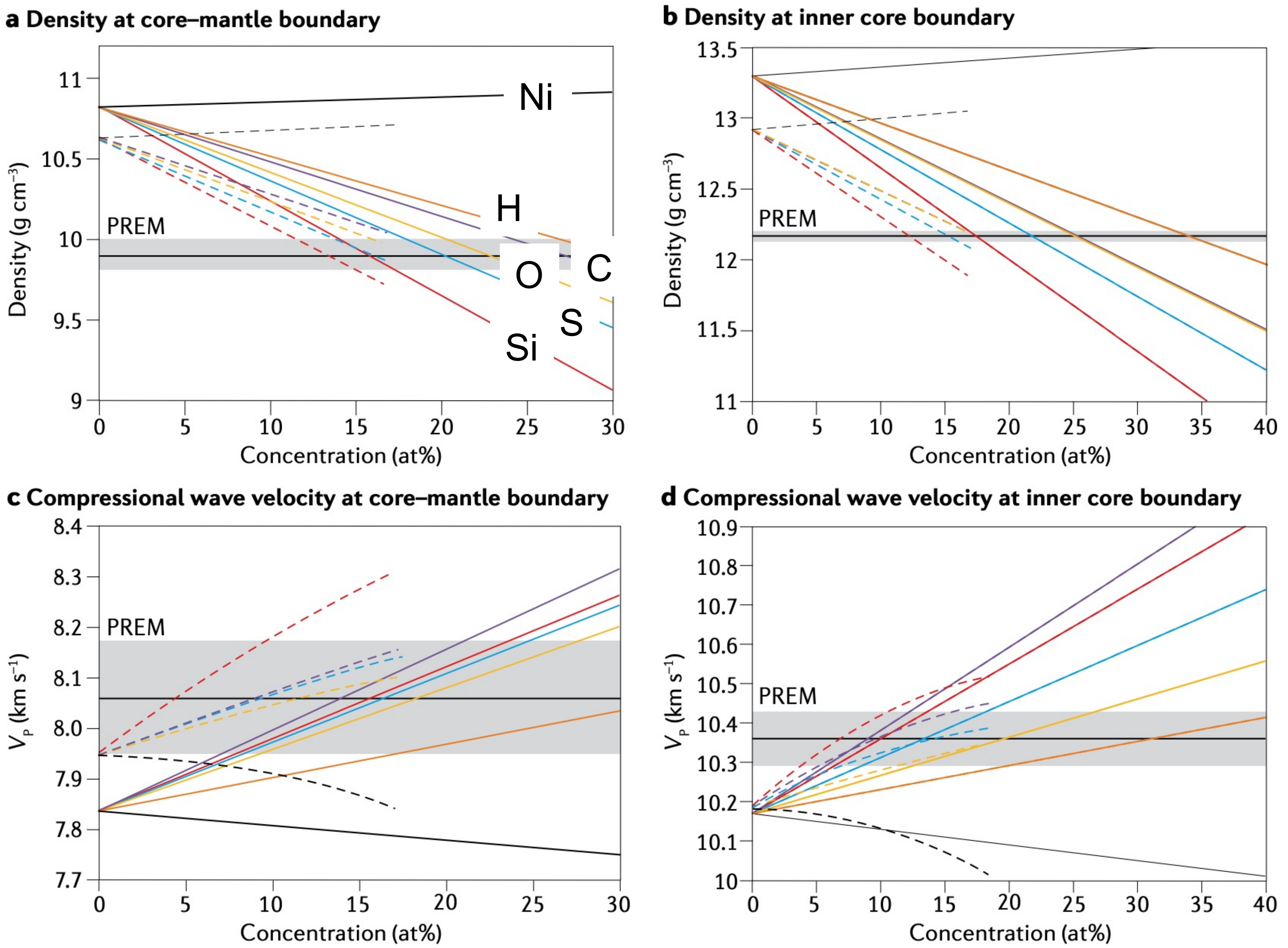


We may employ **cosmochemical and geochemical estimates** of **5 wt% Ni & 1.7 wt% S** in the core.

Difficult to estimate the amounts of highly volatile elements; H, C, & O.

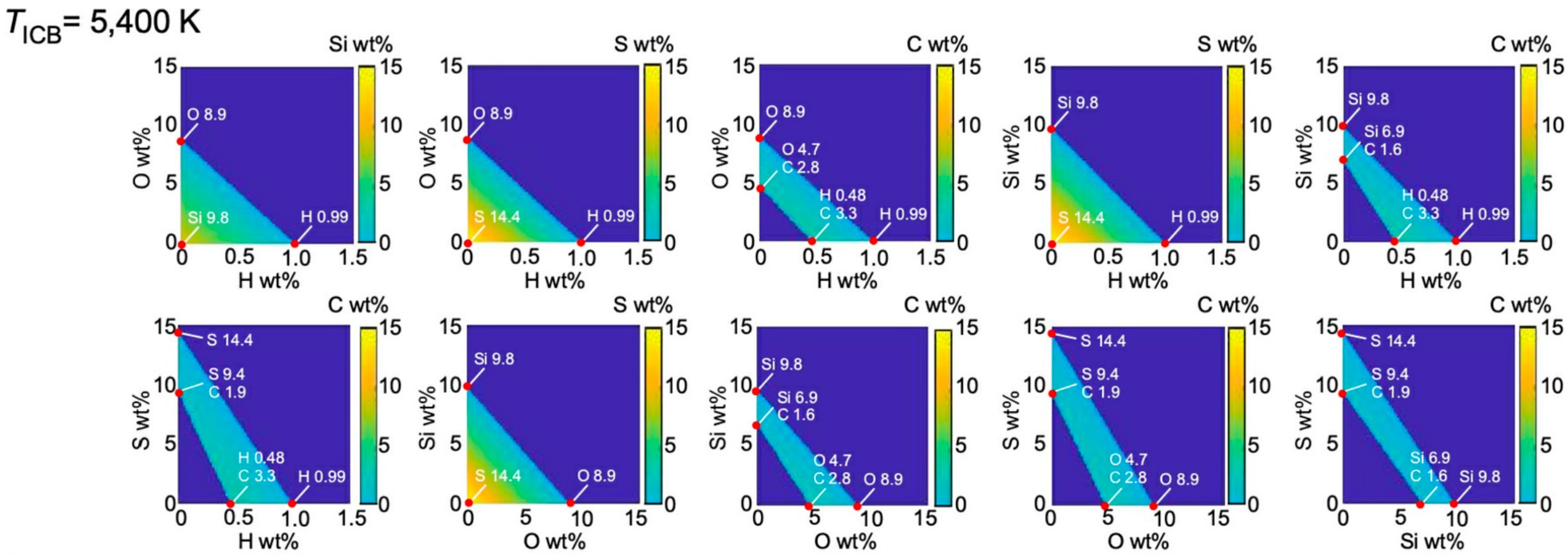
- ✓ ***Hirose, Wood & Vočadlo, 2021 Nature Reviews Earth & Environ.***
- ✓ ***McDonough, 2014 Treatise Geochem.***

II. Constraints from seismological OC observations



Ab initio calculations explored the range of **possible outer core composition** in Fe-Ni-S-Si-O-C-H that **explains the observed density and V_P.**

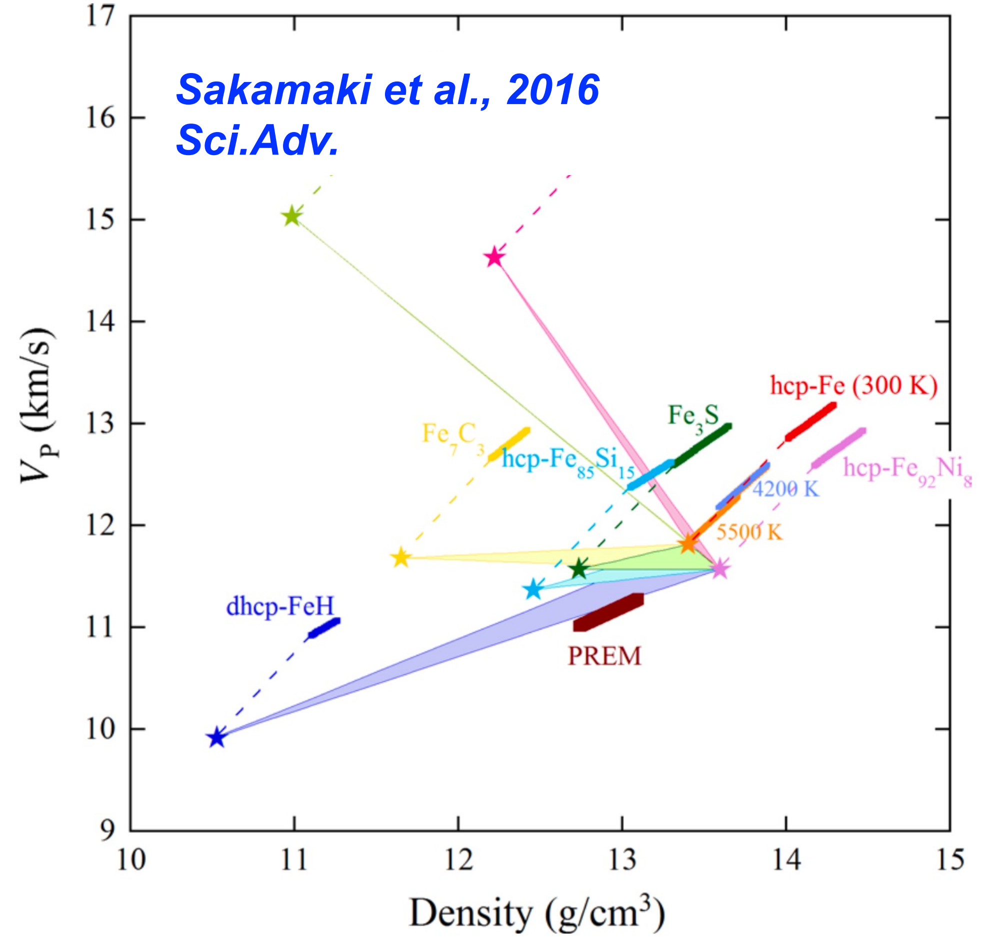
- ✓ ***Badro et al., 2014 PNAS***
- ✓ ***Umemoto & Hirose, 2020 EPSL***

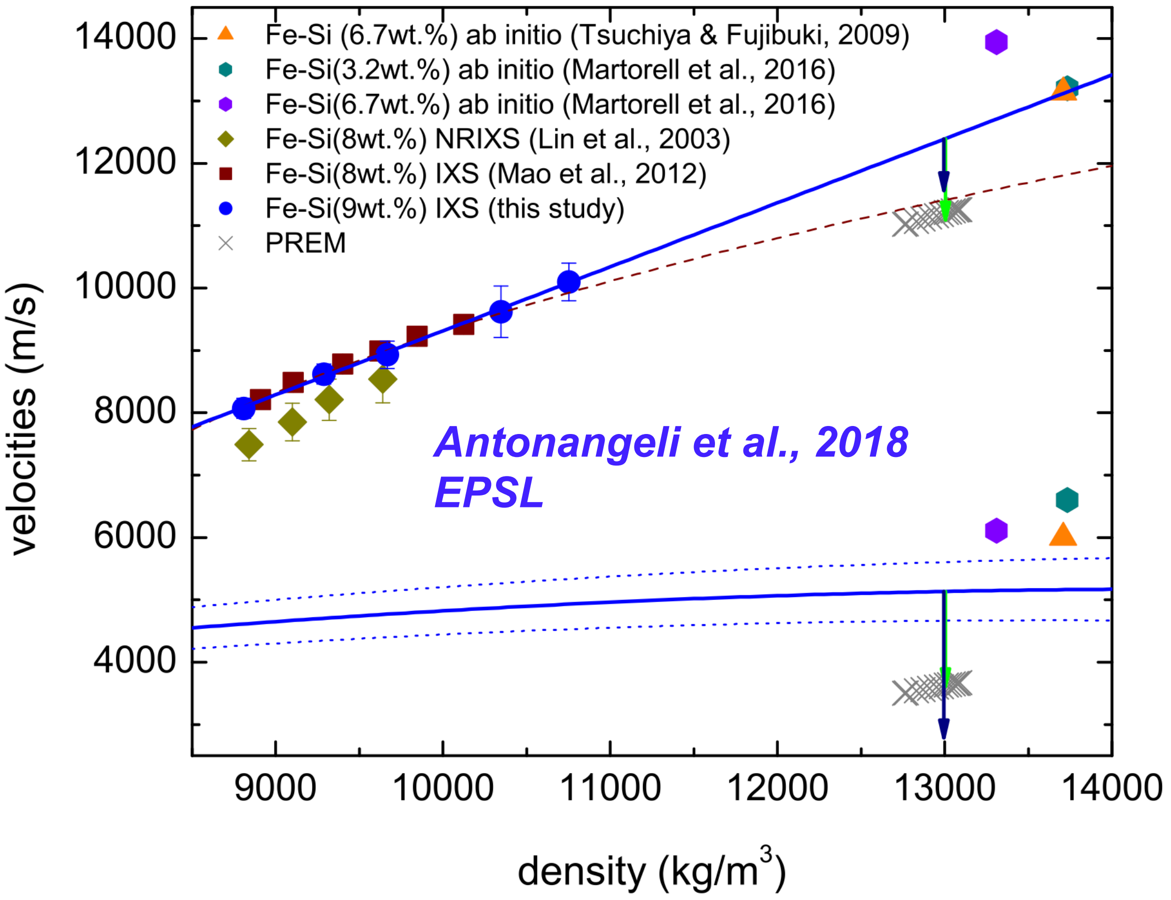


These calculations concluded that **H and O are major outer core light elements when T_{ICB} = 5400 K and >6000 K**, respectively.

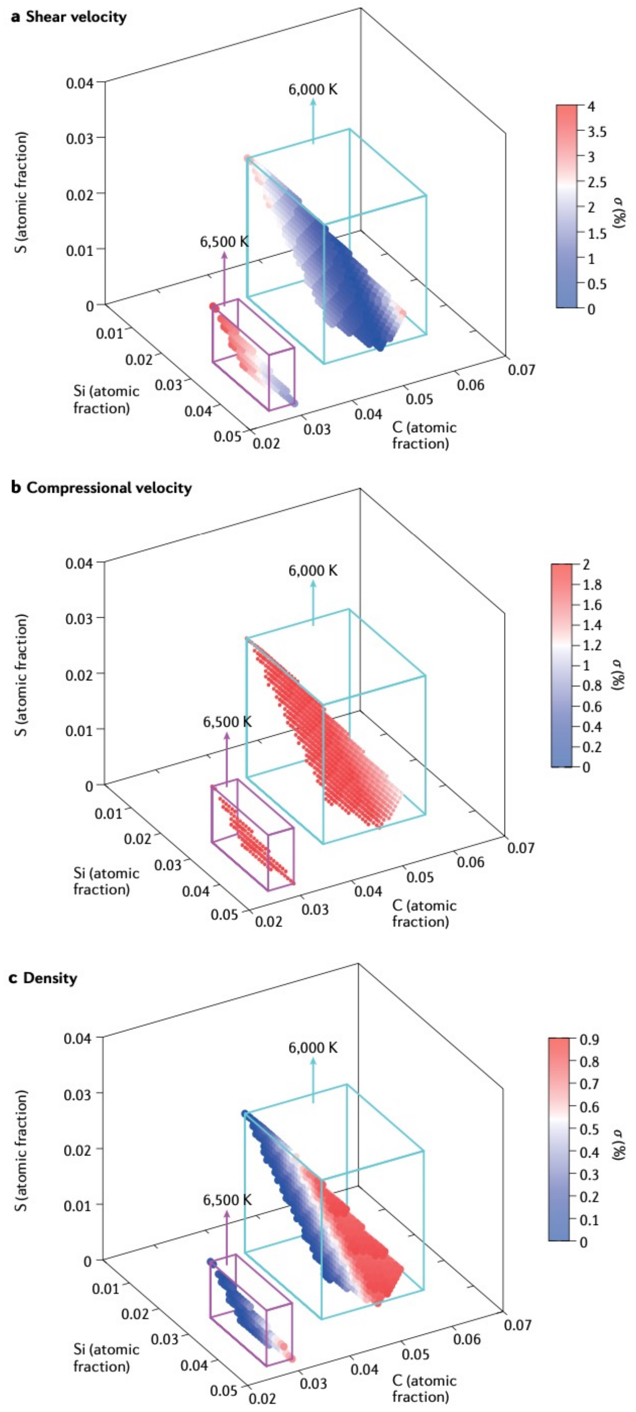
Badro et al., 2014 PNAS; Umemoto & Hirose, 2020 EPSL

III. Constraints from seismological IC observations





The measured density & *Vp* of solid Fe and Fe alloys suggest that **H and/or Si are important inner core light elements**.



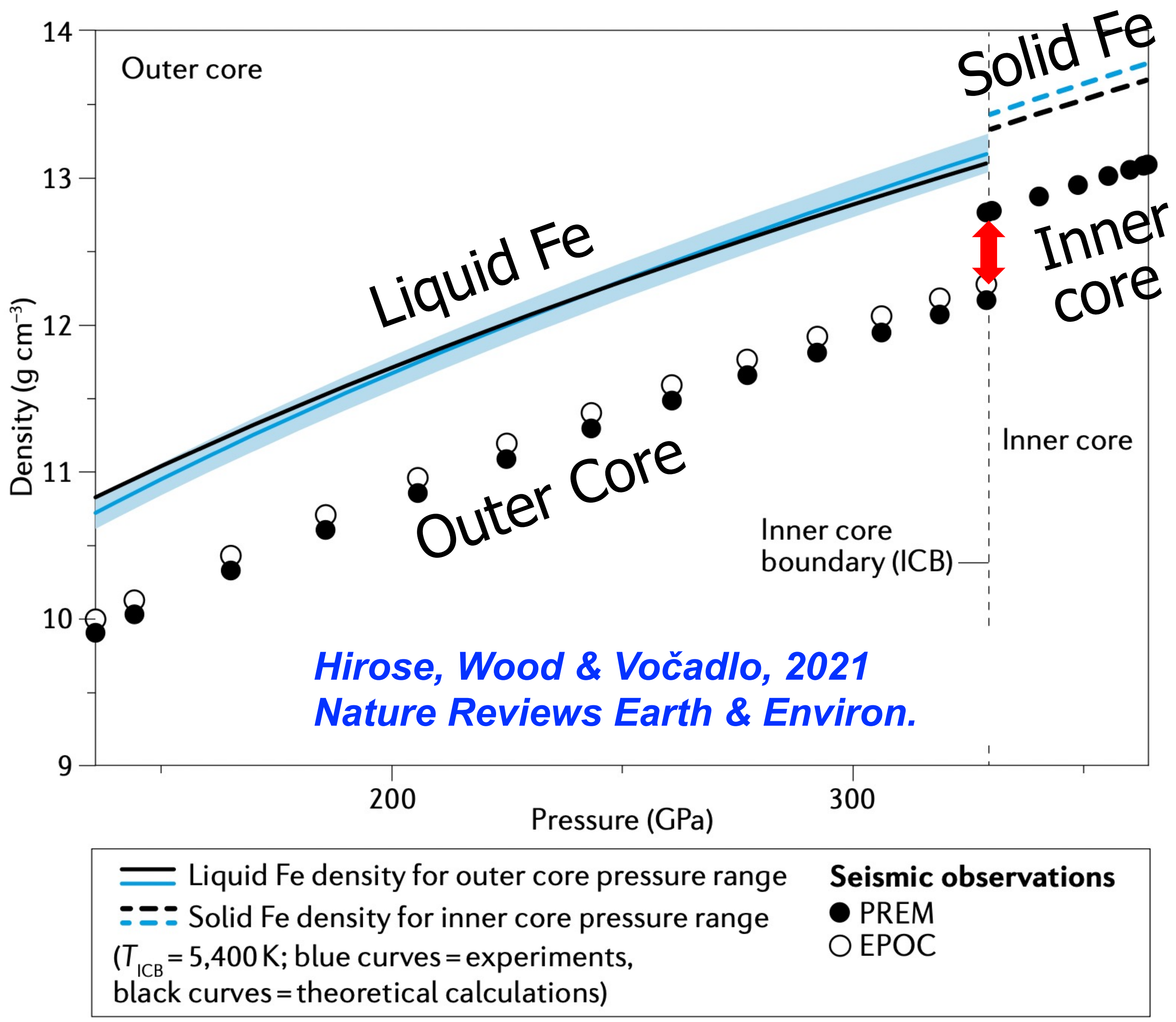
III. Constraints from seismological IC observations

Ab initio calculations proposed the possible range of inner core composition that explains density, V_P & V_S.

C or H are important to account for the high V_P/ V_S ratio of the inner core.

Li et al., 2018 EPSL; Wang et al., 2021 EPSL

III. Constraints from seismological IC observations

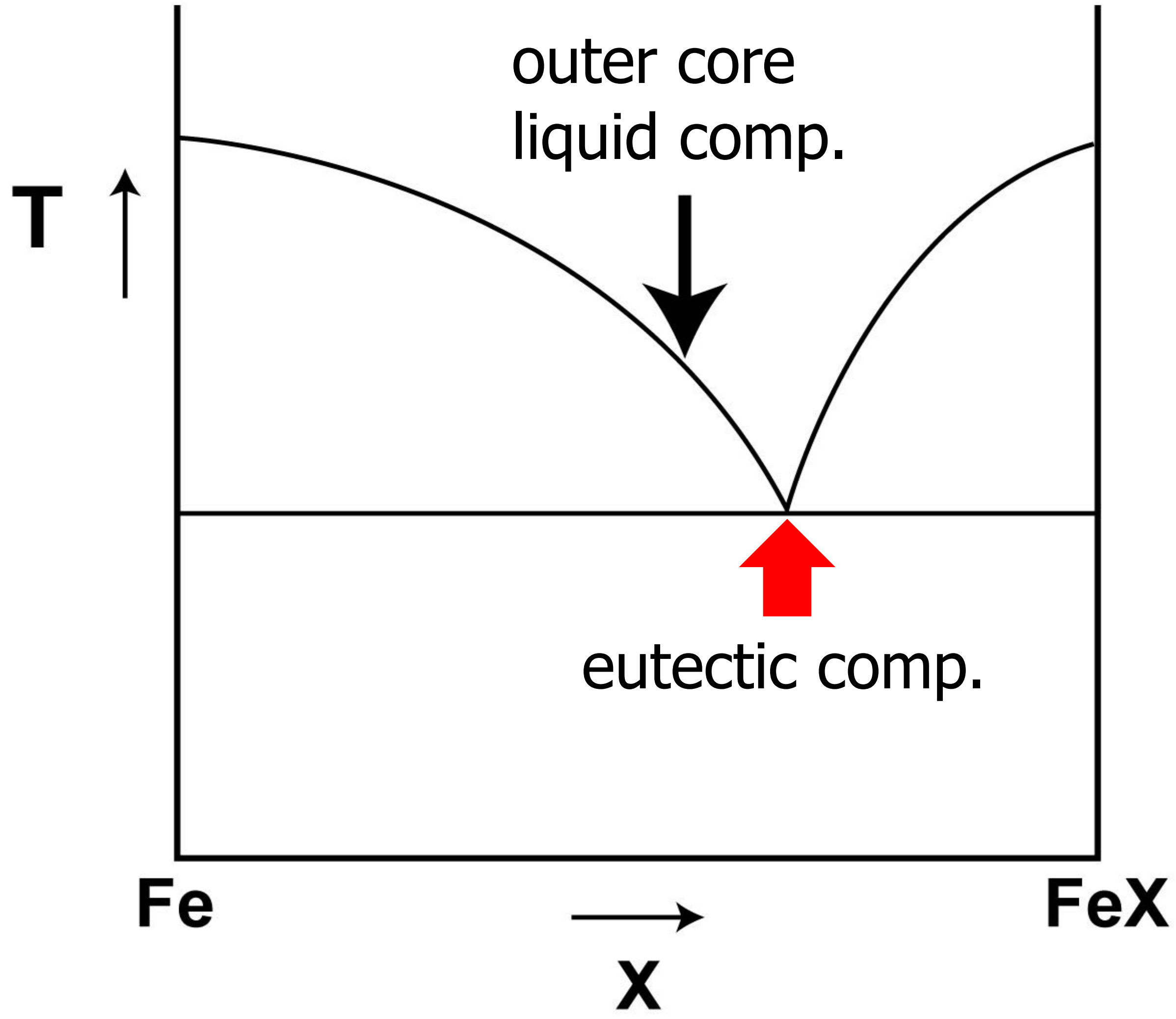


Hirose, Wood & Vočadlo, 2021
Nature Reviews Earth & Environ.

Density jump across the boundary b/w liquid outer core and solid inner core gives the **max O content** in the former because O is not soluble into solid Fe.

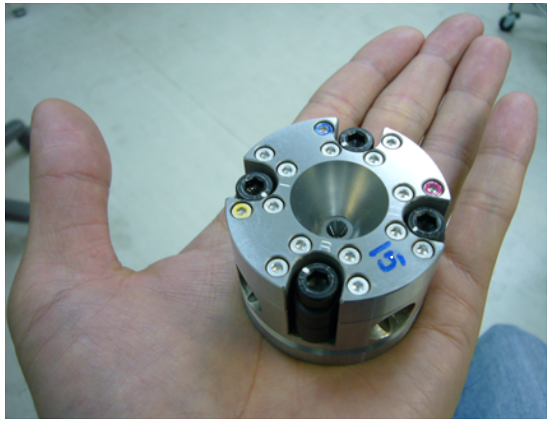
Kuwayama et al., 2020 PRL

IV. Liquidus phase constraints on OC composition

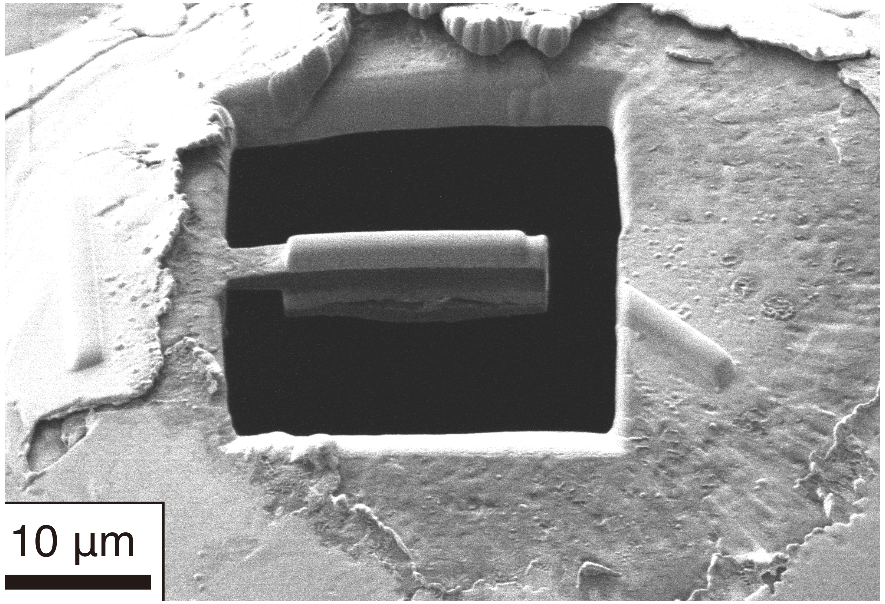


The inner core must be solid Fe that is depleted in light elements. Thus, the outer core liquid should be **on the Fe-rich side of the eutectic** at inner core pressures.

High-pressure melting experiments

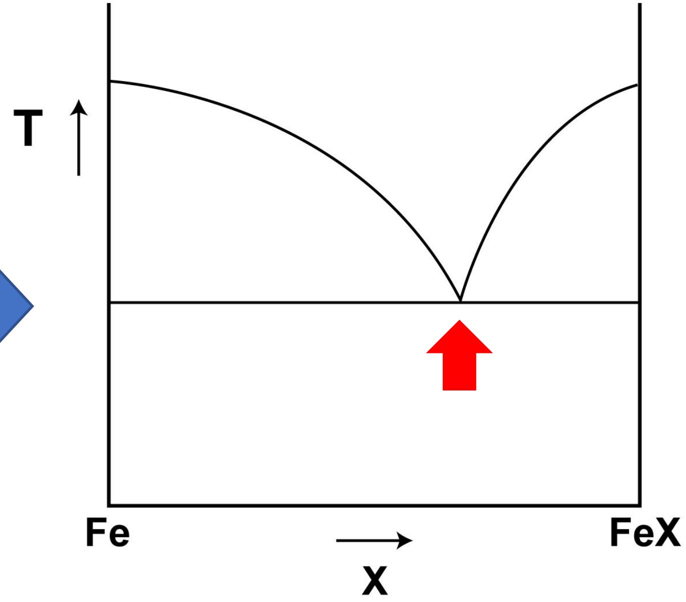


Diamond-anvil cell



Sample cross-section by FIB

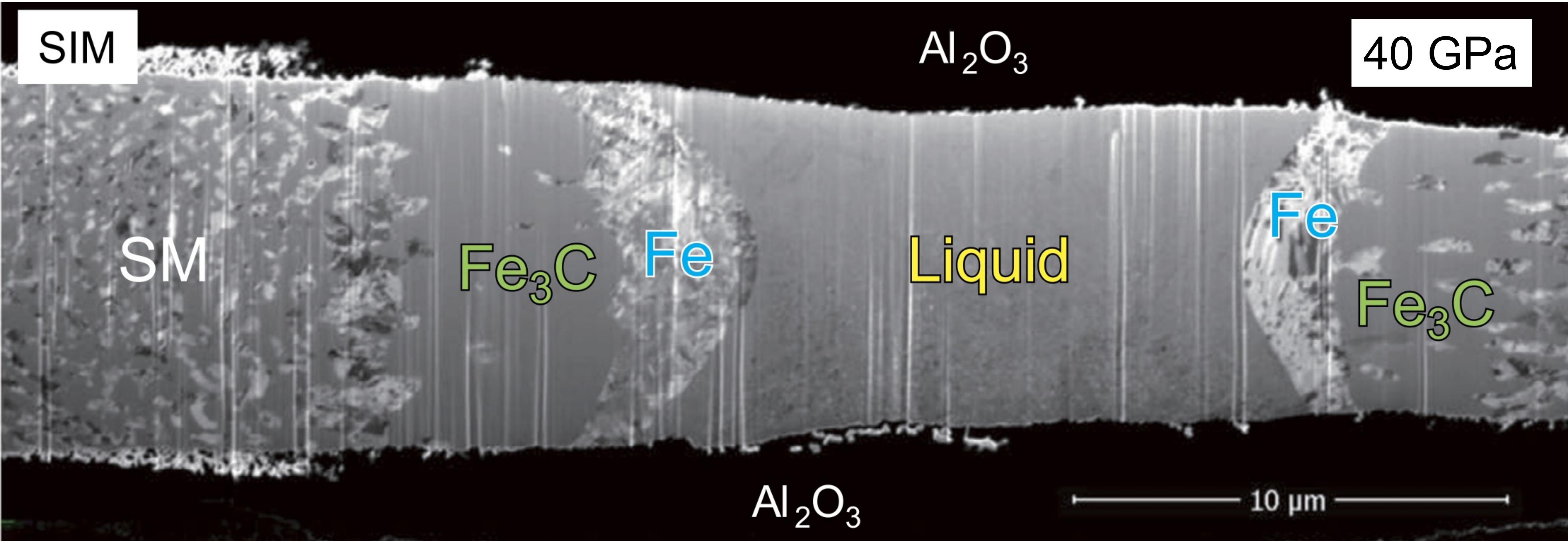
Melting texture & composition by SEM-EDS & FE-EPMA



Determine eutectic liquid composition

Fe-C

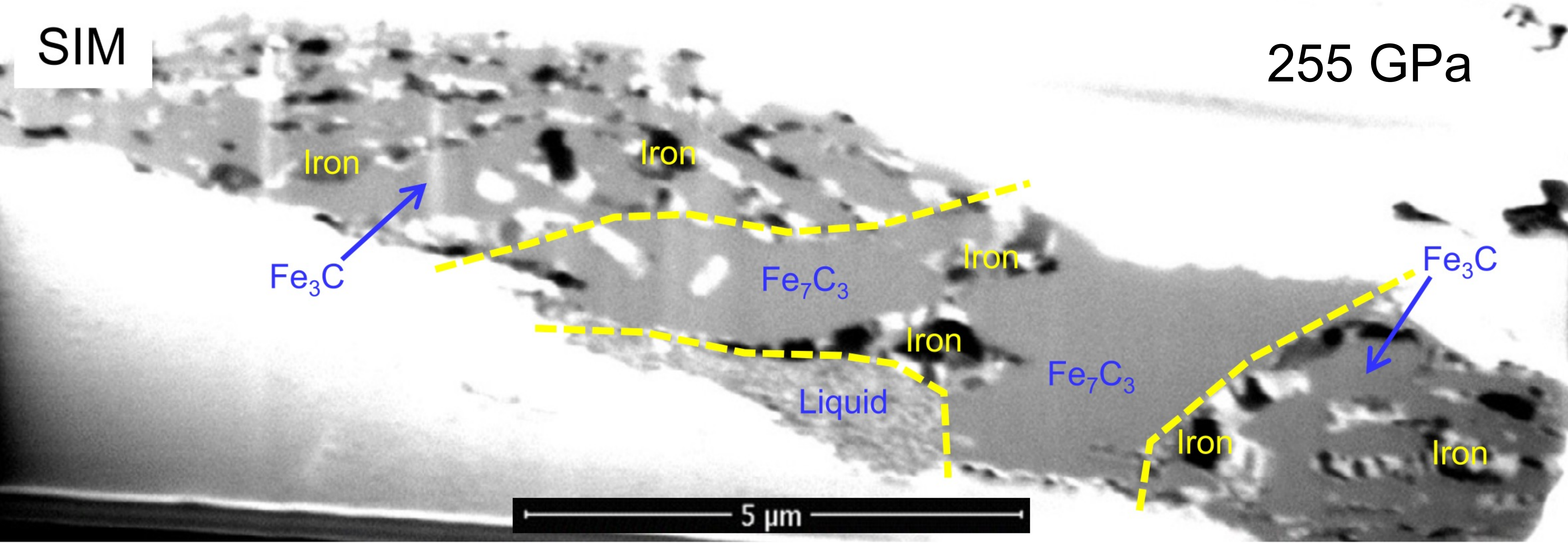
Mashino et al., 2019 EPSL



Fe-C binary eutectic liquid coexisting with Fe and Fe_3C

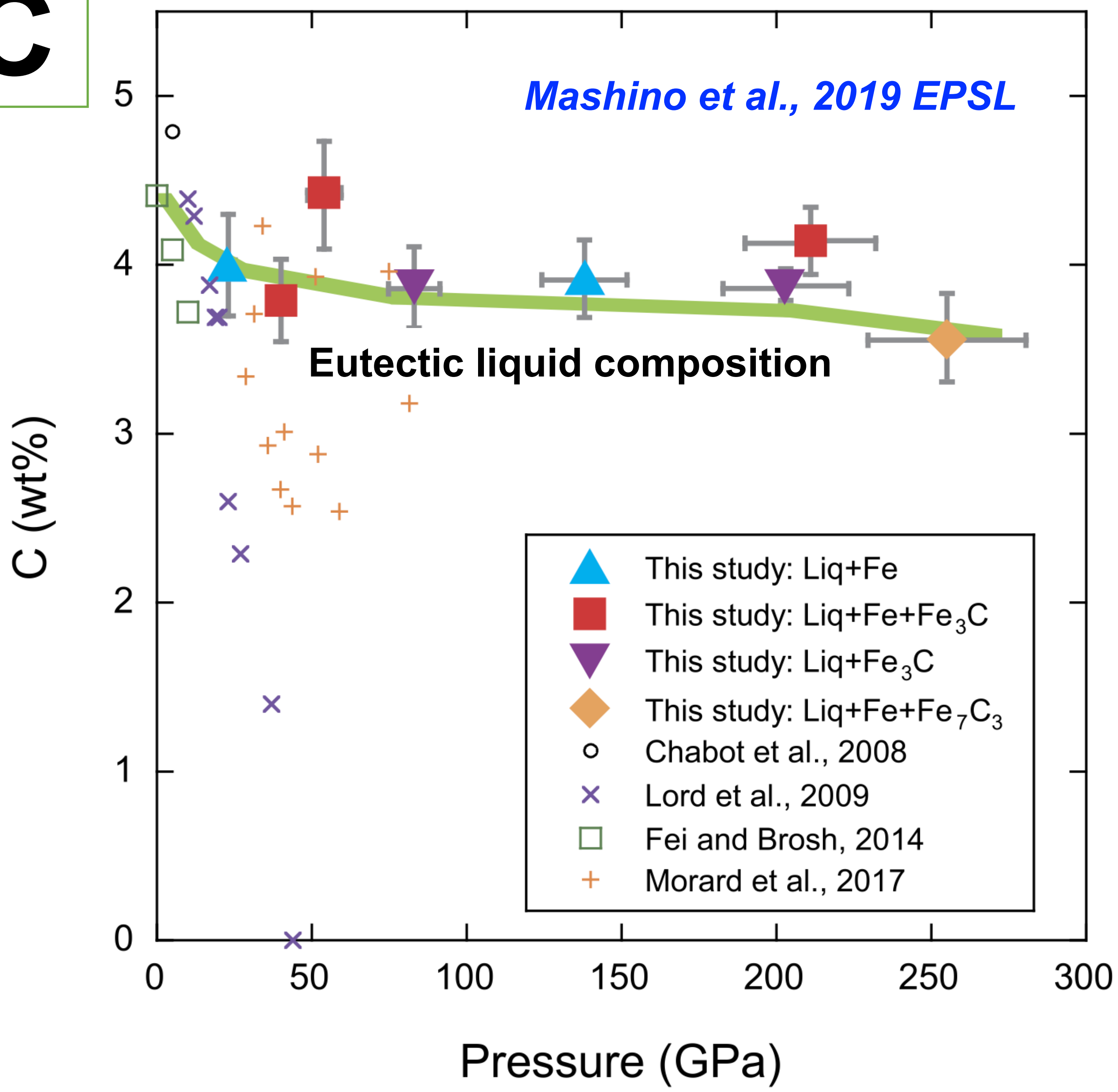
Fe-C

Mashino et al., 2019 EPSL



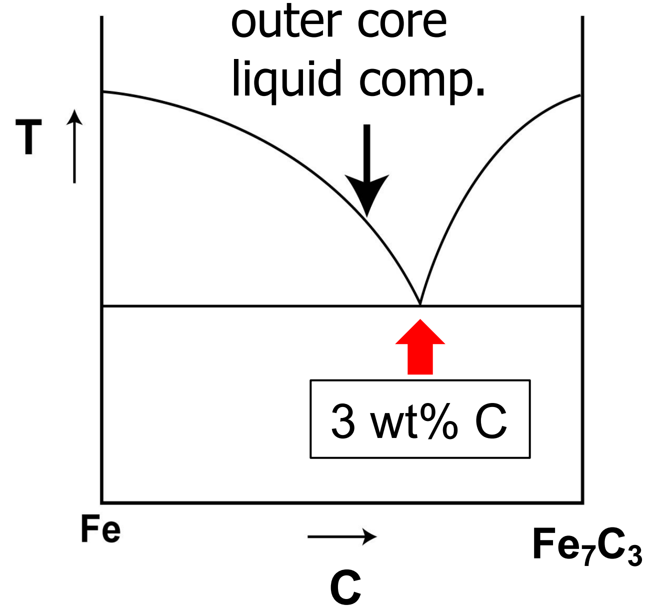
Fe-C binary eutectic liquid coexisting with Fe and Fe_7C_3

Fe-C



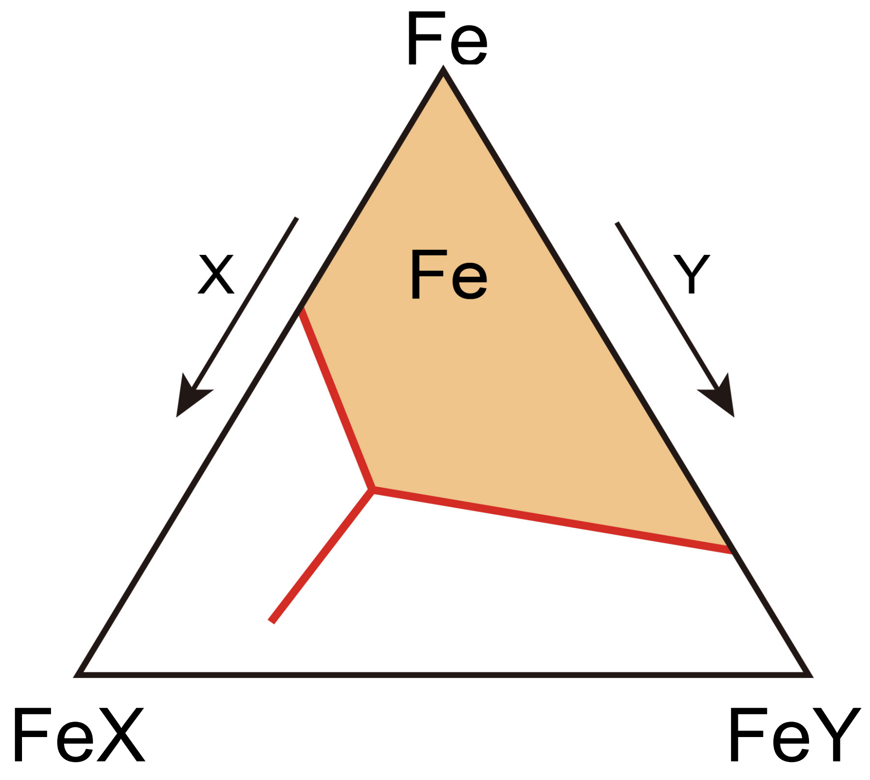
~3 wt% C in the Fe-C eutectic liquid at inner core pressures

It gives **the max C content** in the outer core



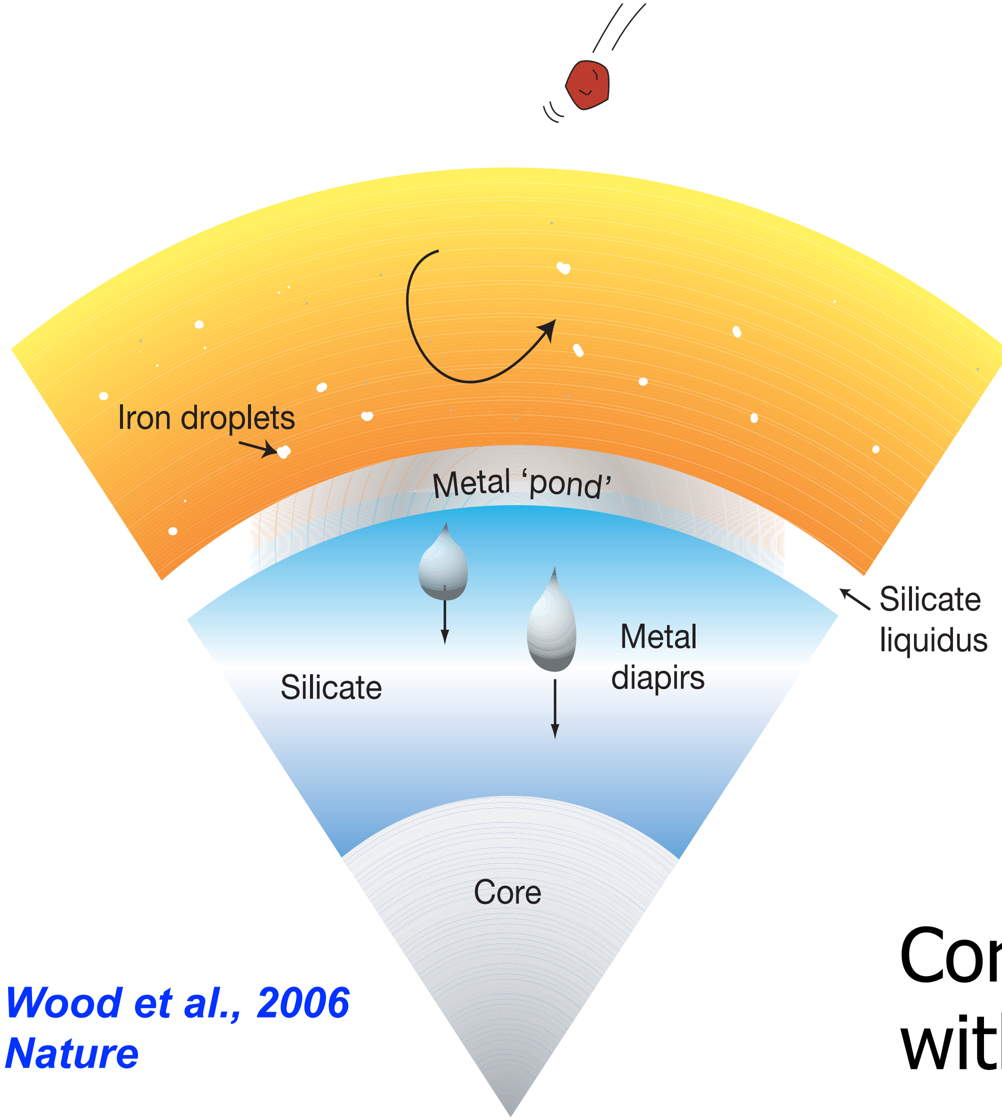
Max amount of each light element:

- <5 wt% S — *Mori et al. 2017 EPSL*
- <8 wt% Si — *Hasegawa et al. 2021 GRL*
- <15 wt% O — *Oka et al. 2019 Am. Mineral.*
- <3 wt% C — *Mashino et al. 2019 EPSL*
- <0.8 wt% H — *Hikosaka et al. 2022 Sci. Rep.*

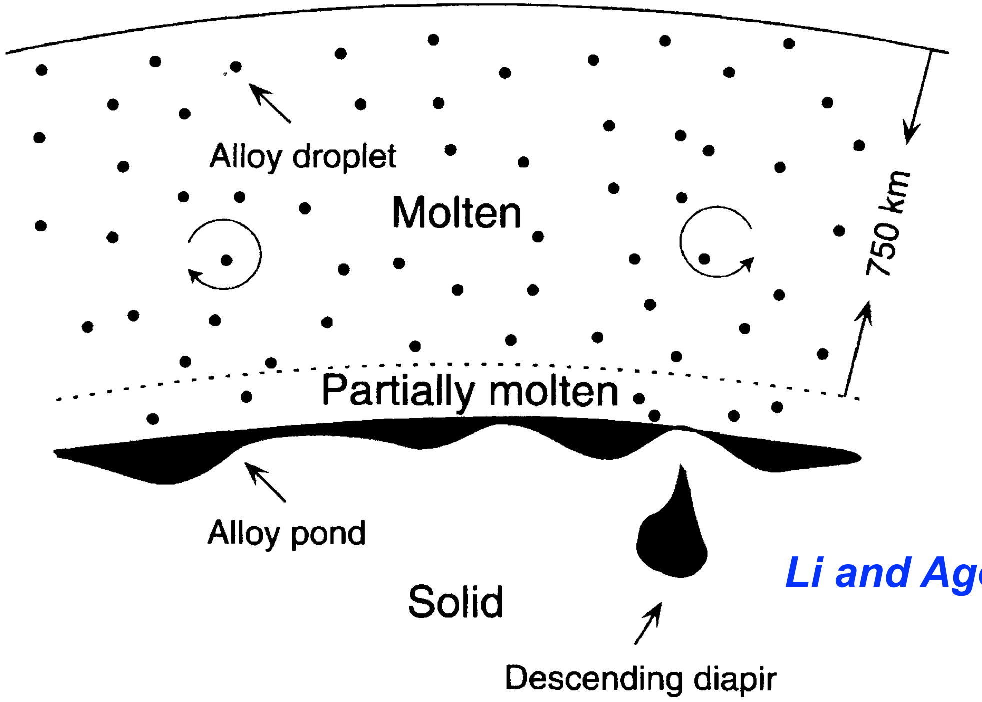


The liquidus field of Fe (the Fe-rich side of any eutectics) **in Fe-S-Si-O-C-H** will narrow down the possible range of the outer core composition.

V. Constraints from core-mantle partitioning



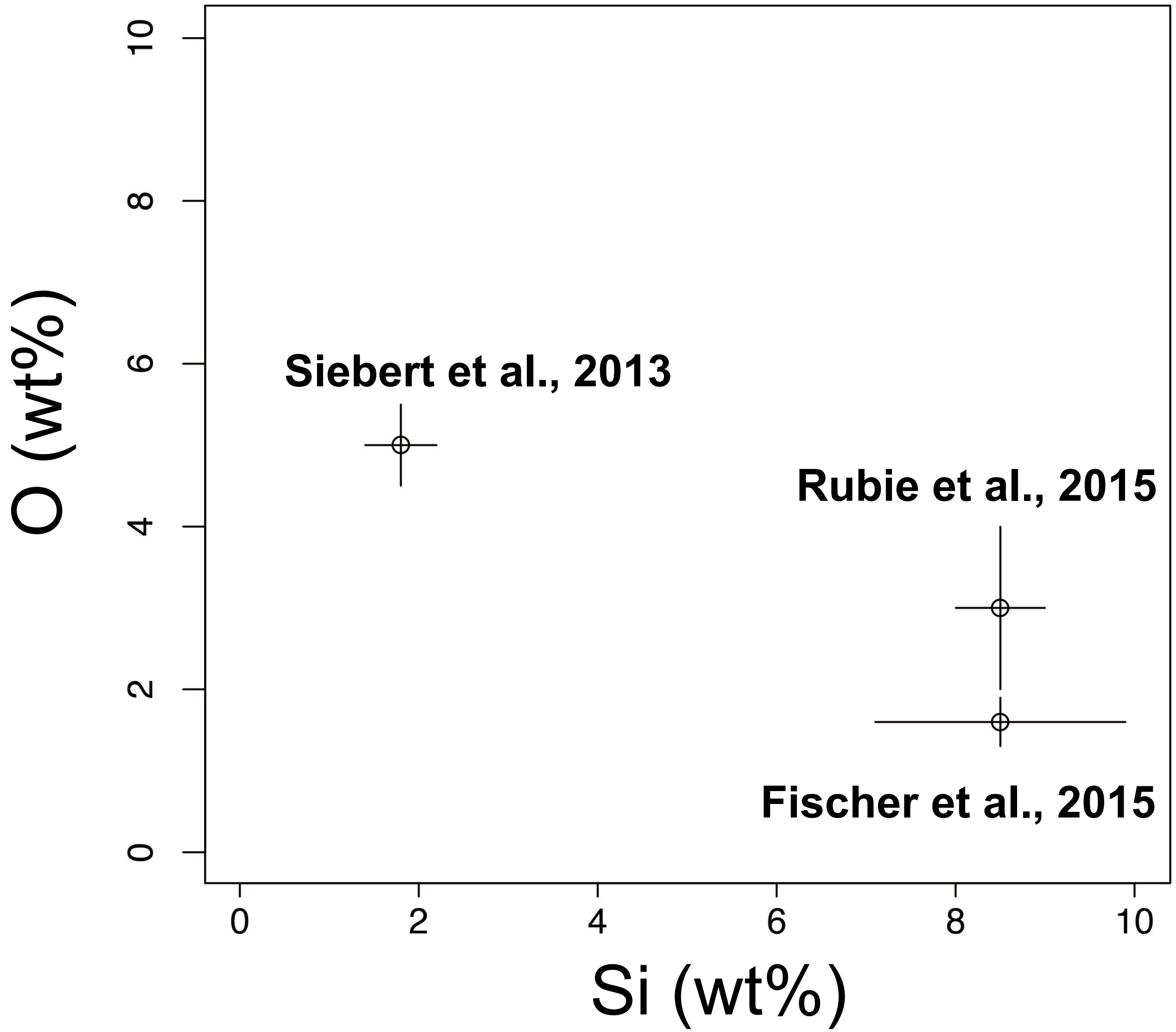
Wood et al., 2006 Nature



Li and Agee, 1996 Nature

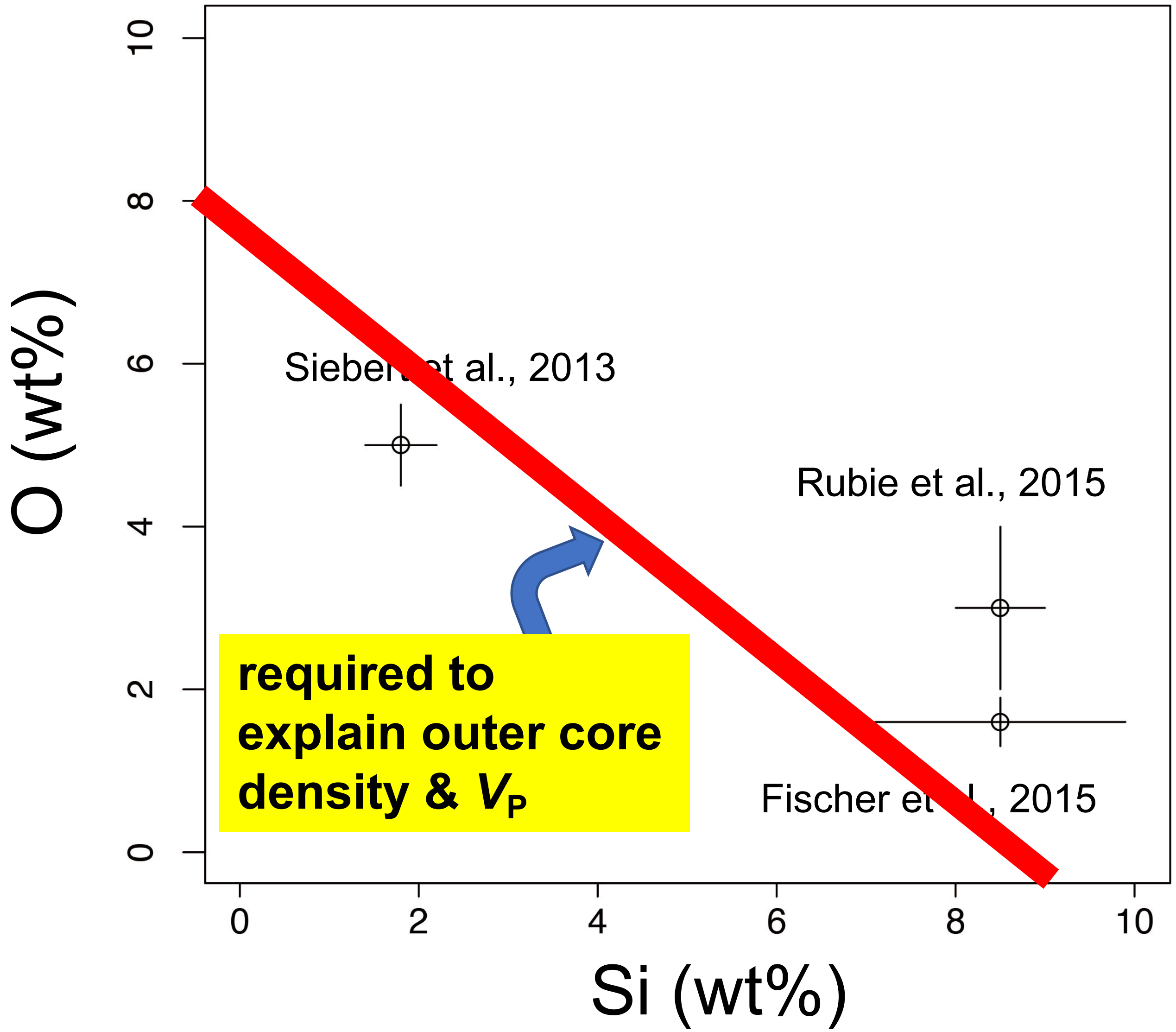
Core-forming metals chemically equilibrated with silicate in a deep magma ocean.

Metal-silicate partitioning of Si & O



Metal-silicate partitioning at high *P-T* in a deep magma ocean should have led to **high Si & O contents in core-forming metals**.

Metal-silicate partitioning of Si & O

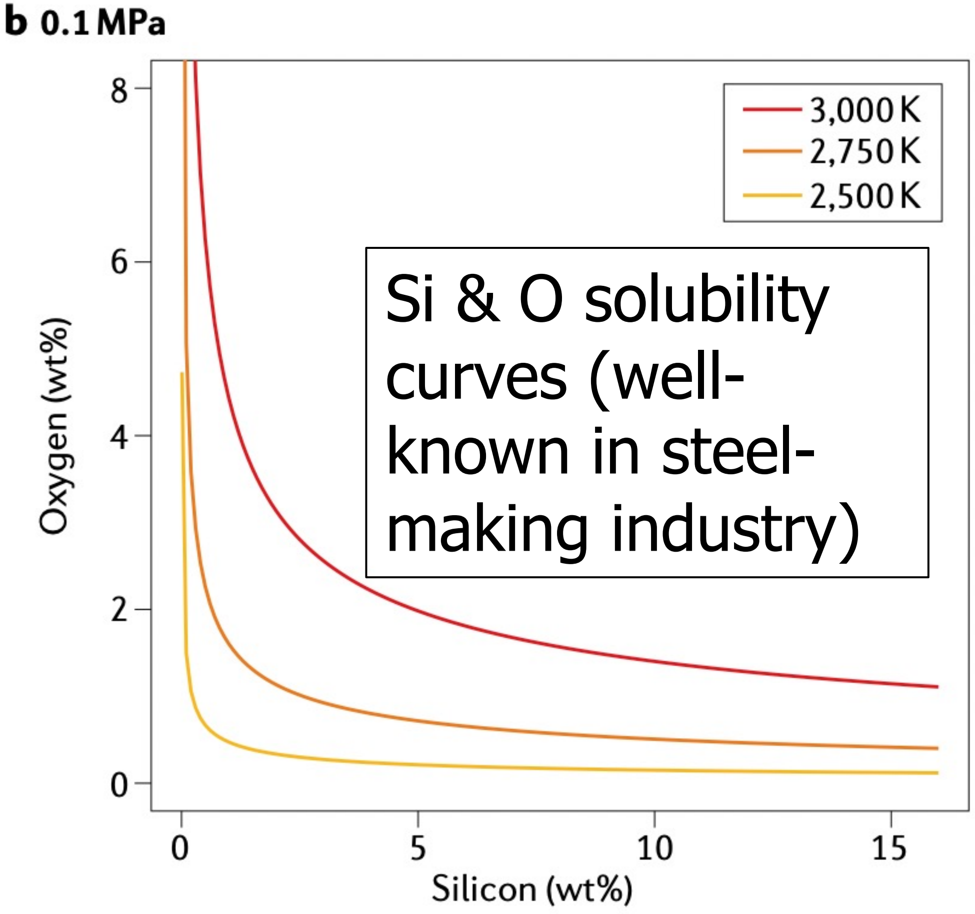


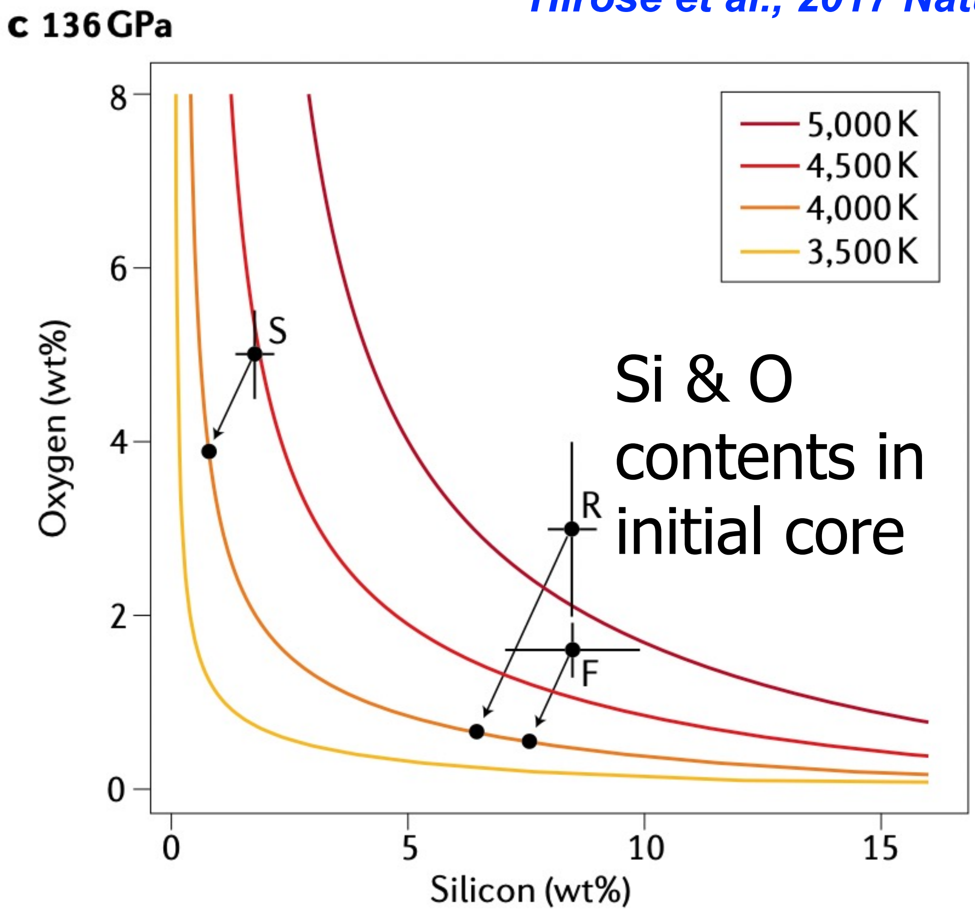
Metal-silicate partitioning in a deep magma ocean should have led to **high Si & O contents in the initial core**.

Already full, no room for other light elements

SiO_2 saturation in liquid core

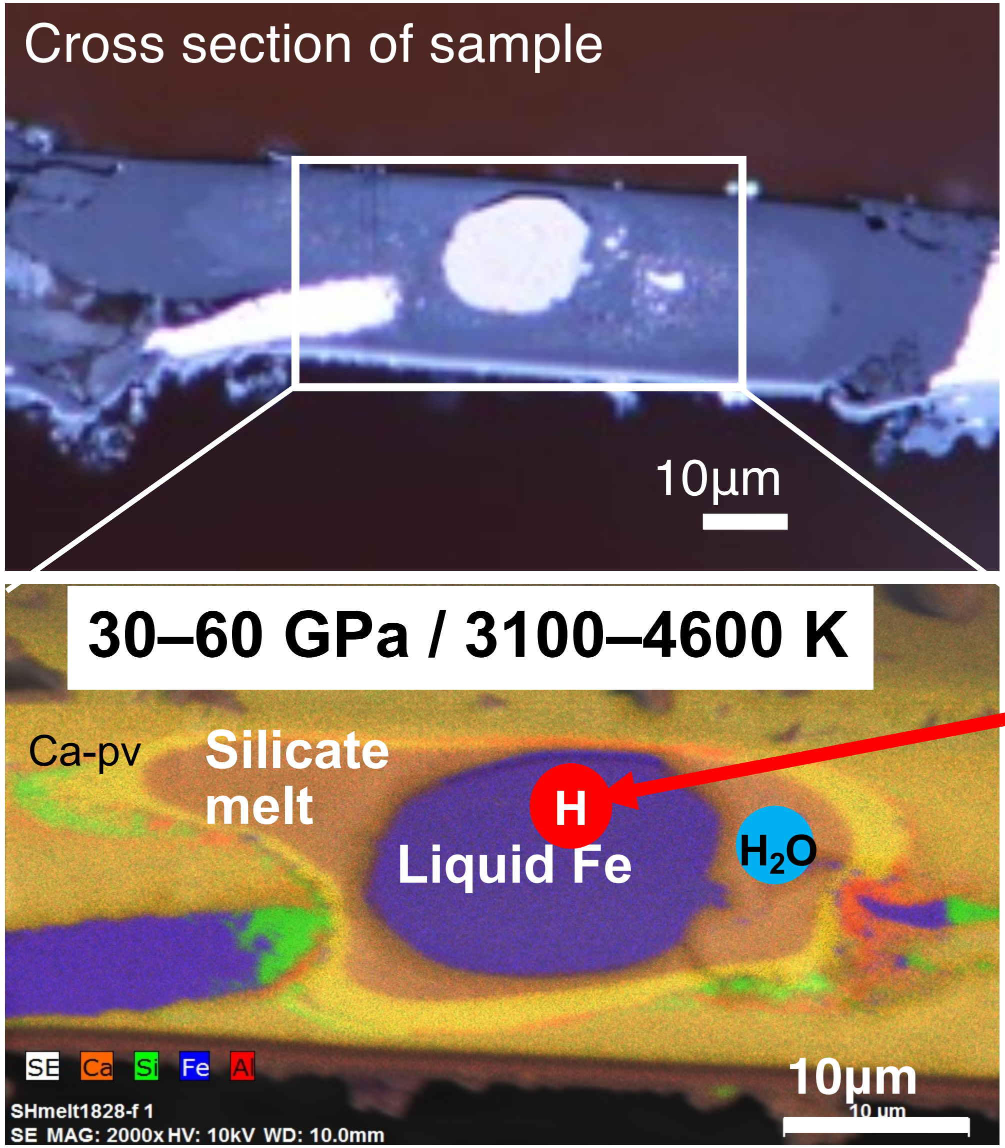
Hirose et al., 2017 Nature

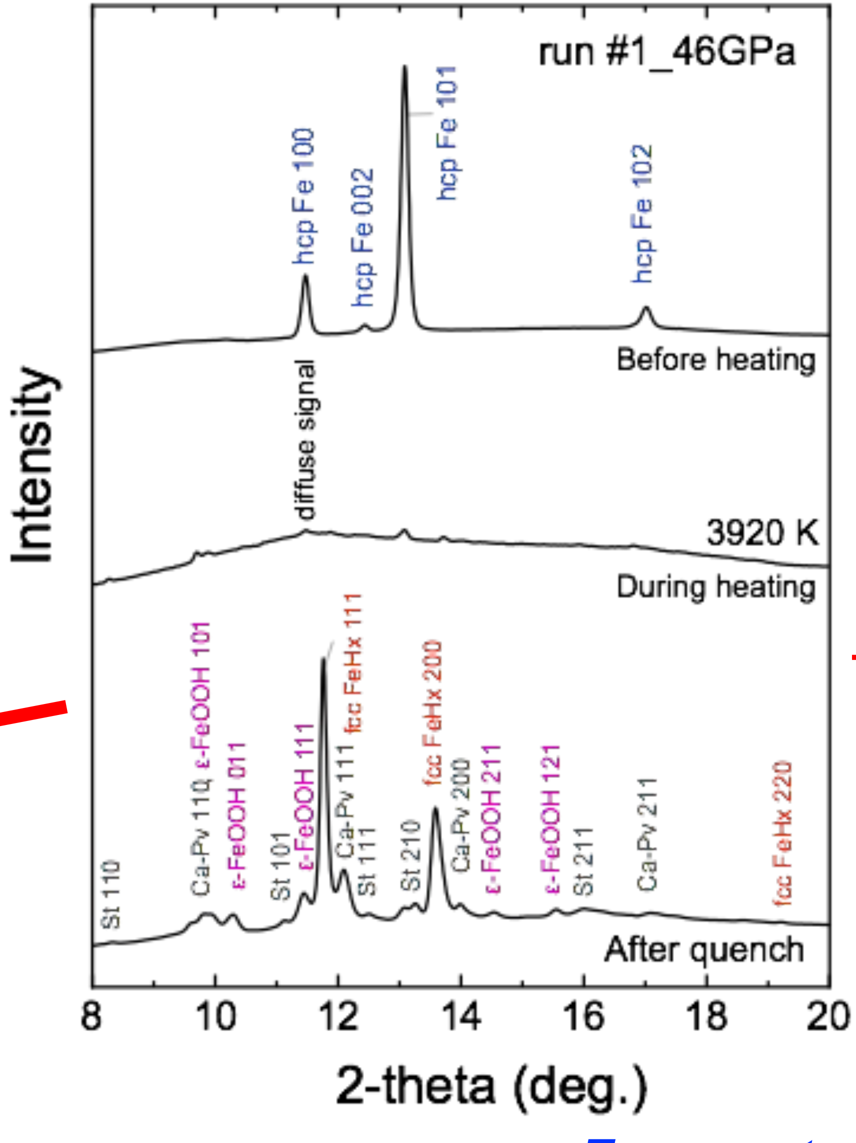




- ✓ Solubility of Si+O in liquid Fe is limited.
- ✓ Present-day liquid core may be **saturated in Si + O**.

Metal-silicate partitioning of H





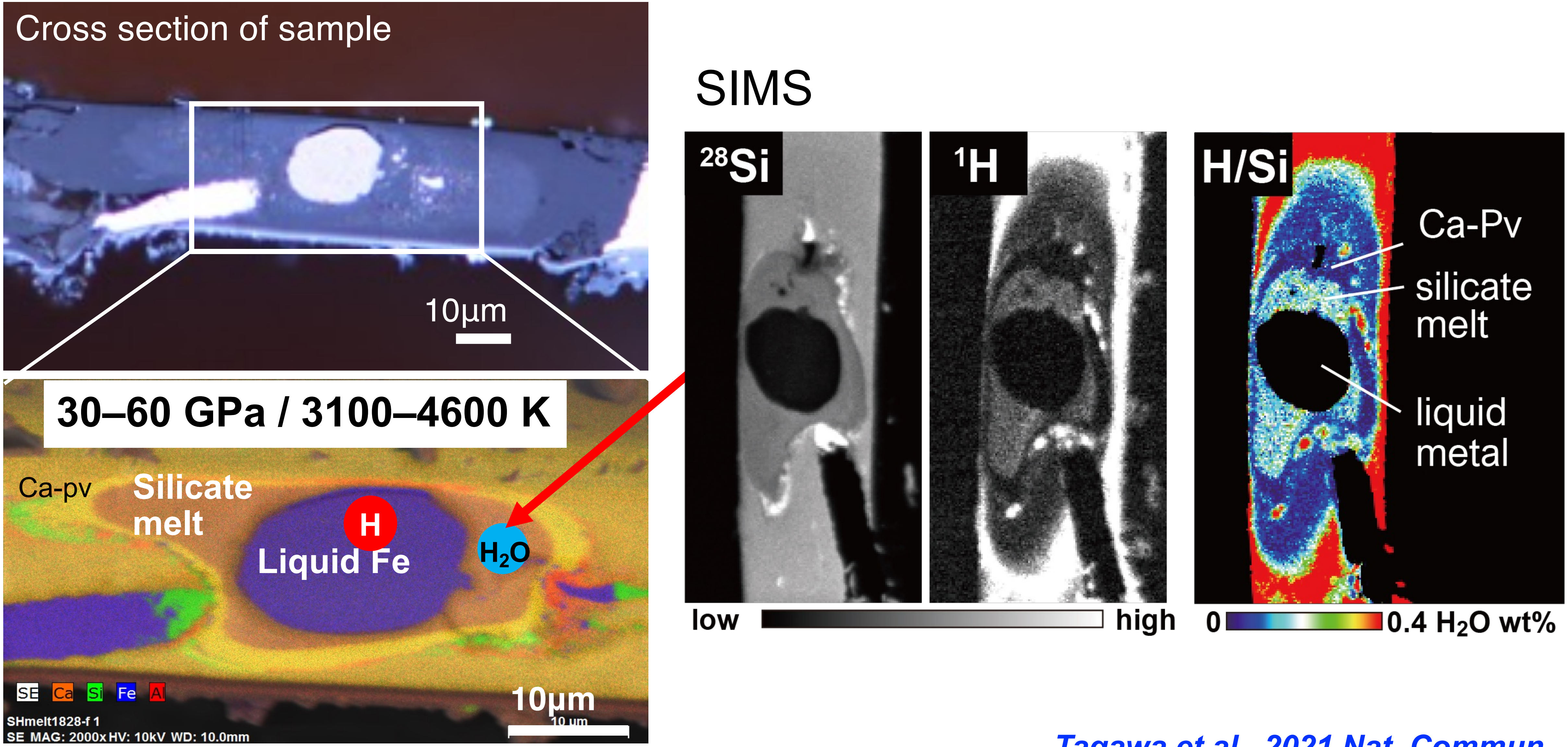
XRD

fcc FeHx

$$x = \frac{V_{FeHx} - V_{Fe}}{\Delta V_H}$$

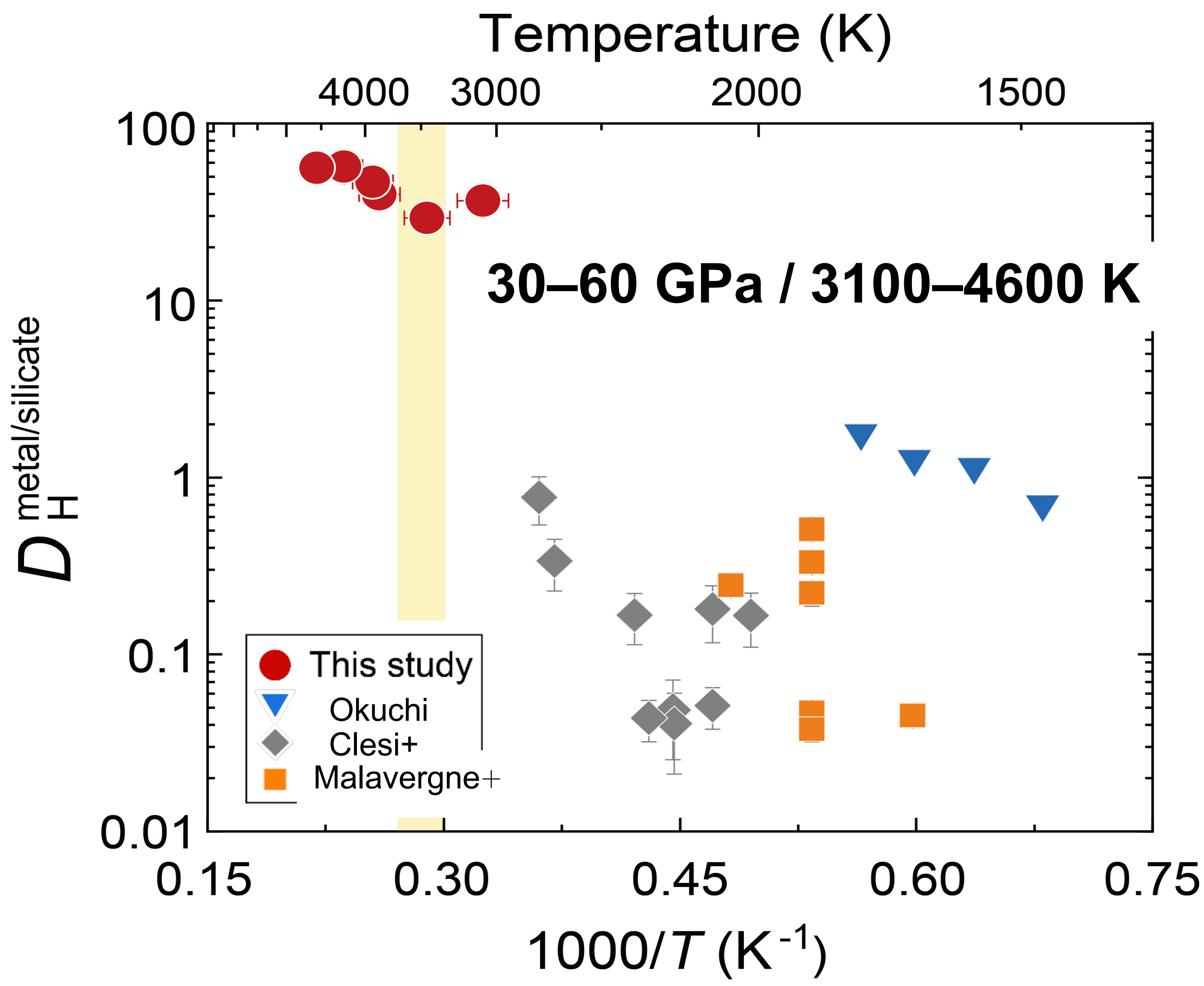
Tagawa et al., 2021 Nat. Commun.

Metal-silicate partitioning of H



Tagawa et al., 2021 Nat. Commun.

Metal-silicate partitioning of H



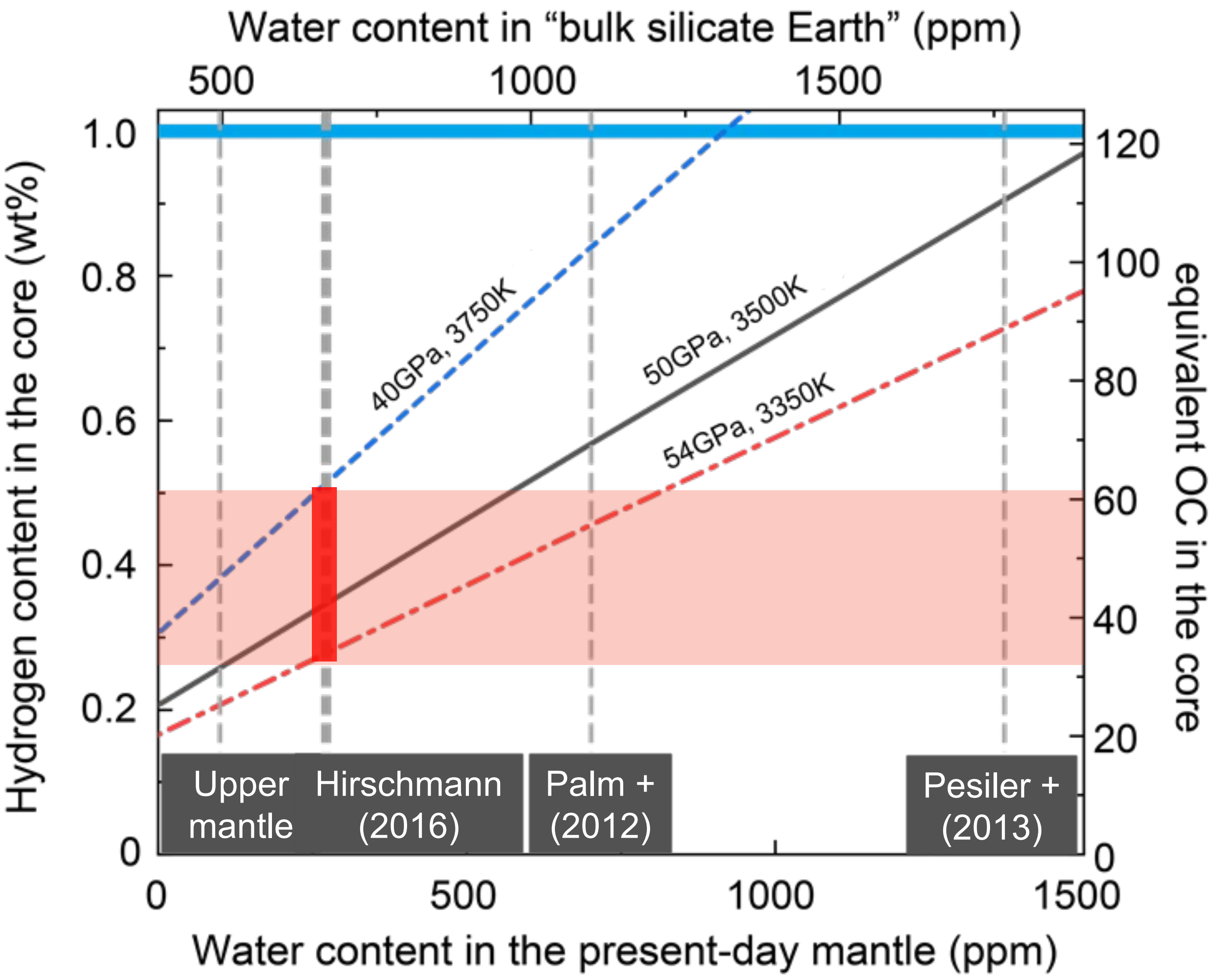
$$D_H = \frac{C^H_{FeH_x\,melt}}{C^H_{Silicate\ melt}}$$

= 29 – 56

Hydrogen is siderophile under high *P-T* conditions of core formation

Tagawa et al., 2021 Nat. Commun.

How much H in the core?



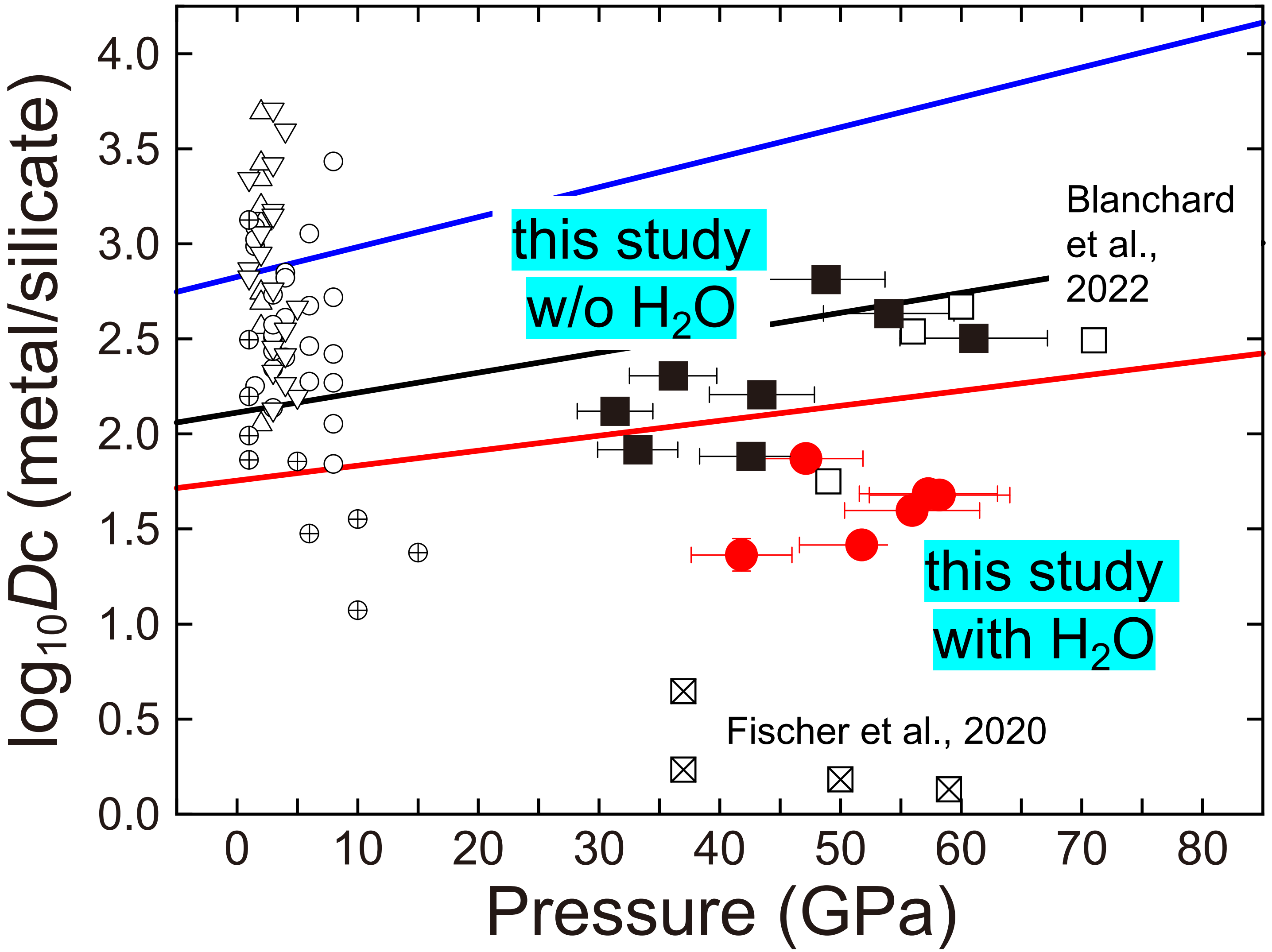
Core may include 0.29–0.53 wt% H

(explains ~30–50% of outer core density deficit and velocity excess)

Such amount is equivalent to H in 35–63 times ocean water

Tagawa et al., 2021 Nat. Commun.

Metal-silicate partitioning of C



$D_c\ (\frac{\text{metal}}{\text{silicate}})$ = 76–650 (dry)

= 23–74 (hydrous)

suggesting

>0.8 wt% C with no H

>0.5 wt% C with 0.6 wt% H

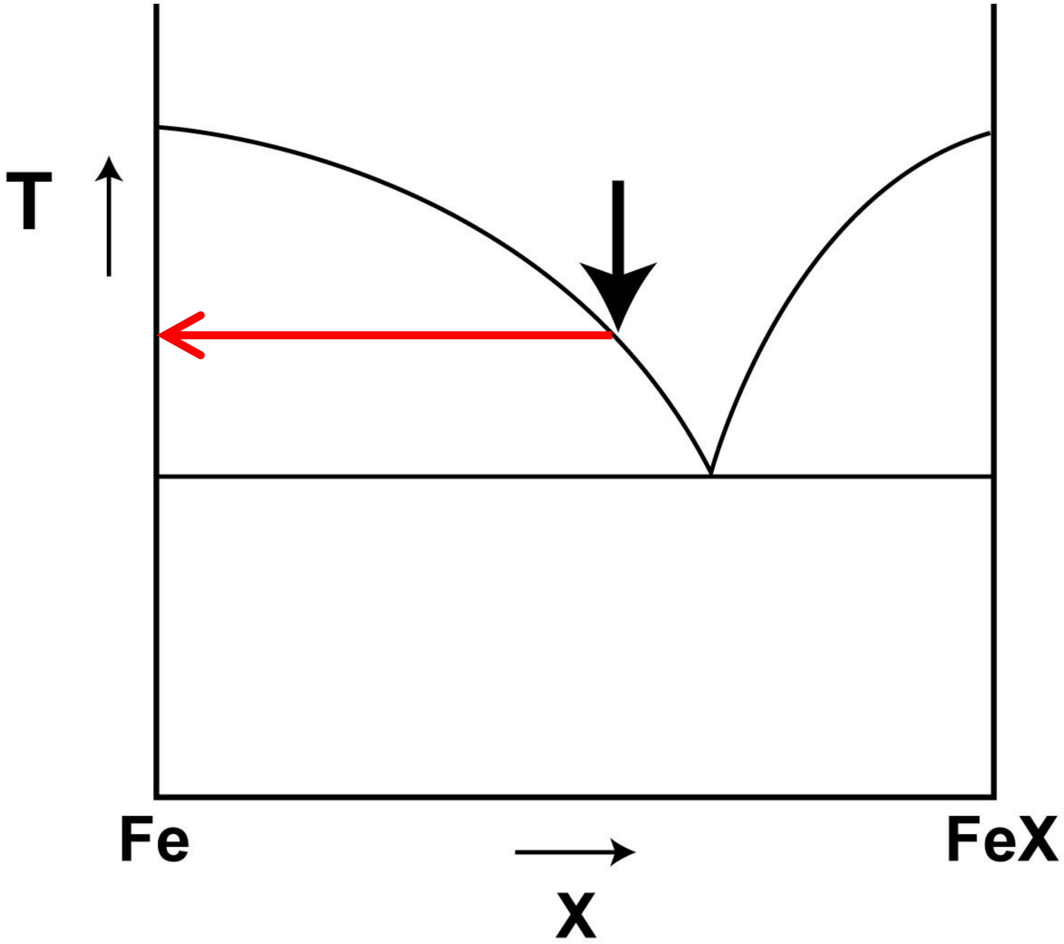
in the core.

Tsutsumi et al., OL01_5 IMA 2022

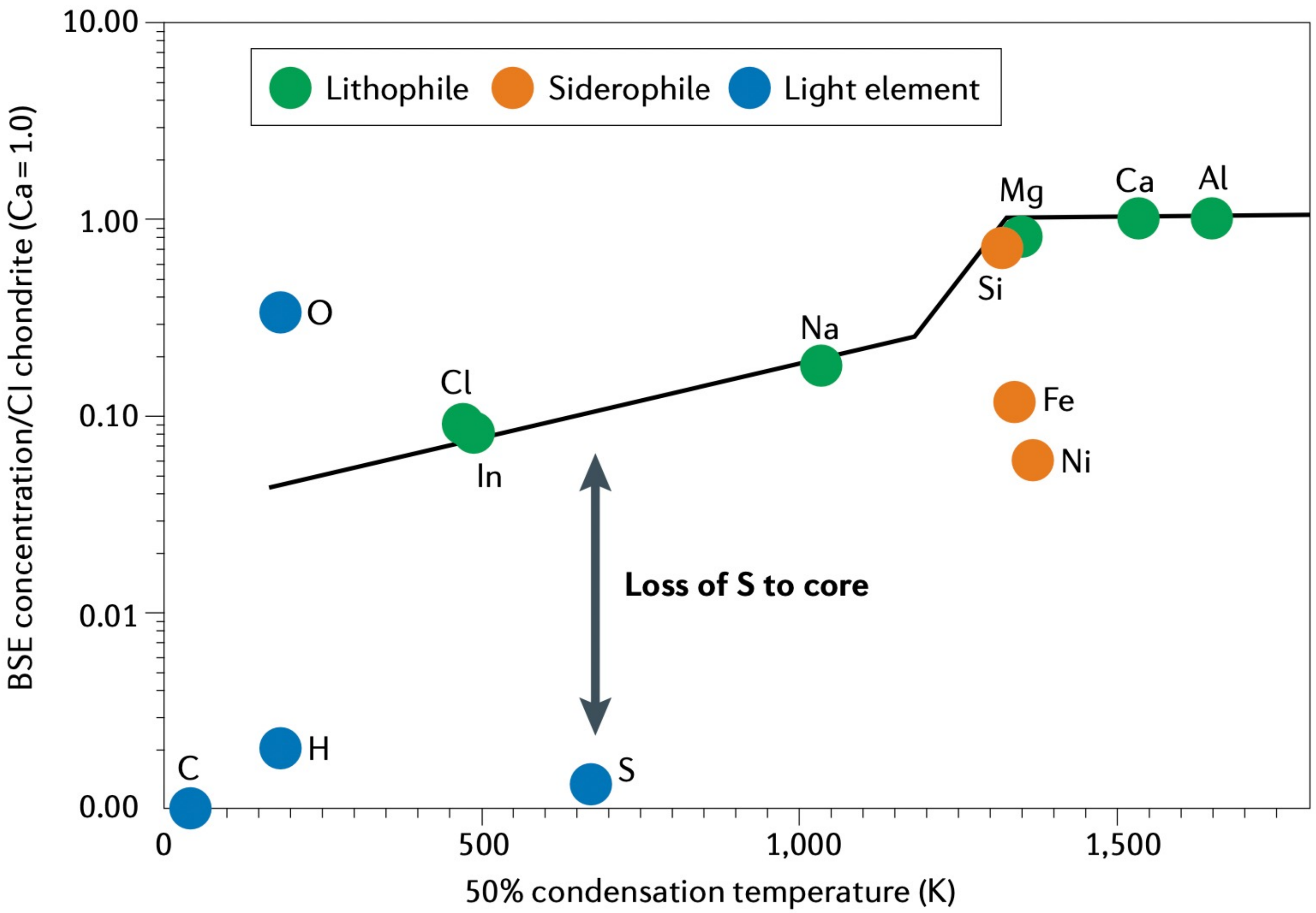
VI. Possible range of outer core composition

1) Assume T_{ICB} = 5400 K, corresponding to ~4000 K at CMB

(T_{ICB} is the liquidus T of the outer core liquid and thus constrained simultaneously with liquid core composition)



VI. Possible range of outer core composition

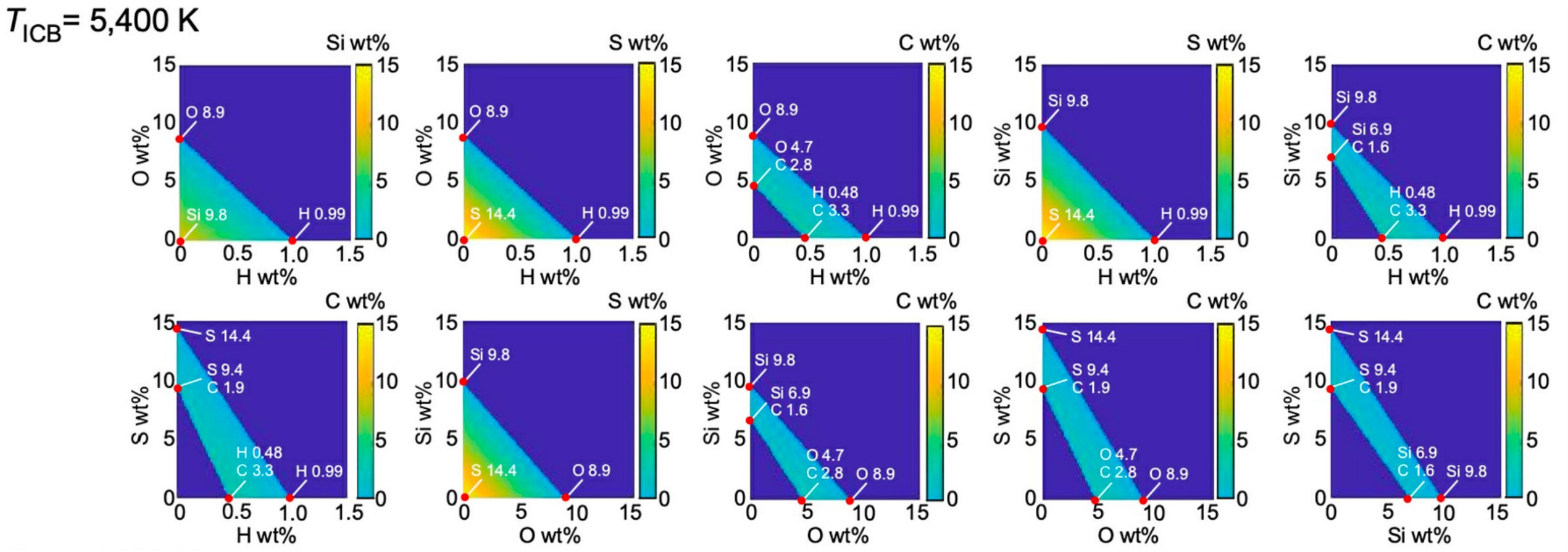


2) Employ cosmo-/geochemical estimate of 1.7 wt% S in the core

Dreibus & Palme, 1996 GCA

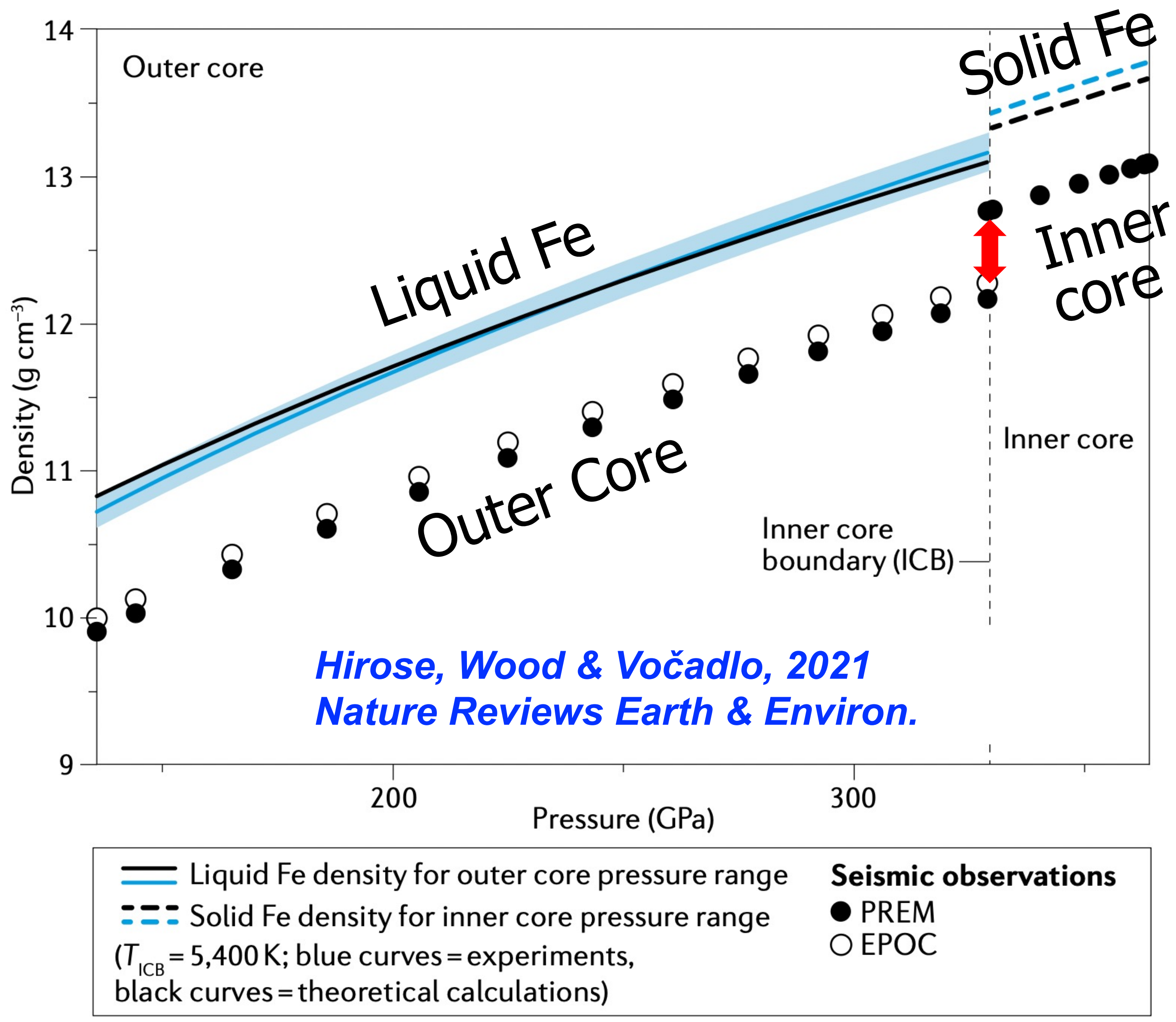
VI. Possible range of outer core composition

3) Employ the possible range of liquid core composition that explains outer core density & V_P



Umemoto & Hirose, 2020 EPSL

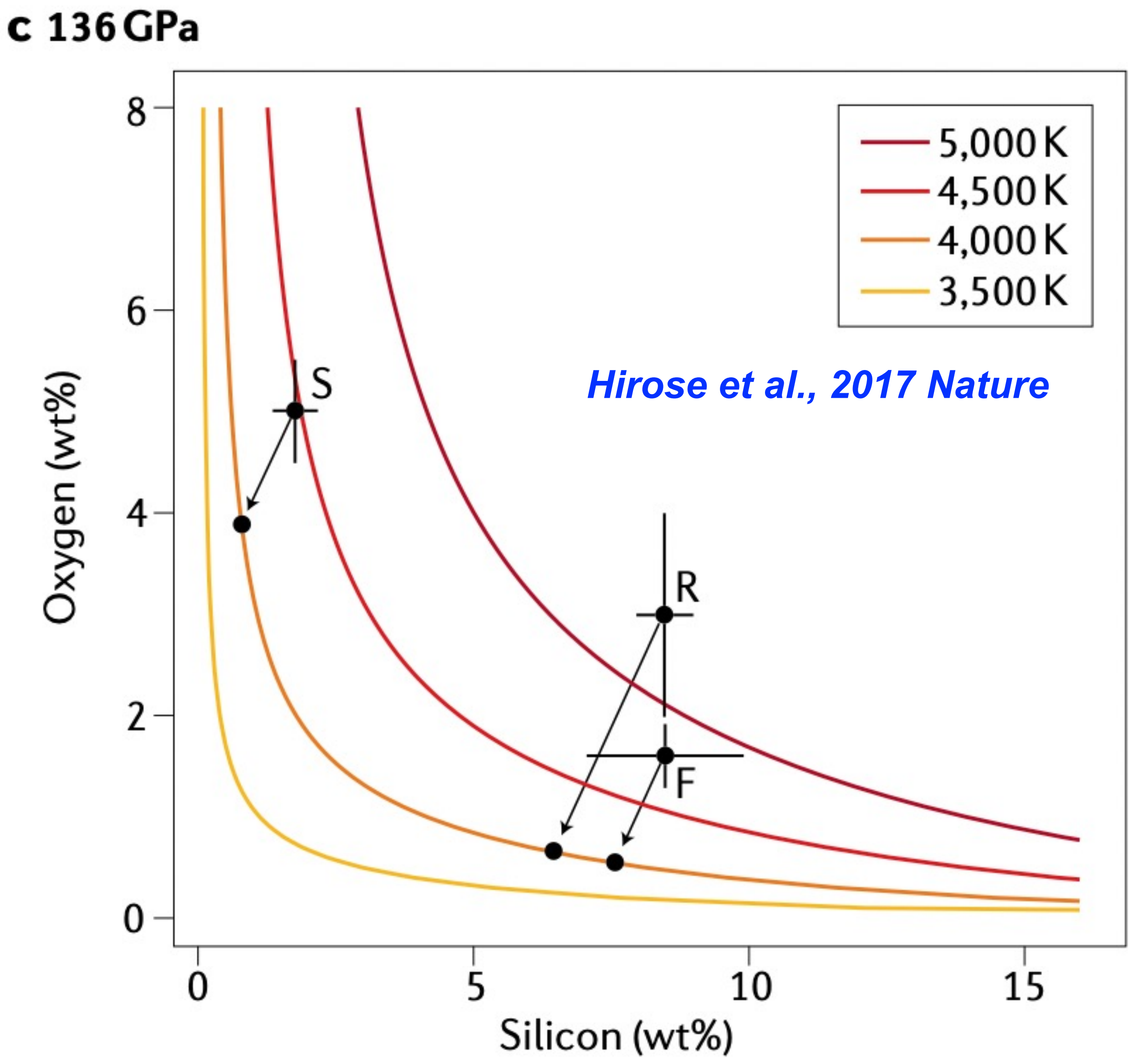
VI. Possible range of outer core composition



4) Employ max 3.8 wt% O in the outer core to explain the density jump across the ICB

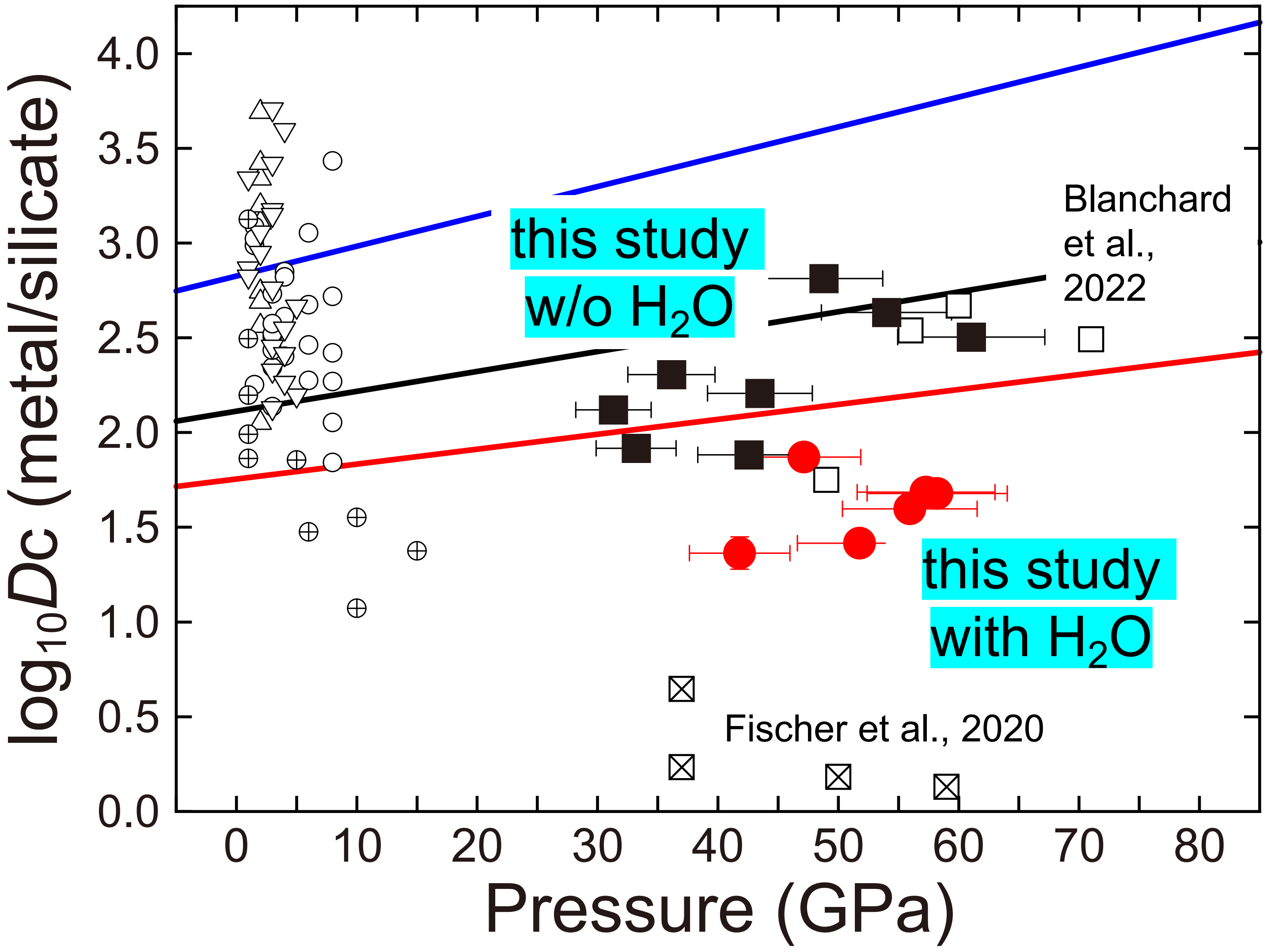
Kuwayama et al., 2020 PRL

VI. Possible range of outer core composition



5) Employ Si + O saturation limit at T_{CMB} = 4000 K

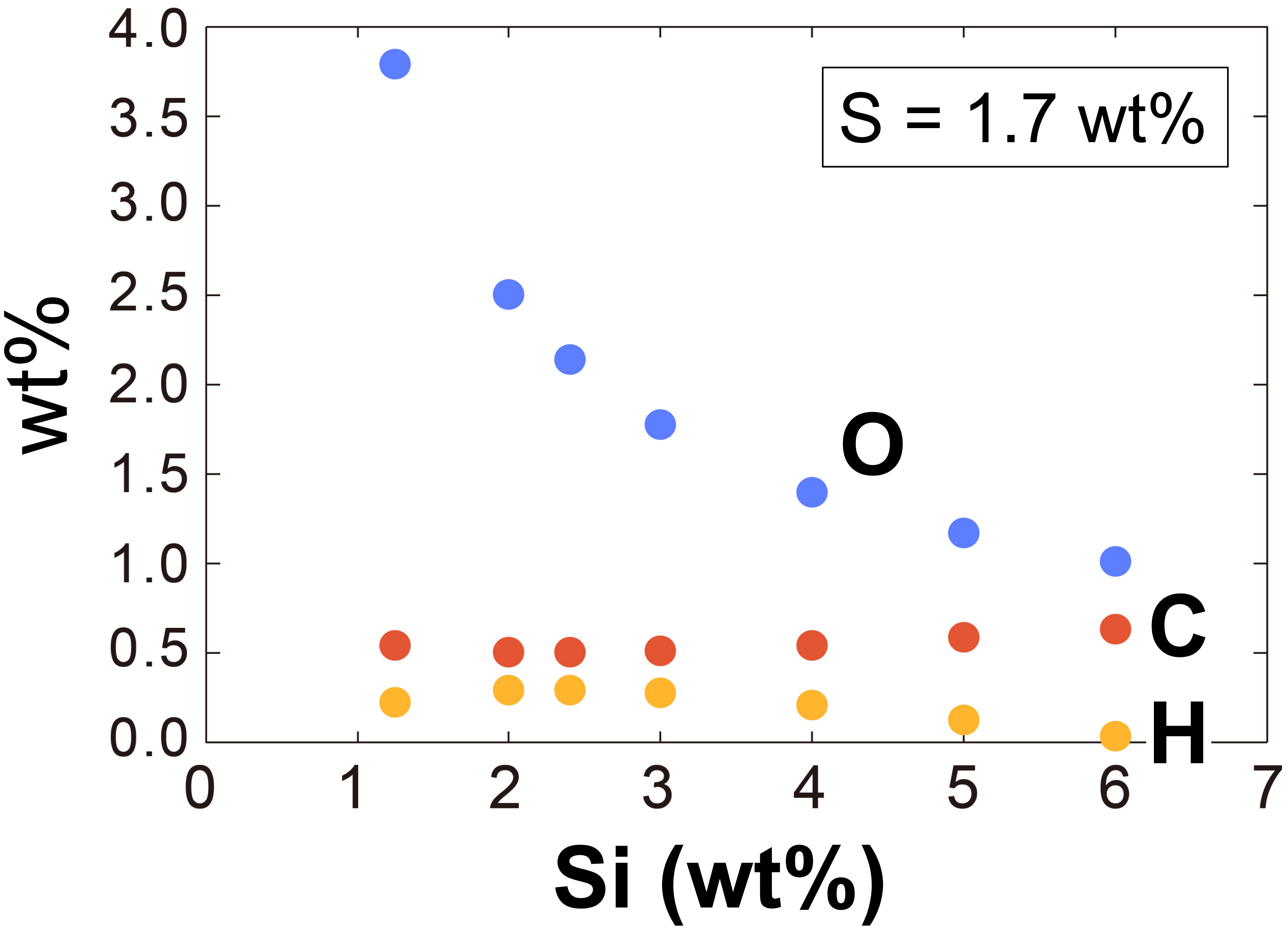
VI. Possible range of outer core composition



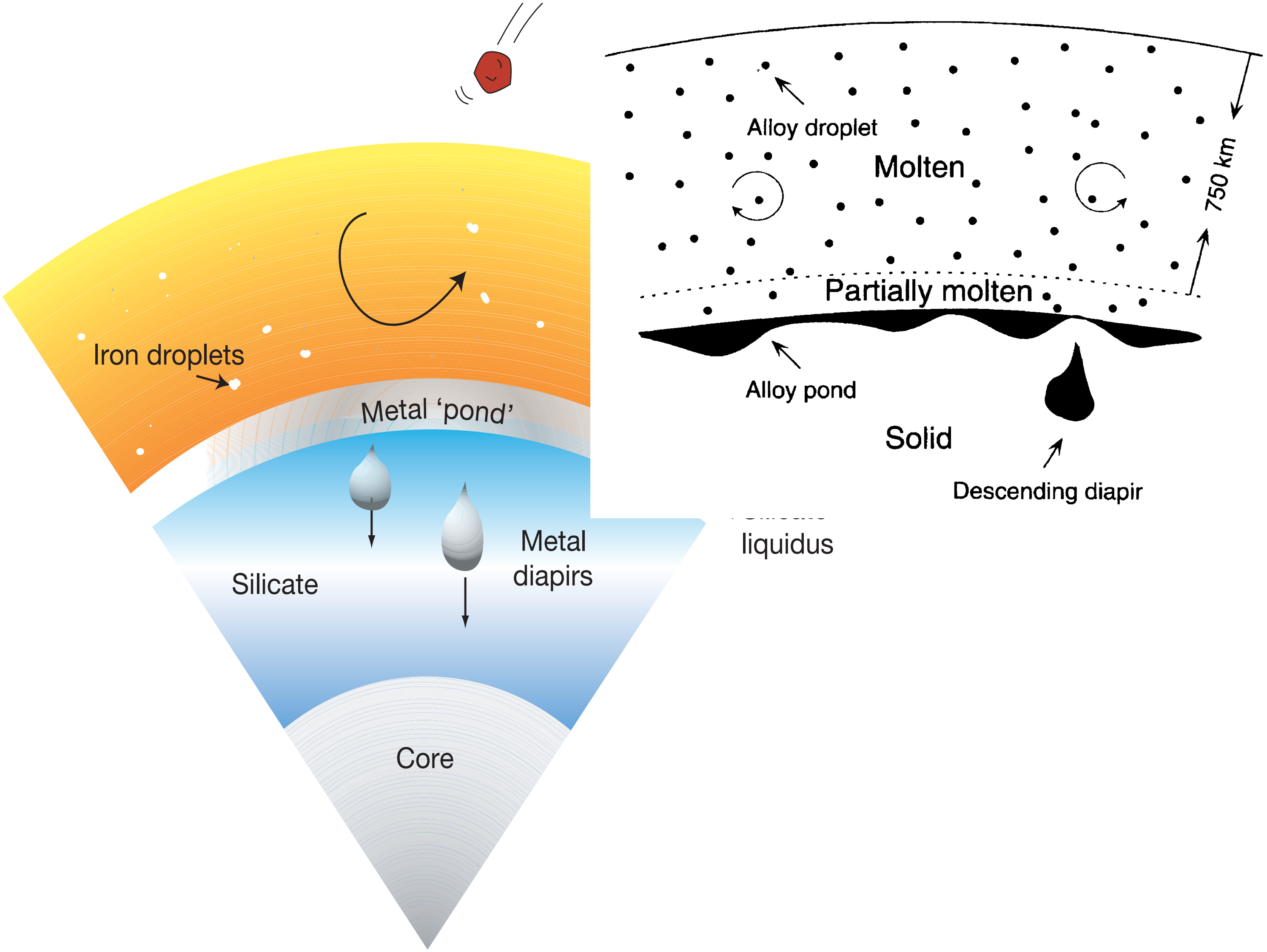
6) Employ core-mantle partitioning of C that depends on metal H concentration

Tsutsumi et al., OL01_5 IMA 2022

VI. Possible range of outer core composition



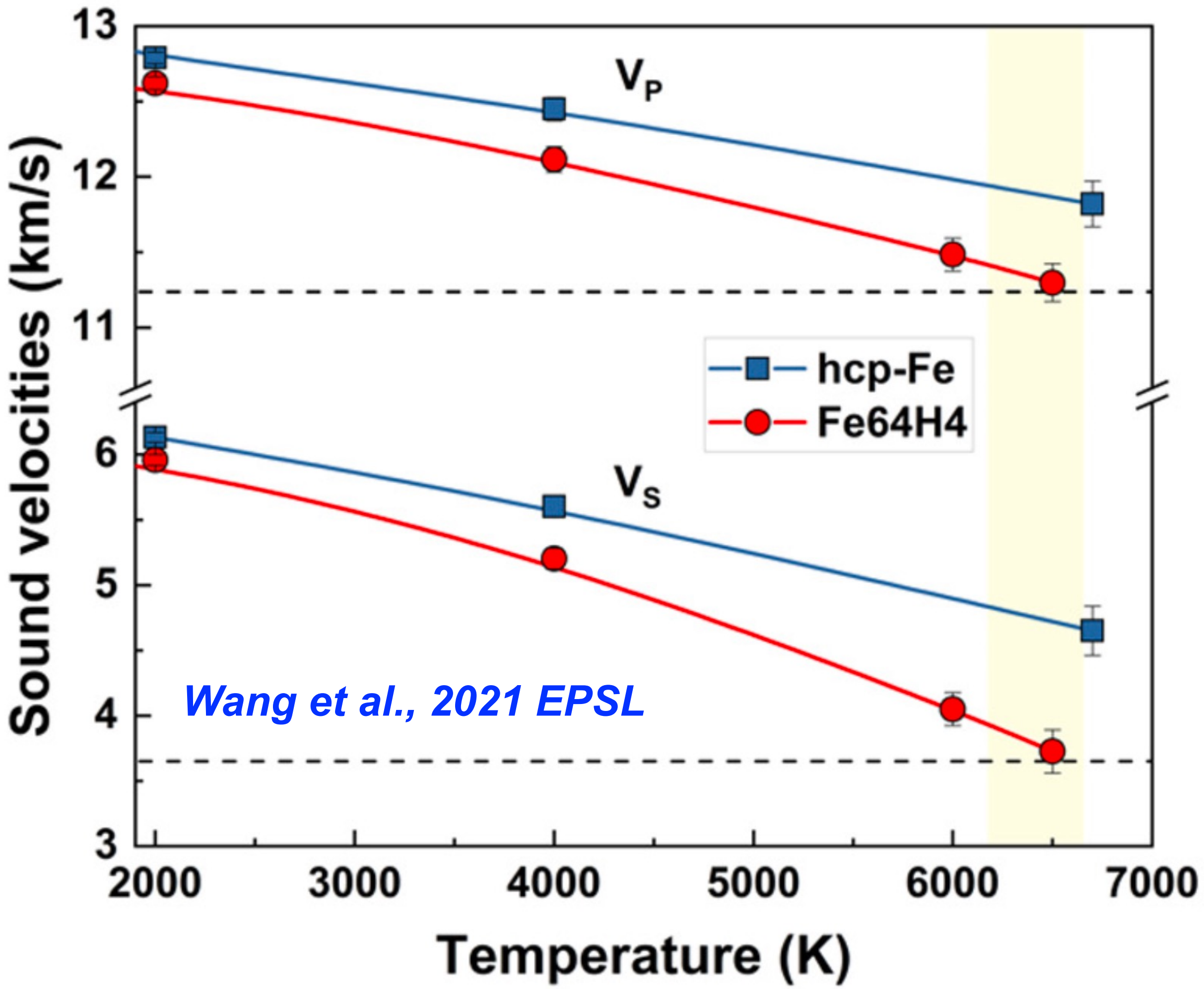
VI. Possible range of outer core composition



7) If we employ ≥0.3 wt% H in the core from the core-mantle partitioning study,

Tagawa et al., 2021 Nat. Commun.

Hydrogen is important for both OC & IC



- ✓ Density & V_P of liquid Fe-H are compatible with outer core observations when T_{ICB} = 5400 K.

  Umemoto & Hirose, 2020 EPSL

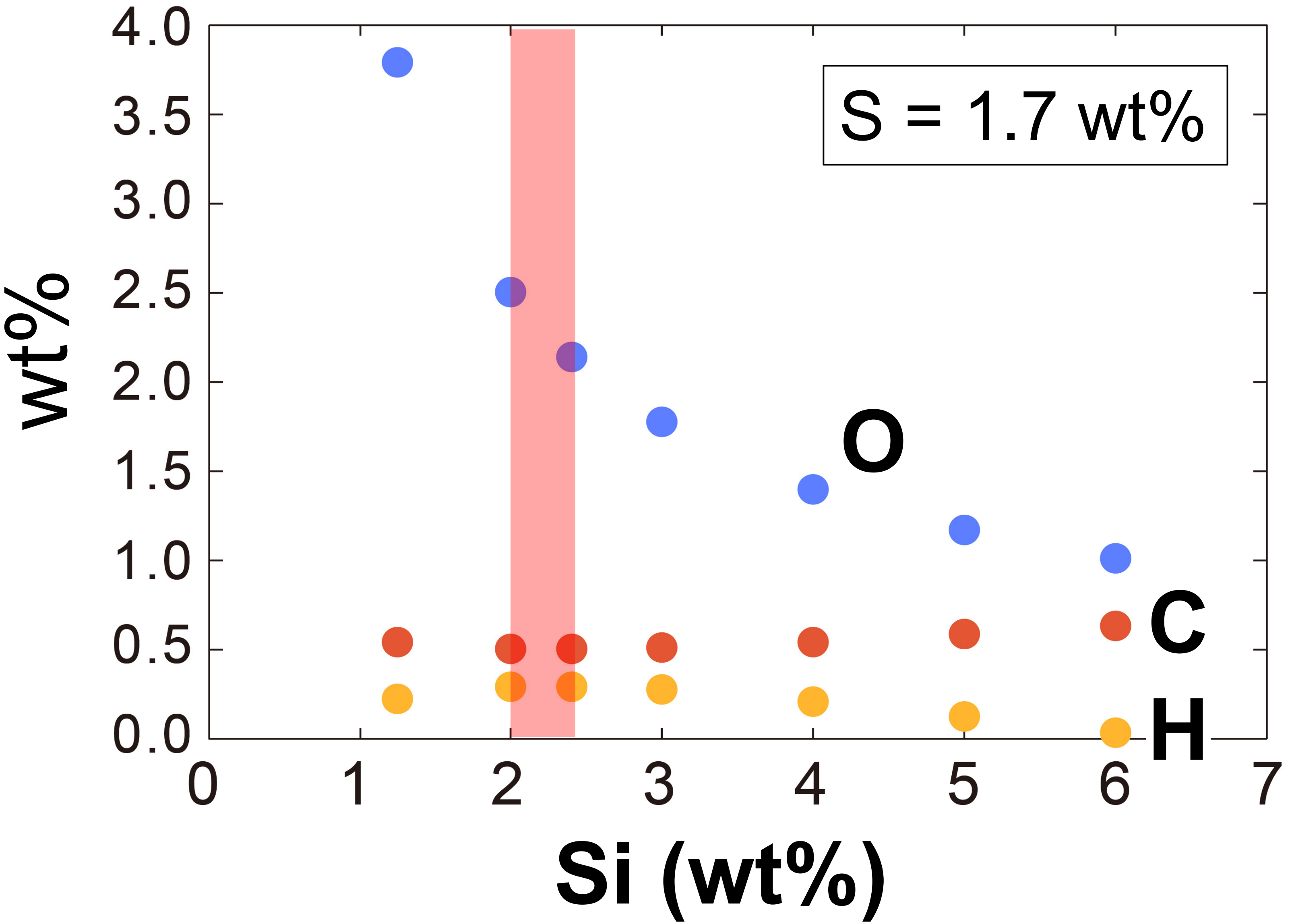
- ✓ Super-ionic solid Fe-H explains high V_P/V_S, characteristic of the inner core.

  Wang et al., 2021 EPSL
  He et al., 2022 Nature

- ✓ Large amount of H_2O may have been delivered to the growing Earth and mostly sequestrated in the core.

  Walsh et al., 2011 Nature
  Raymond et al., 2007 Astrobiology

VI. Possible range of outer core composition



7) If we employ ≥0.3 wt% H in the core, the outer core may include:

2.0–2.4 wt% Si
2.1–2.5 wt% O
0.6 wt% C
0.3 wt% H
with 1.7 wt% S

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H & O may largely contribute to the outer core density deficit.

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Reservoirs of hydrogen

Oceans	1
Mantle + Crust	2 – 10
Core	**37**

Hirschmann, 2016 Am. Mineral.

Peslier et al., 2017 Space Sci. Rev.

Most of hydrogen (77–93%) on Earth may be present in the core.

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Note, however, that this estimate is strongly dependent on the Earth accretion scenario. More observational constraints, possibly from neutrino observations, are very welcome!

Conclusions

- ✓ H (H_2O) concentrations in the deep Earth still remain largely unknown.
- ✓ Nevertheless, large amounts of H, equivalent to H in **>2 and ~40 ocean mass of water**, may be present in the mantle and the core, respectively.
- ✓ It is supported by recent **planet formation theories**.