INSTITUTE OF GEOLOGY
AND MINERALOGY SB RAS

IGM UHP
LABORATORY OF ULTRA-HIGH
PRESSURE

TOHOKU
UNIVERSITY

SPring-8

Litasov, Shatskiy, 2016 RGG
Takahashi et al., in prep.

Recent progress in understanding the composition of the Earth's core

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International Seminar “High-Pressure Mineralogy: Theory and Experiment”
Moscow State University, Geological Faculty – October 21-23, 2015 (Room 415)

Ultra-high pressure Lab in IGM SB RAS, Novosibirsk

http://uhplab.igm.nsc.ru/

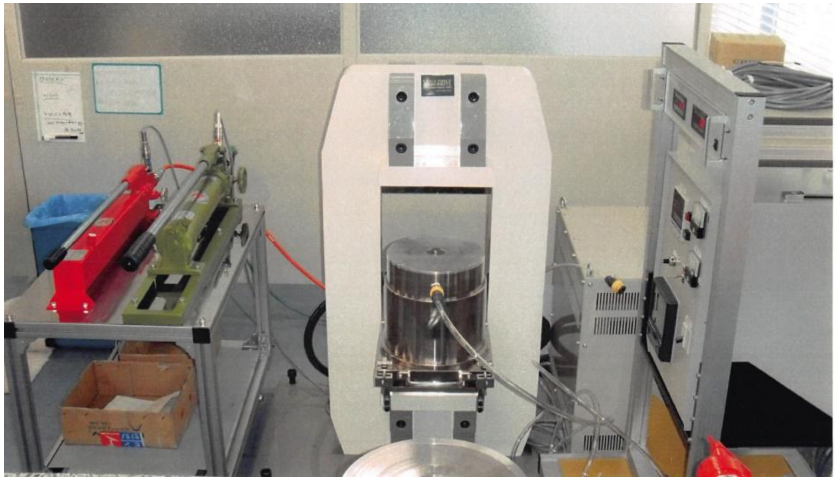
Crisis (1990-2012)

Mid-1970ths
Hydraulic press and piston
cylinder apparatus

Rejuvenation at 2013-2015
Modern lab equipped with all
technical facilities

Ultra-high pressure Lab in IGM SB RAS, Novosibirsk

Piston-cylinder apparatus (end of 2015)



Machine shop

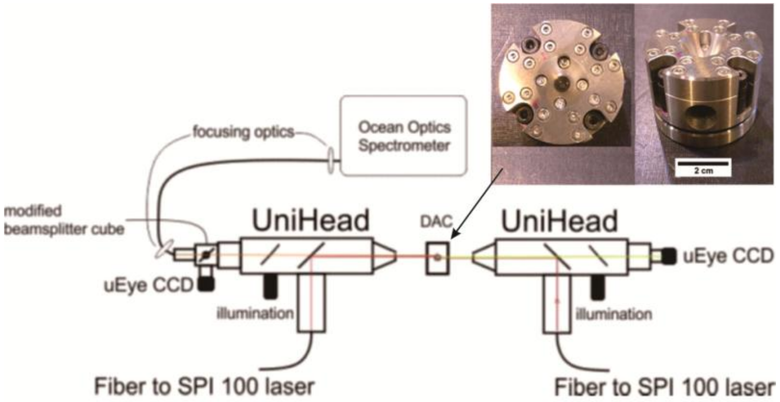
1500-tons multianvil press (installed)

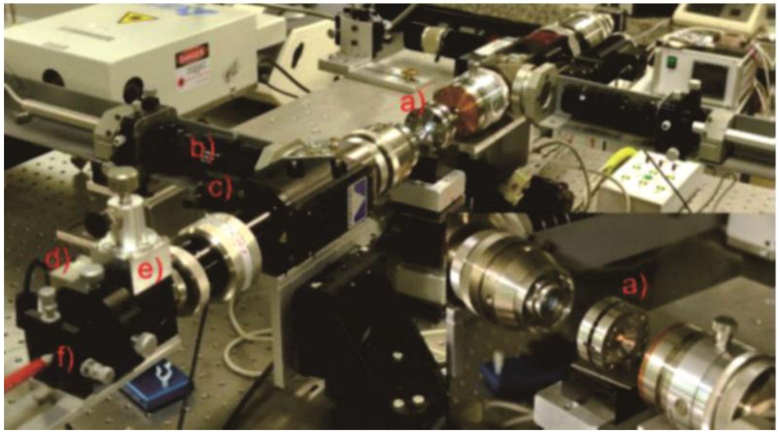
Sample preparation

Ultra-high pressure Lab in IGM SB RAS, Novosibirsk

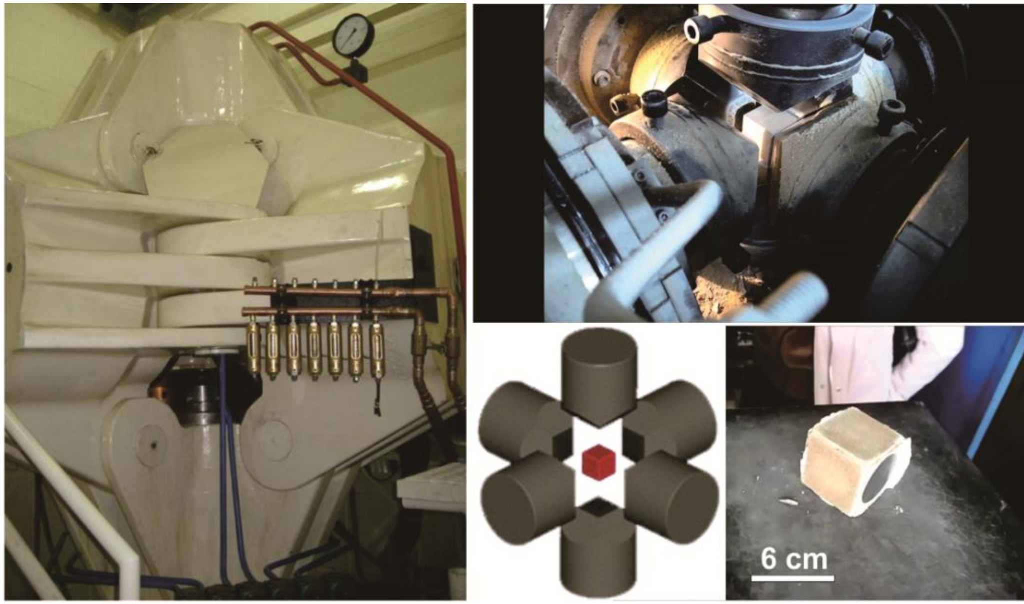
Further development in 2016-2017

Lab laser-heated DAC system





Cubic press for diamond technology



Local computational cluster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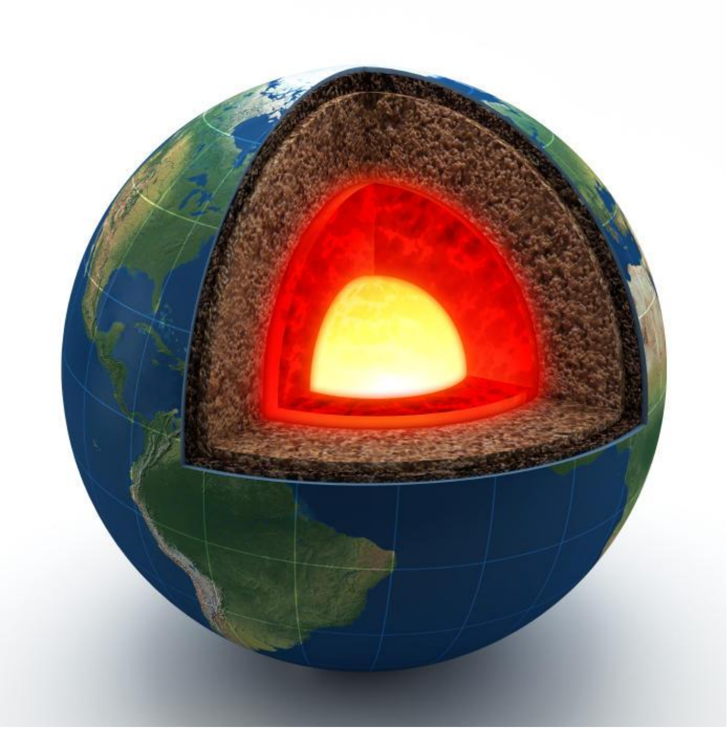
Earth’s core: methods



Seismic wave propagation, attenuation and scattering

Thermal physics modeling of energetics and evolution

Modeling of geomagnetic field and geodynamo

Cosmochemical calculations

Short and long-lived radiogenic isotope systems, Hf-W

Stable isotope systems, Si, O, Fe, Mg, …

Geoneutrino

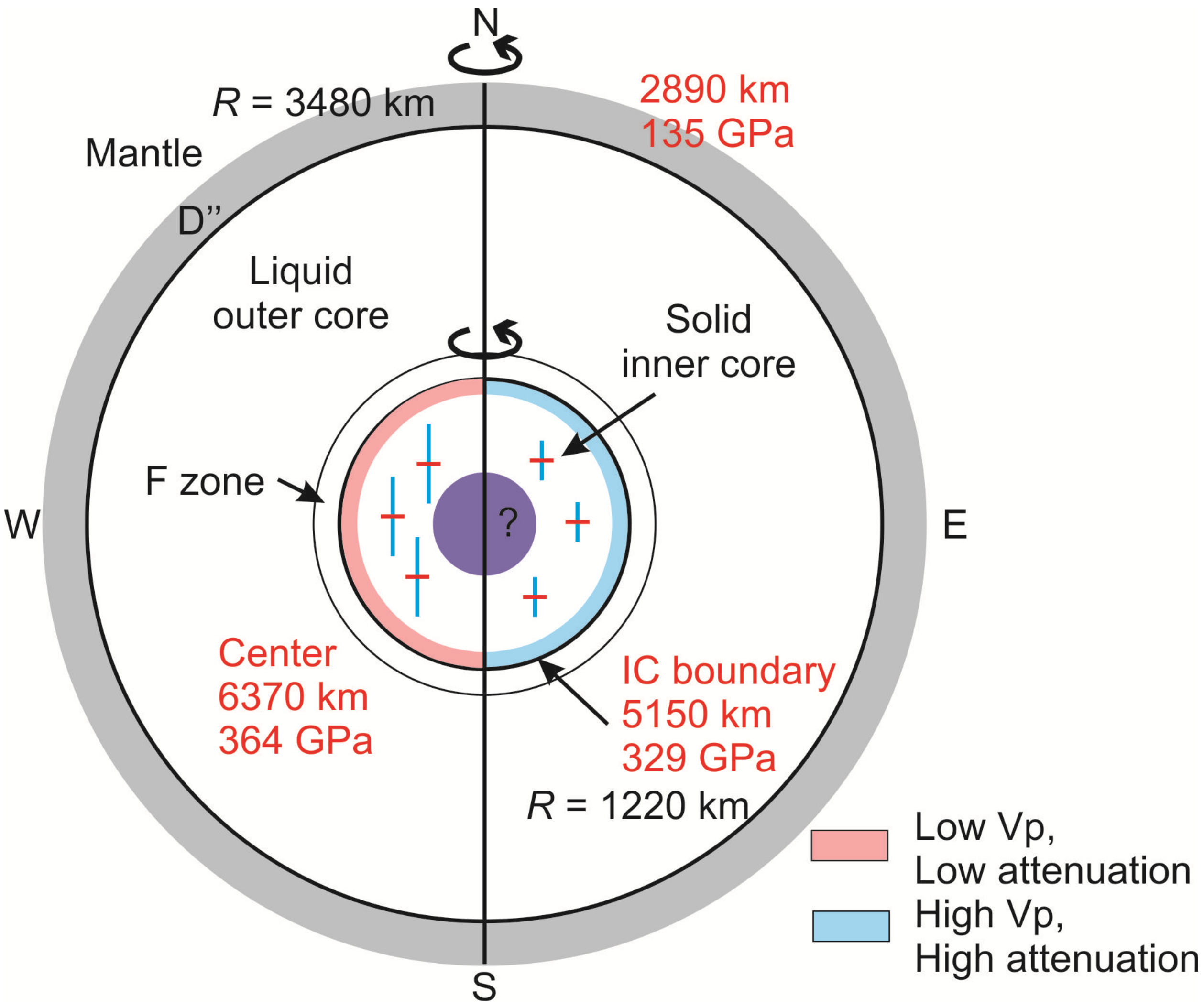
<u>High-pressure experiments and</u>
<u>Ab initio theoretical computations:</u>

Metal/silicate partitioning of elements

Phase diagrams of Fe-Ni and their alloys

Equations of state and sound velocity of Fe-Ni and alloys

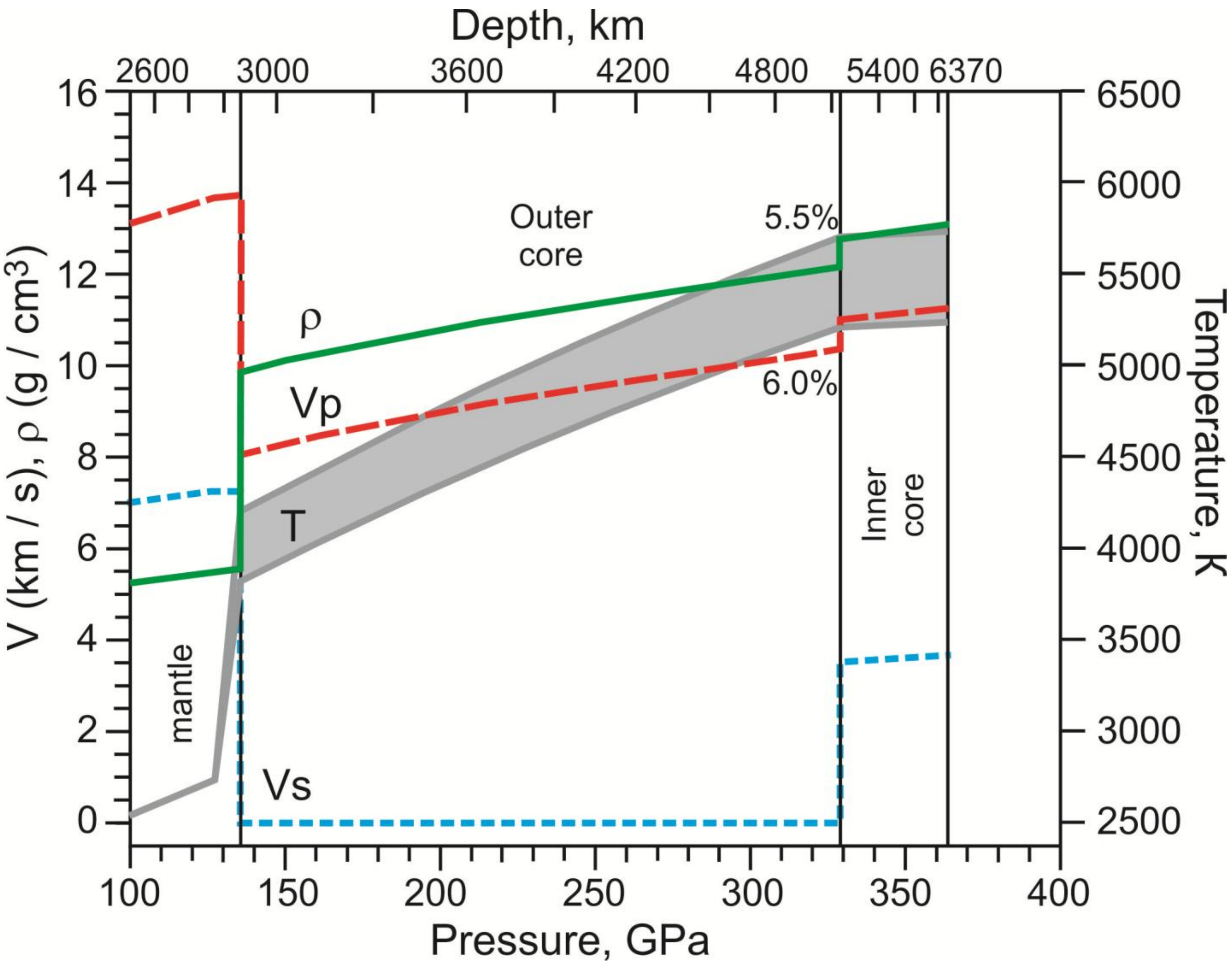
Seismological features of the Earth's core



Sources (Souriau and Calvet, 2015 Tr Geophys II; Deuss, 2014 Ann Rev EPSL)

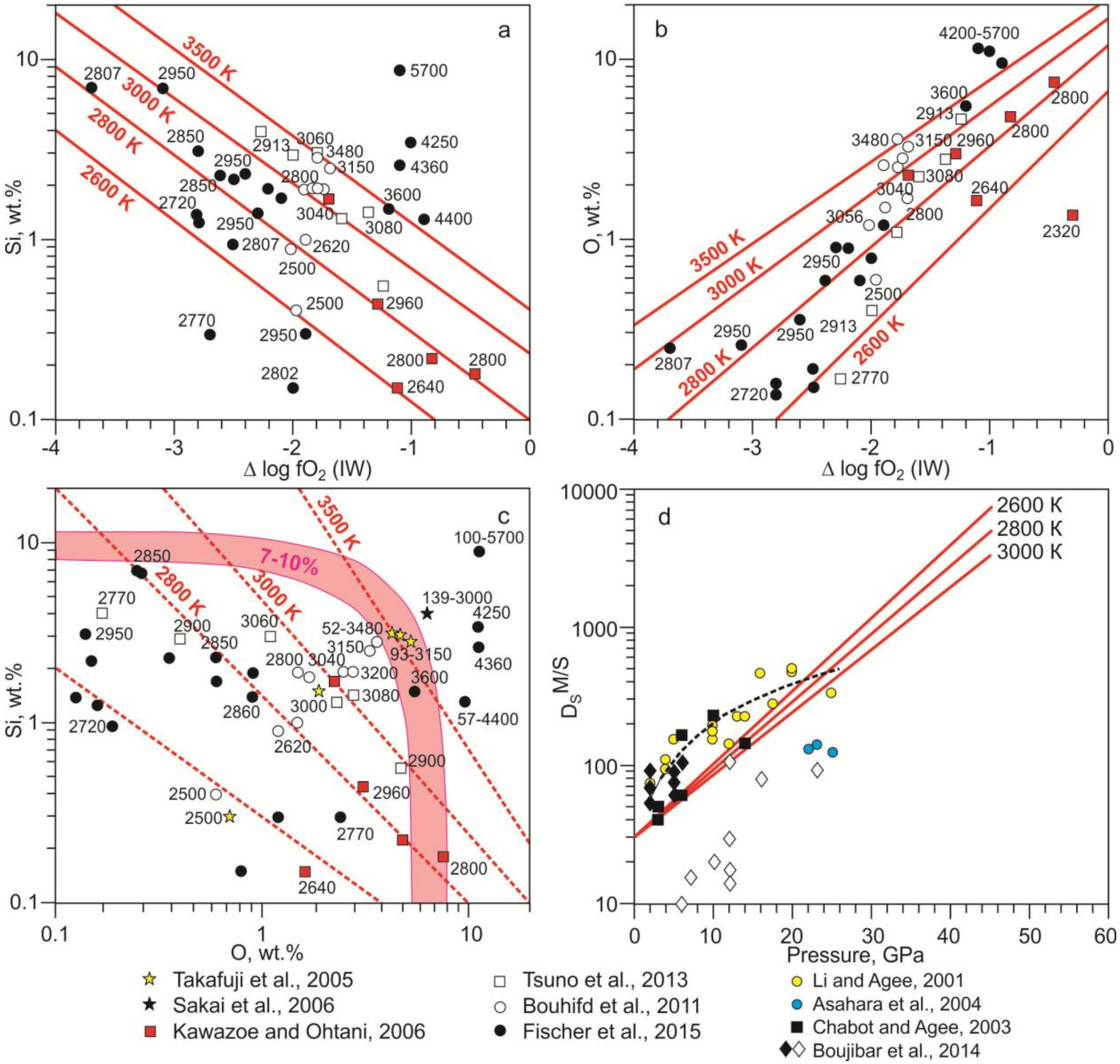
Density and velocity profile in the Earth’s core

PREM Model (Dziewonski and Anderson, 1981)



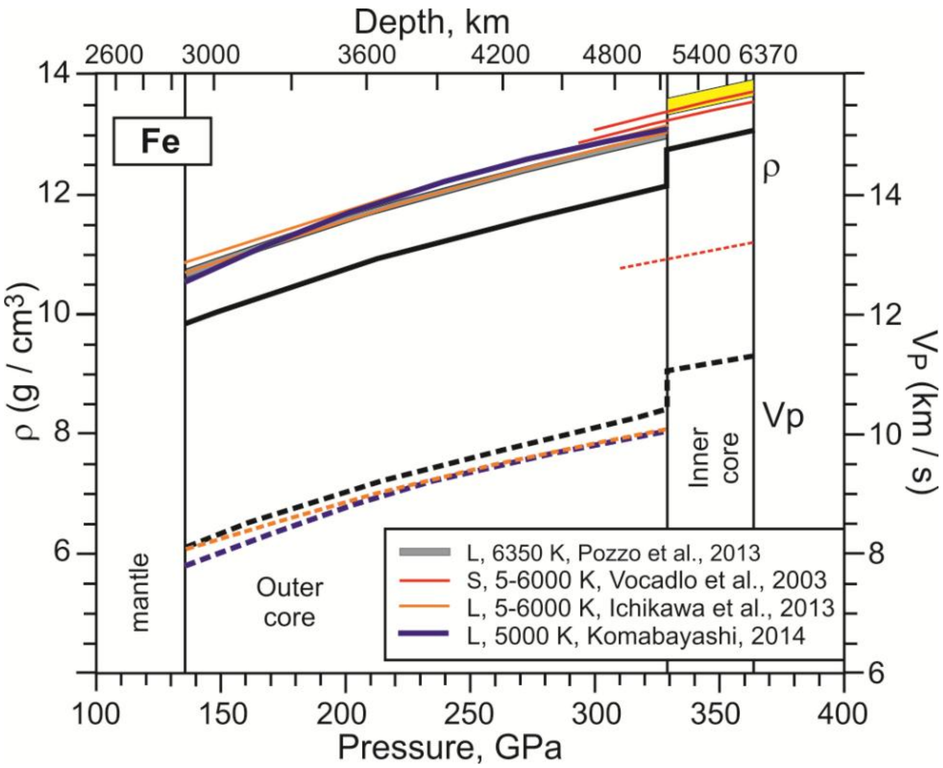
Metal-silicate partitioning experiments

Si and O should be major light elements in the core. However the role of other elements may be underestimated



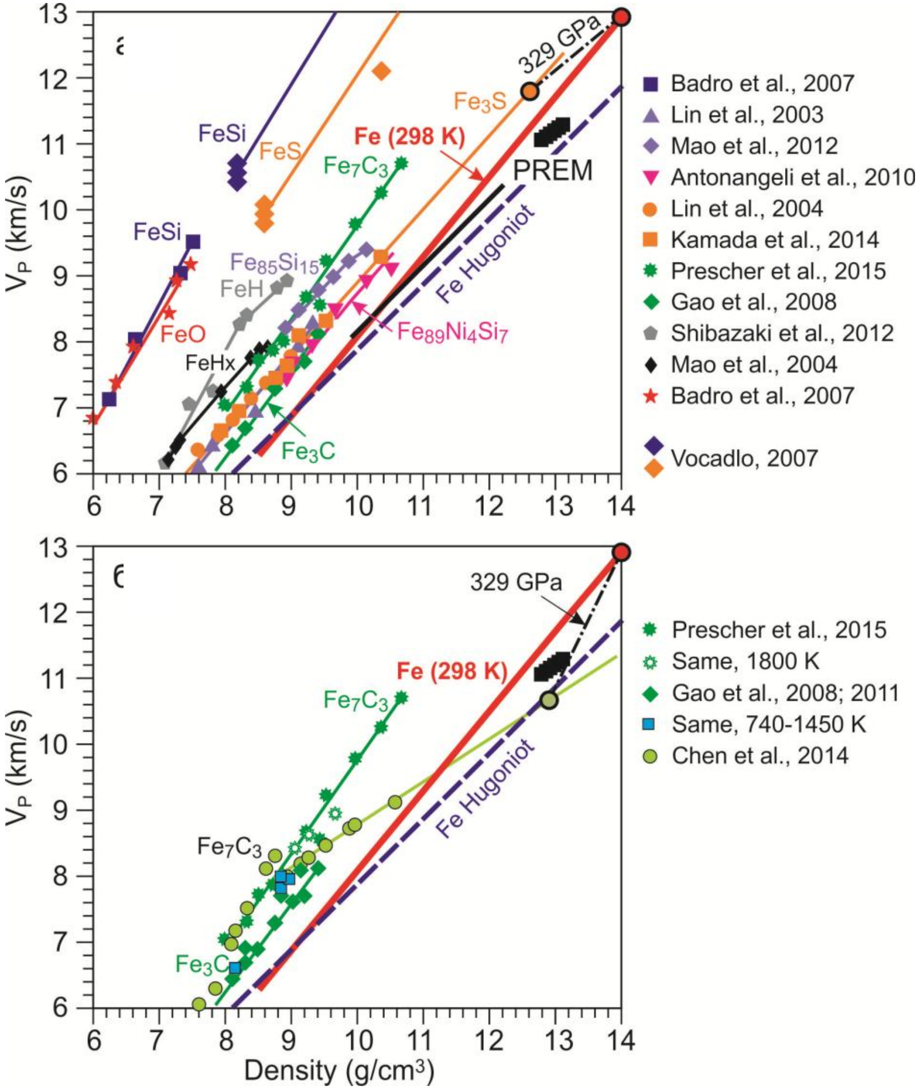
Density deficit in the Earth’s core

Comparison of Fe EOS and PREM

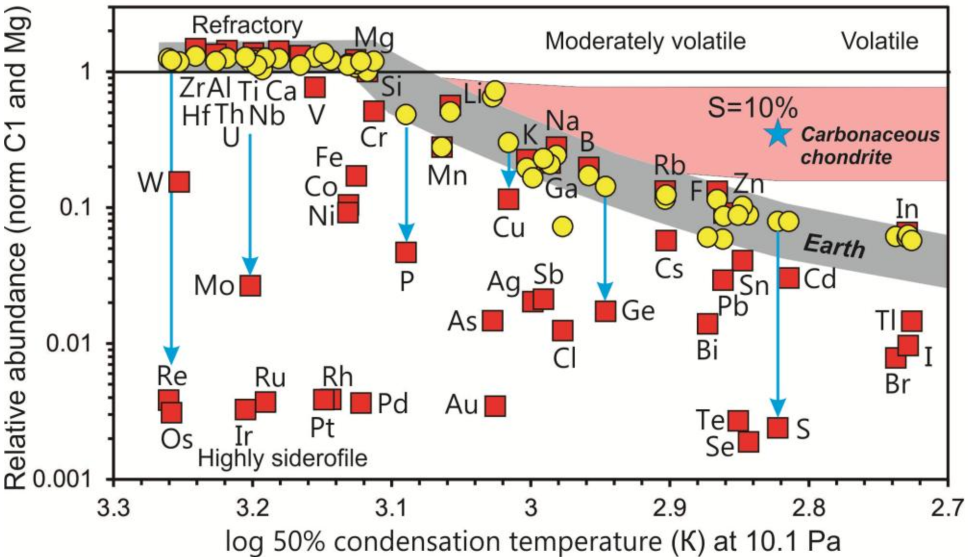


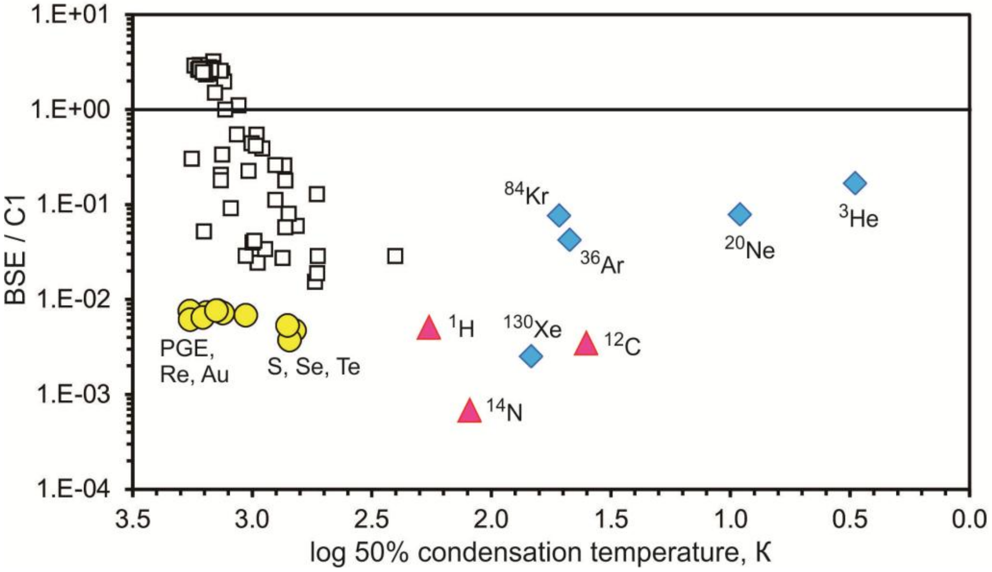
Density deficit
5-10 % liquid outer core
3-6 % solid inner core

Birch diagram



Earth volatility trend and core composition



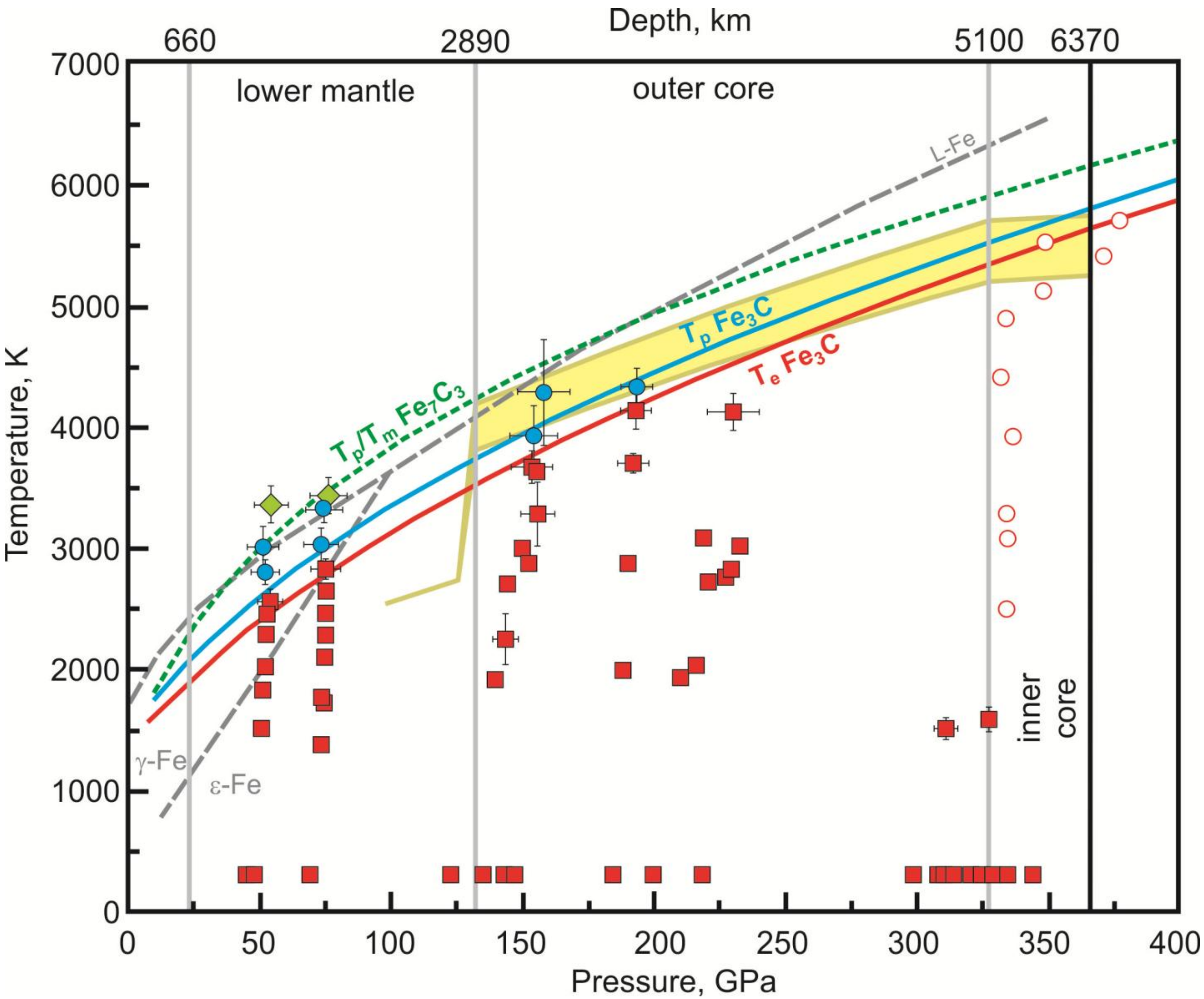


McDonough, 2014 Tr Geochem II

Models of core composition

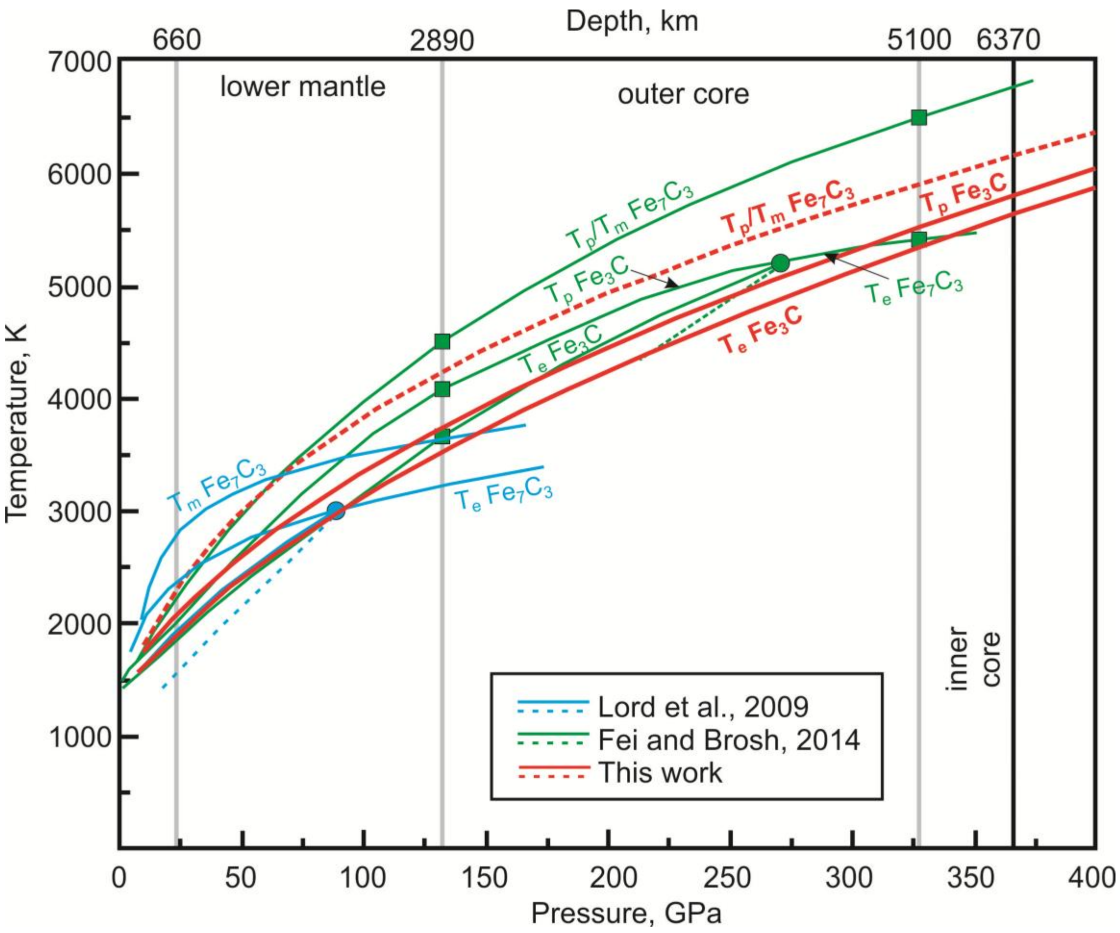
	Model		**% Core**	**% BSE**
	Si	O		
H	600		**74.1**	25.9
C, %	0.2		**88.8**	11.2
N	75		**94.7**	5.3
O, %	0	3.0	3.3*	96.7*
Si, %	6.0	0	12.0*	88.0*
P, %	0.2		**91.4**	8.6
S, %	1.9		**97.3**	2.7
Cl	200		**84.9**	15.1
V	150		50	50
Cr, %	0.9		62.1	37.9
Mn	300		12.1	87.9
Fe, %	85.5	88.3	86.7	13.3
Co, %	0.25		93	7
Ni, %	5.2	5.4	92.7	7.3
Cu	125		65	35
Mo	5		98	2
Pd	3.1		98	2
W	0.47		91	9
Re	0.23		98	2
Pt	5.7		98	2

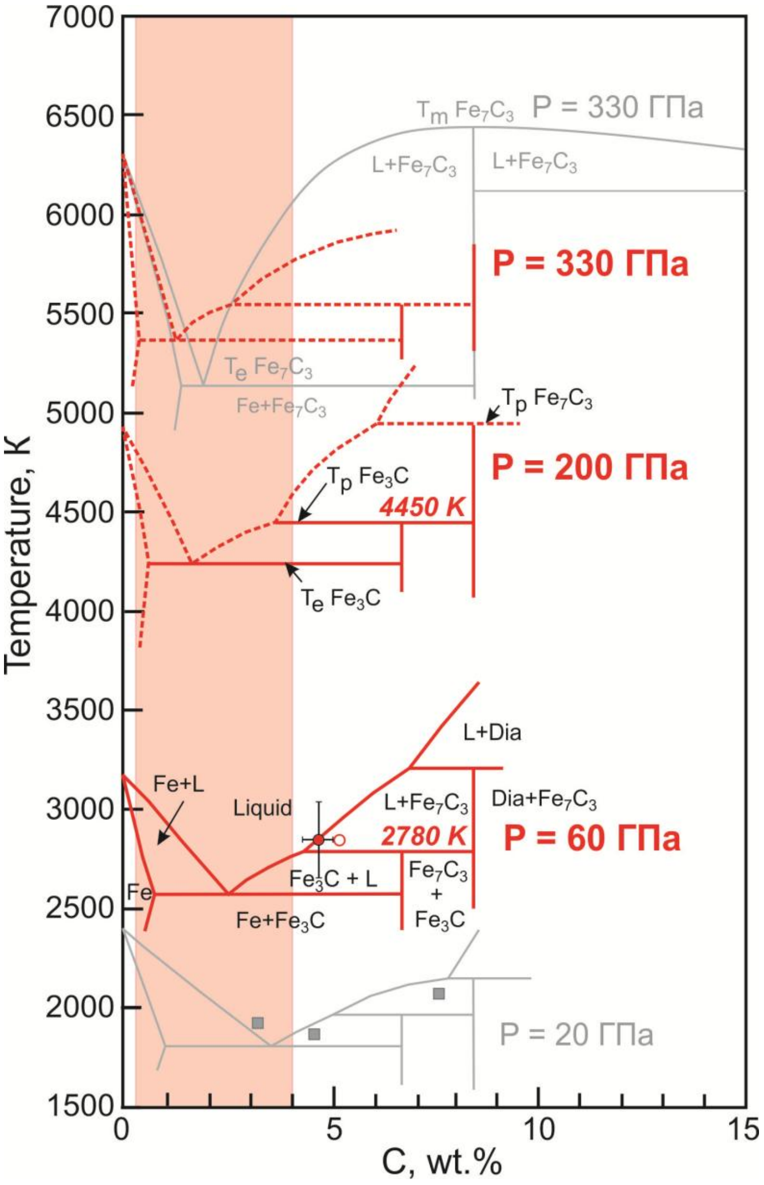
Carbon in the core. Fe_3C melting to 200 GPa



Takahashi et al., submitted

Carbon in the core. Comparison

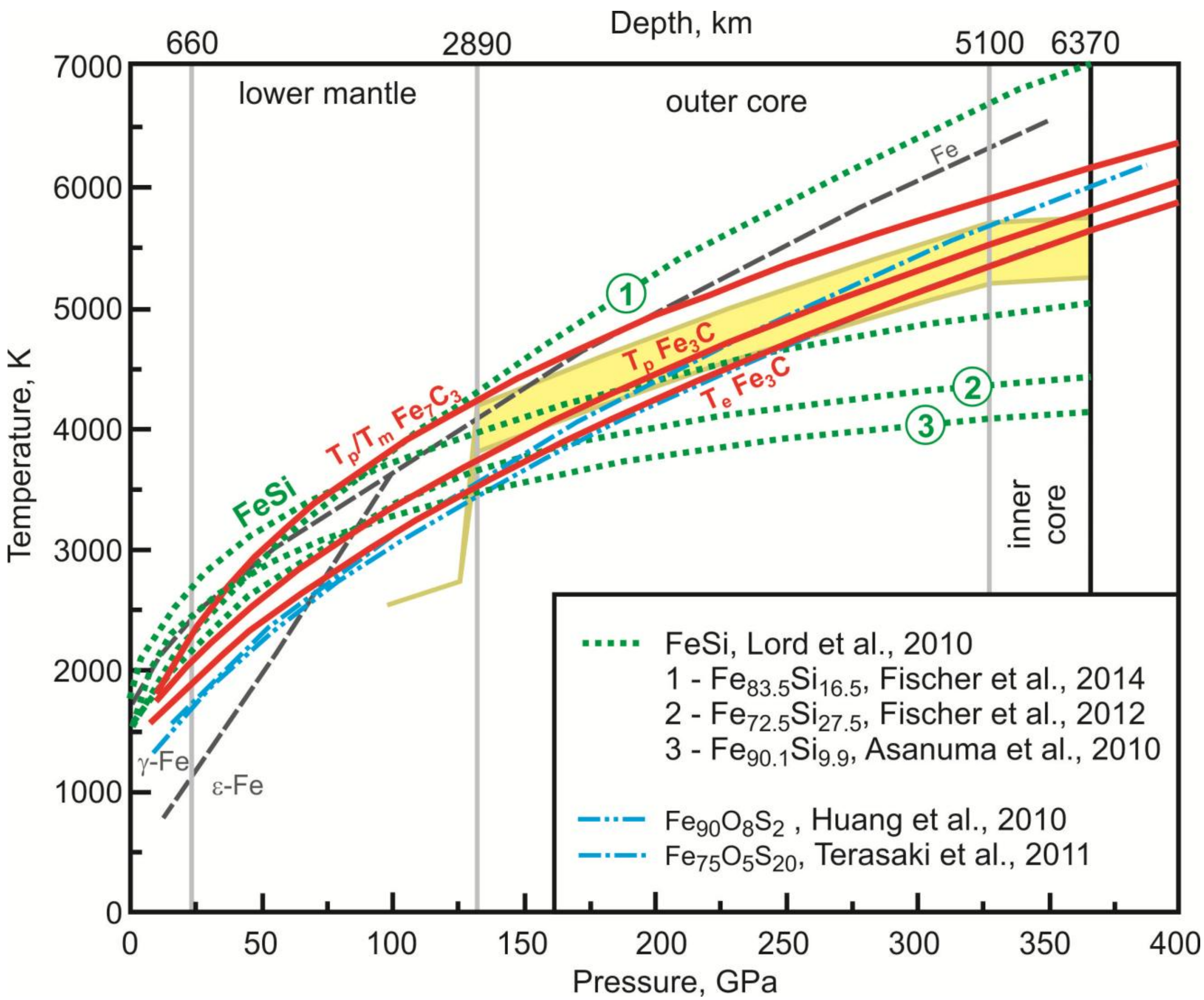




0.5-4 wt % C is acceptable for crystallization of Fe carbide in the core

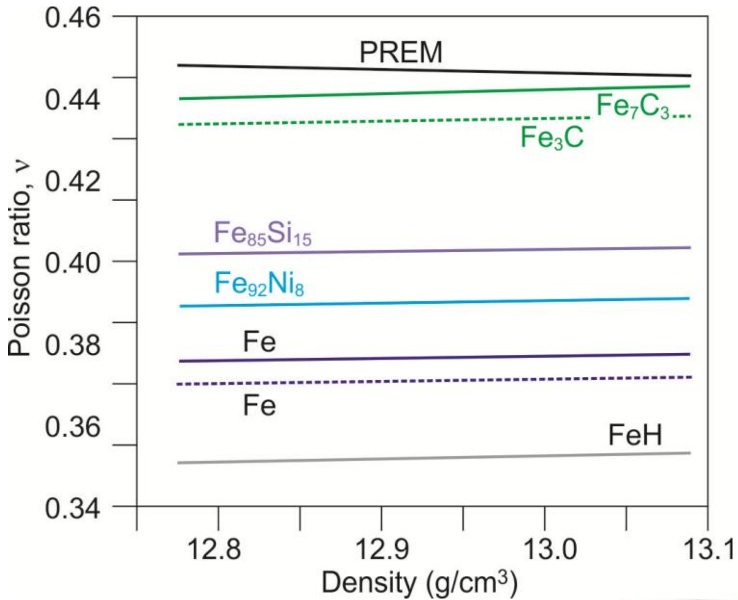
Liquidus phase for inner core crystallization

Comparison of melting in Fe-Si, Fe-O, and Fe-C systems. Liquidus Fe-carbide is possible.

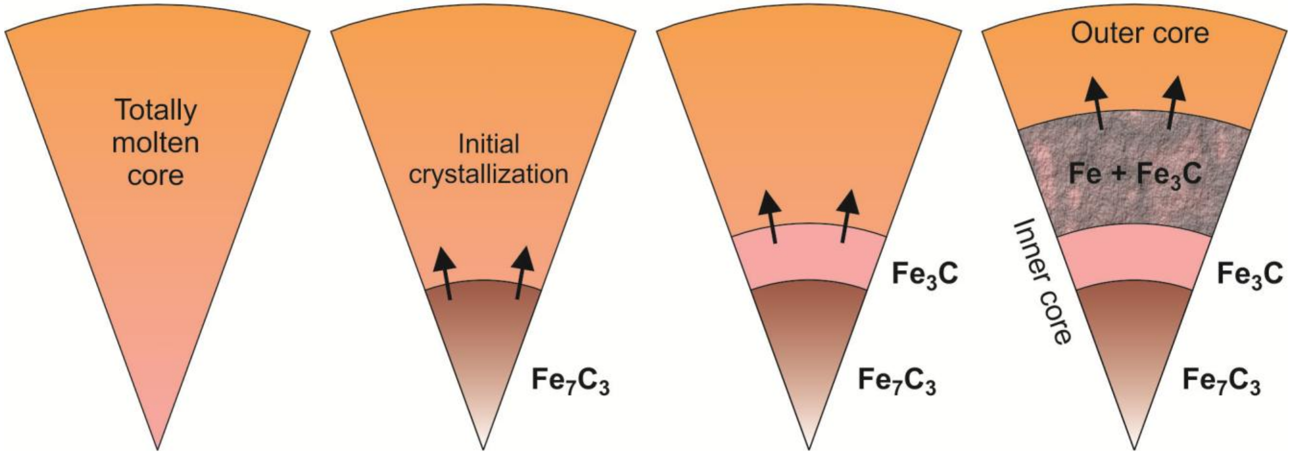


Fe carbide in the inner core

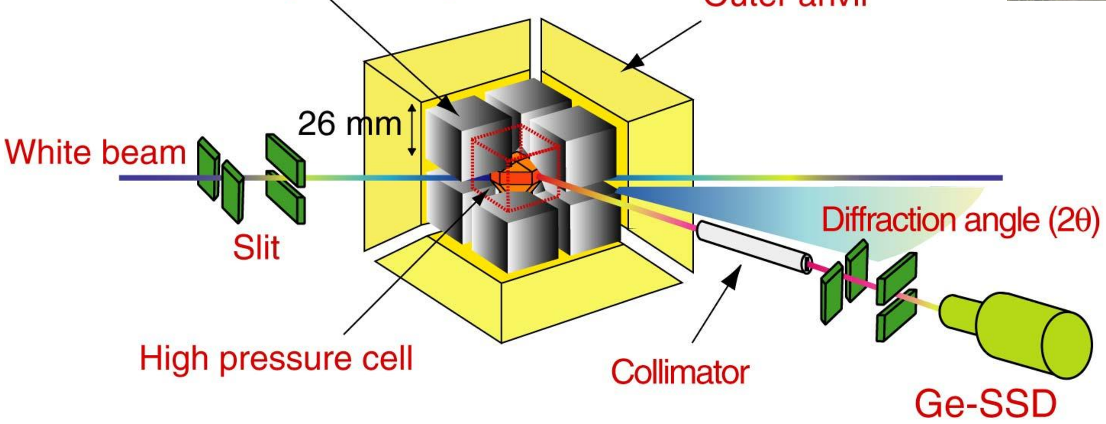
Poisson ratio and shear modulus of Fe-carbides
(Prescher et al., 2015 Nat Geosci)



Model for Fe carbide in the core based on the phase diagram
(Takahashi et al., submitted)

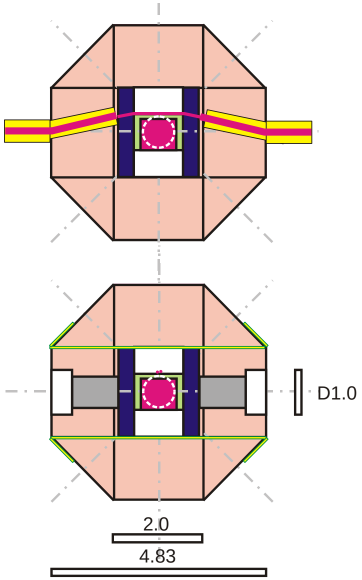


In situ X-ray diffraction experiments at SPring-8



6.24/2.0 cell Co-MgO   Gaskets th.2.0, width 3.4

Anvils 26.0 Toshiba (Tungalloy) TF05, TEL 2.0



■ TiB_2 D 1.8/1.1, l =2.0 = 0.8+1.2

□ MgO

■ $MgCO_3$:SiO_2(Qu) = 1:1 mol

▬ WRe(3/25) D0.15

— WRe(3/25) D0.05

■ Diamond powder 5mkm D=0.7

🟩 BN

— Mo 2.0*6.0, th.=0.05

■ Co doped MgO

▭ BN D=0.5/0.3 (in Gasket)

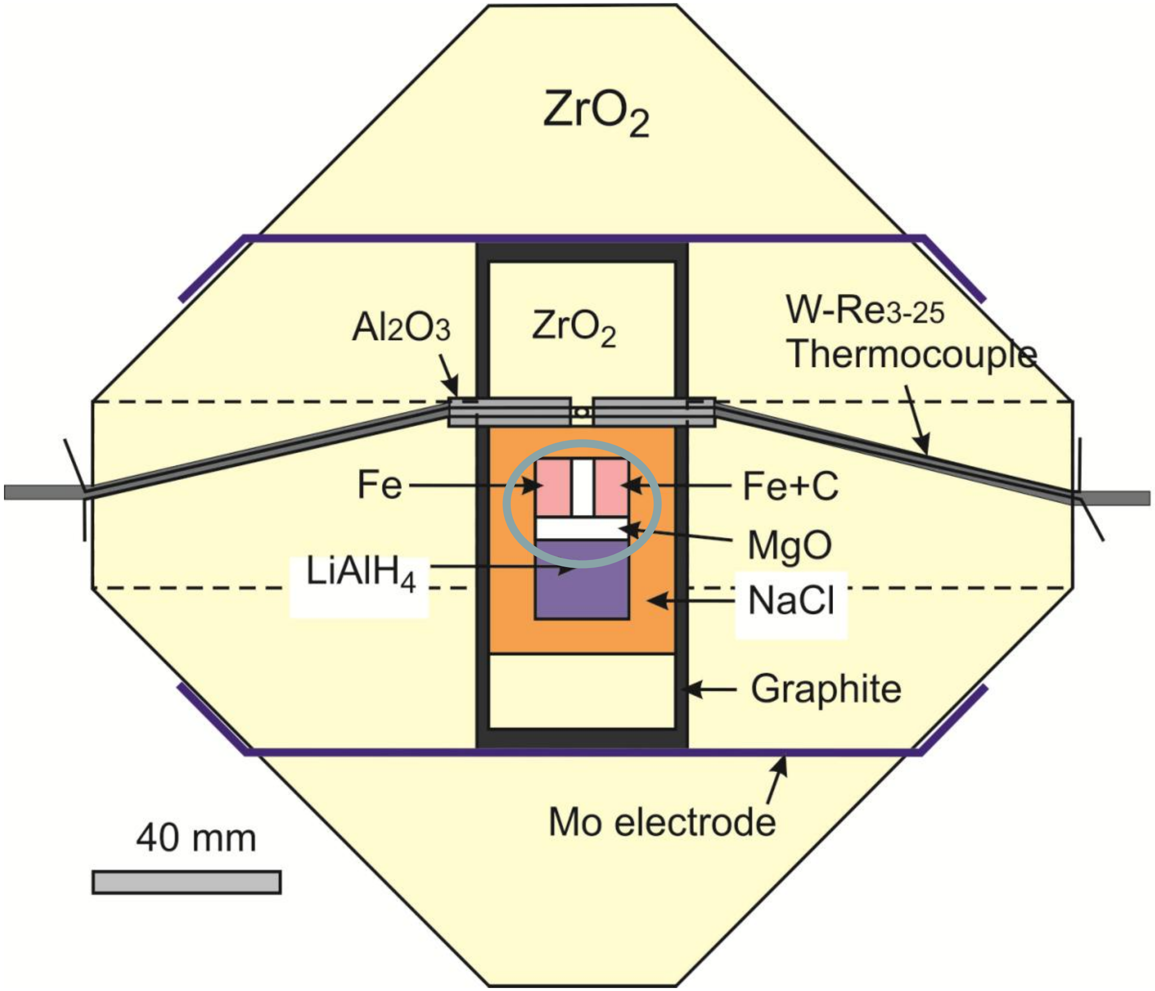
▭ BN D=0.4/0.2 (in PM)

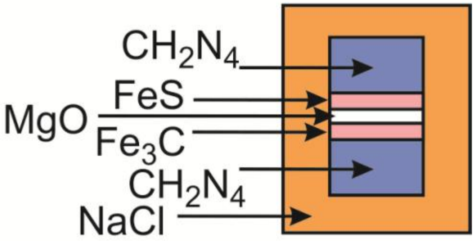
Speed Mk-II with oscillation system

Examples of cell assemblage for experiments

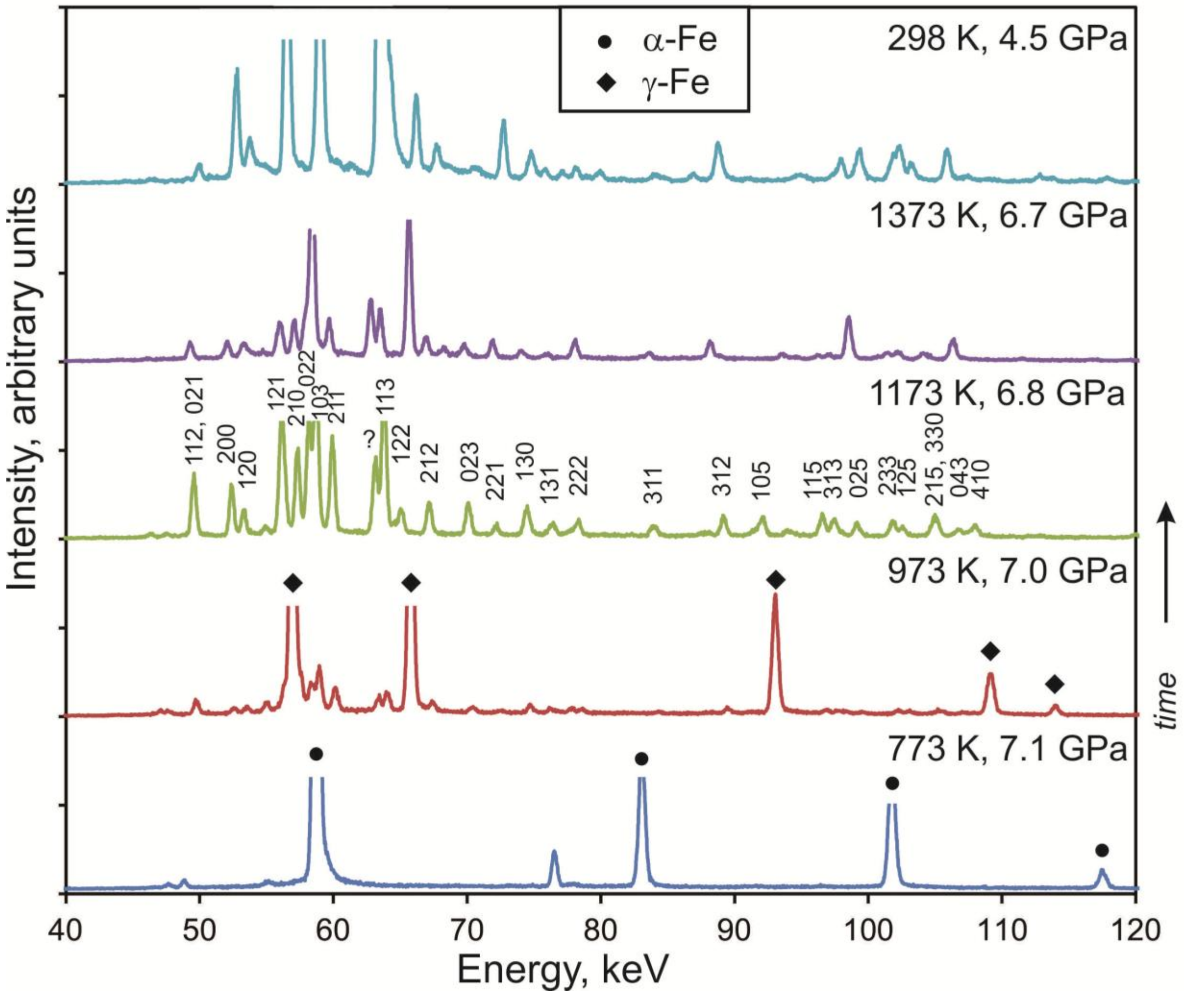
TEL 12 mm for 6-7 GPa
TEL 3.5 mm for 17-20 GPa

H-source: $LiAlH_4$
NH-source: explosive



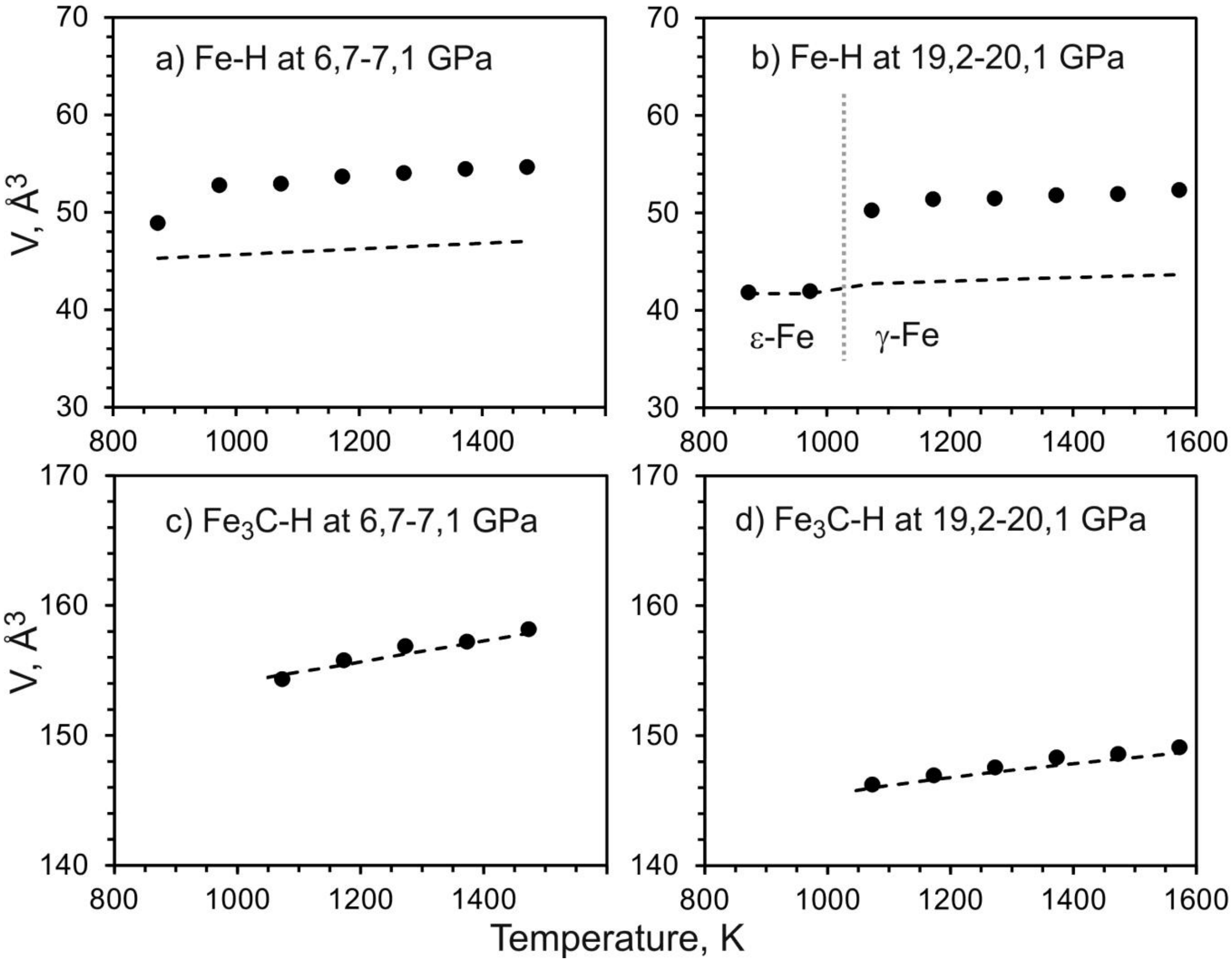


Formation of Fe_3C carbide from Fe+C+H source



Hydrogenation of Fe_3C carbide

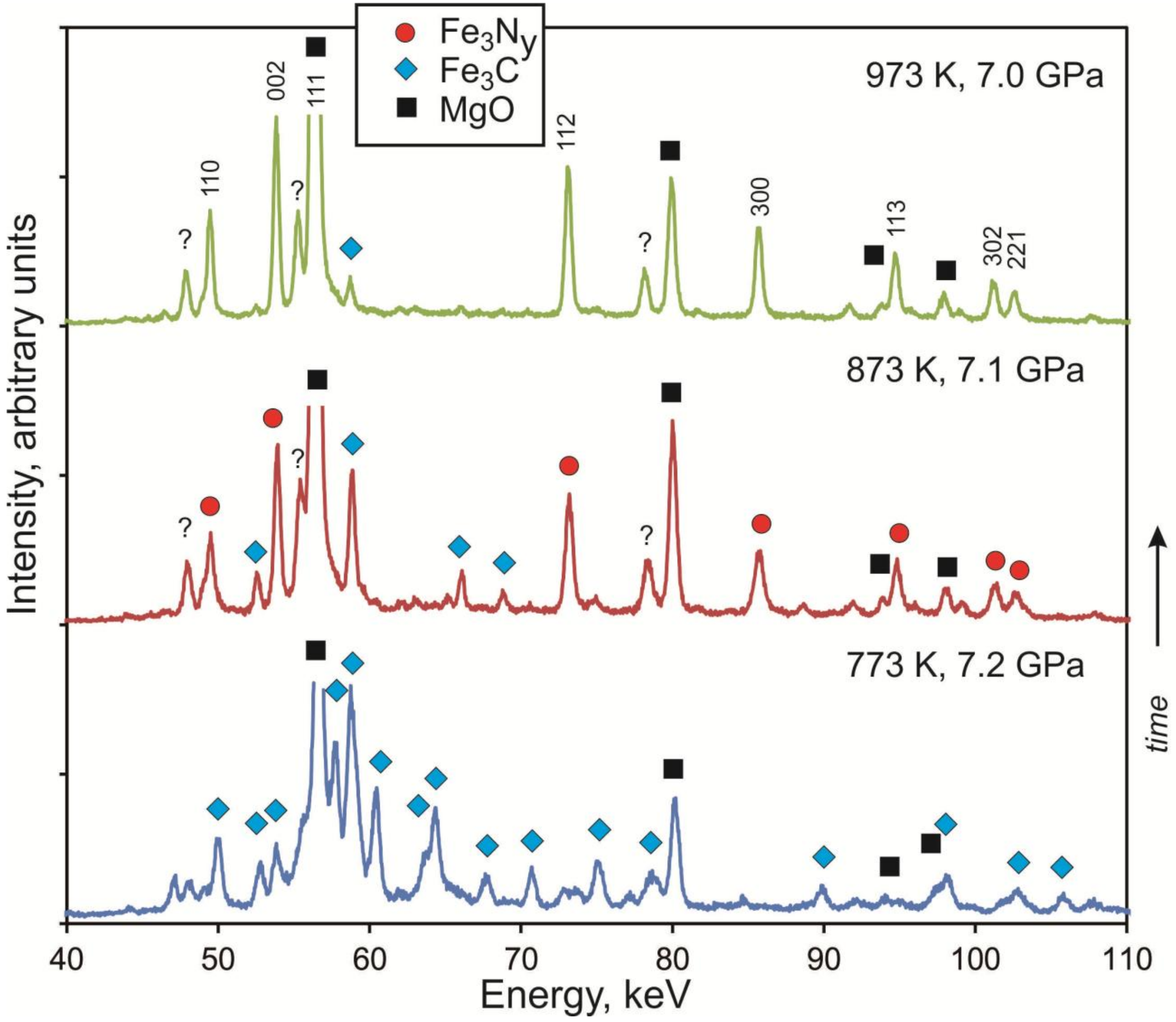
X_H in Fe_3C carbide is below 0.05 at.%



Similar with the results of Terasaki et al., 2014

Nitrogenation of Fe_3C carbide

Fast formation of ε-Fe_3N_y at 873-973 K



Nitrogenation of Fe_3C and FeS by CH_2N_4

T, K	V_{MgO}, Å^3	P_{MgO}, GPa	Fe_3C	FeS
Run #3				
673	72.53 (3)	7.2 (1)	Fe_3C	V
773	72.78 (3)	7.2 (1)	Fe_3C	V
873	73.07 (2)	7.1 (1)	$Fe_3C \rightarrow Fe_3N_y$	V
973	73.38 (3)	7.0 (1)	Fe_3N_y	V
1073	73.69 (2)	6.9 (1)	Fe_3N_y	V
1173	73.97 (3)	6.9 (1)	Fe_3N_y	V
1273	74.30 (2)	6.8 (1)	Fe_3N_y	V
Run #4				
873	69.16 (6)	17.9 (2)	Fe_3C	IV
973	69.68 (5)	16.9 (2)	$Fe_3C \rightarrow Fe_3N_y$	IV
1073	69.95 (3)	16.7 (1)	Fe_3N_y	IV
1173	70.23 (1)	16.5 (1)	Fe_3N_y	V
1273	70.51 (2)	16.3 (1)	Fe_3N_y	V
1373	70.77 (2)	16.2 (1)	Fe_3N_y	V
1473	71.03 (2)	16.1 (1)	Fe_3N_y	V

IV and V are stable phases of FeS

Conclusions

- Core remains most enigmatic layer in the Earth's deep interior. The problem of light element is not solved. Silicon and oxygen may be major light elements according to metal-silicate partitioning experiments, however other elements are poorly studied.

- Fe-carbides are reliable candidates for inner core according to new phase relations and EOS studies even if the total carbon content in the core is ca. 1wt.%.

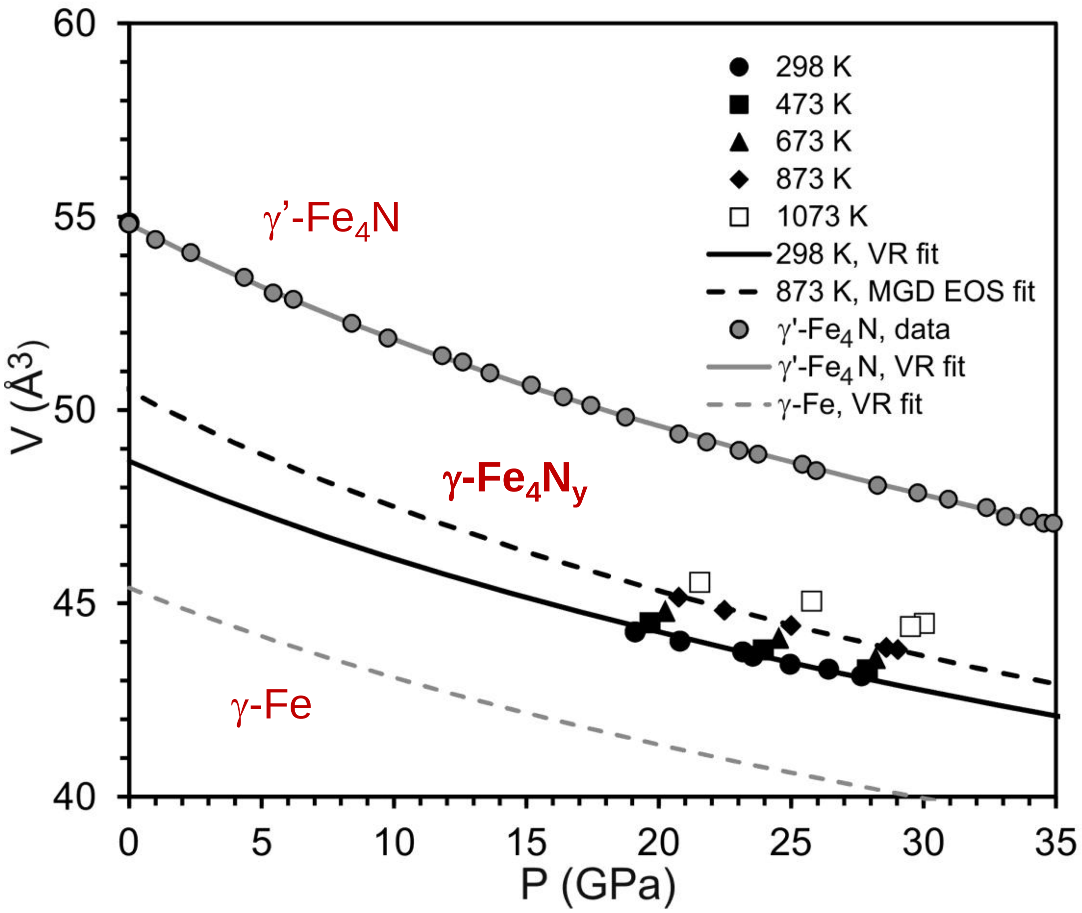
- Further complications arrived from hydrogenation and nitrogenation experiments. From experiments at 6-20 GPa and temperatures up to 1600 K we obtained following sequence of relative reactivity/stability of Fe-compounds in the studied PT-range: Fe-S > Fe-N > Fe-C > Fe-H > Fe. Fe-nitride are ready to replace Fe-carbides at high pressures.

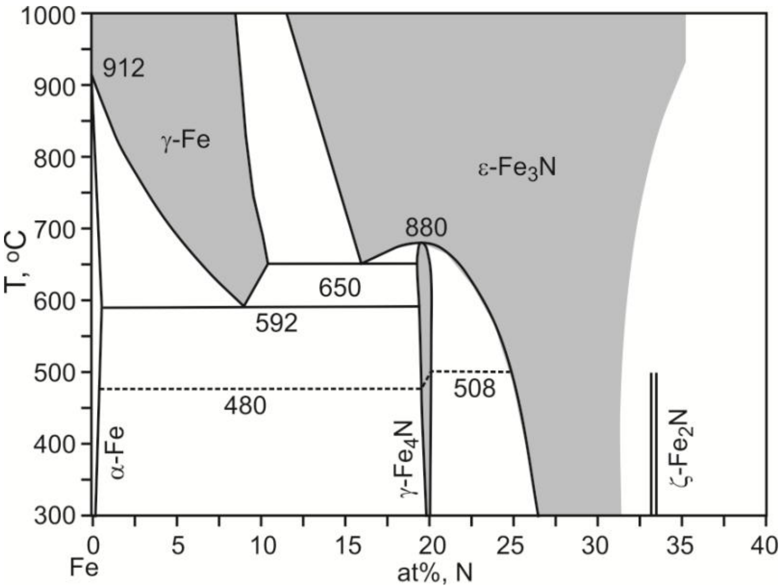
- For future research we need to determine liquidus surfaces in Fe-Si-C and Fe-O-C systems.

- Blank

Nitrogen effect on γ-Fe at 20-30 GPa

Compressibility of γ-Fe_4N_y , y = 0.35(1) (N = 1.8 wt.%)





Fe-N phase diagram at 1 atm

γ'-Fe_4N (Guo et al., 2013)
γ-Fe (Komabayashi and Fei, 2010)

Conclusions

- In situ X-ray diffraction experiments were conducted at SPring-8 synchrotron radiation facility on hydrogenation and relative stability of Fe, Fe_3C, FeS and Fe_3N_x at 6-20 GPa and temperatures up to 1600 K. We obtained following sequence of relative reactivity/stability of Fe-compounds in the studied PT-range:

  Fe-S > Fe-N > Fe-C > Fe-H > Fe.

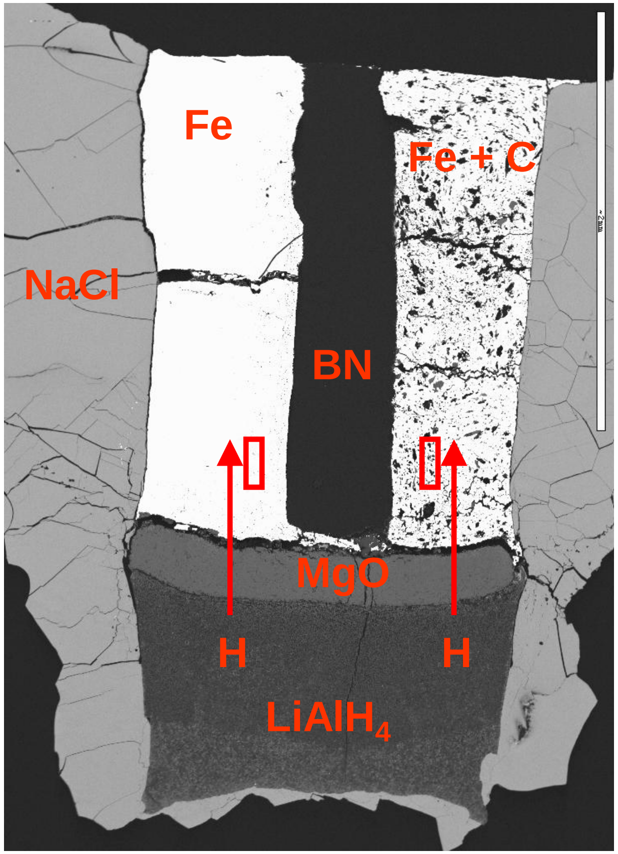
- We determined hydrogen content of Fe-carbide, Fe-sulfide, and Fe. The data for Fe is consistent with FeHx stoichiometry with $x \approx 1$. The data for sulfide indicate $x = 0.2$-0.3 in FeSHx. In carbide $x<0{,}04$-$0{,}05$.

- We also tried to study hydrogen incorporation to Fe-nitride, however, the results are qualitative at present, because Fe-nitride have non-stoichiometric composition, which can vary from PT-conditions.

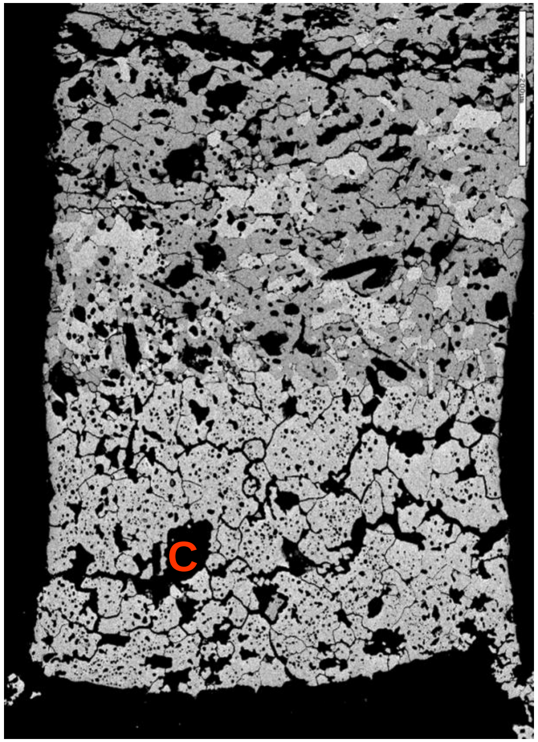
- If extrapolate the results to the Earth core conditions we can suggest that carbon and hydrogen and carbon and nitrogen are poorly consistent in the Earth’s inner core. Although partial substitution of carbon by nitrogen is possible in the case of nitrogen deficit in the system.

Fe + C + H. 6.5 GPa

Fe + C + H, 6.8 GPa, 1473 K

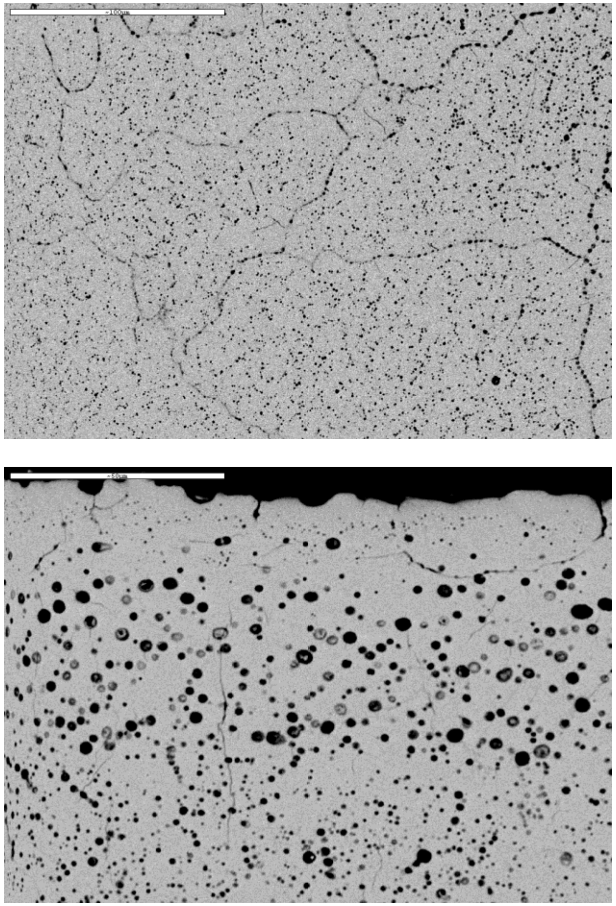


Fe + C



See top-bottom difference:
Not yet determined

FeHx



Fe + C + H. 6.5 GPa

P, GPa	T, K	Fe, Å^3 *	FeH_x, Å^3 *	X_H	Fe_3C, Å^3 *	Fe–C–H	X_H
7.1	773	(α) 11.45	11.57	0.06		(α) 11.57	0.06
6.8	1073	(γ) 11.49	12.04	0.28		(γ) 11.78	0.15
6.5	1373	(γ) 11.63	12.20	0.31	13.01	13.12	**0.06**
4.5	27	(γ) 11.27	11.82	0.29	12.63	12.74	**0.06**

* Atomic volume.

α-Fe and γ-Fe are calculated from EOS. Fe_3C is measured in other exp.

$X_H = [\ V\ (FeH_x) - V\ (Fe)\ ]\ /\ \Delta V_H$

ΔV_H = 1.9 Å^3 – volume increase per hydrogen atom (from Antonov et al., 1979)

1. Fe_3C is preferable relative to FeH
2. H solubility in Fe_3C is most likely very low