Neutron diffraction experiments
under high-pressure and high-temperature conditions at J-PARC:
Hydrogenation of Fe and its implication
for the density deficit of the Earth's core

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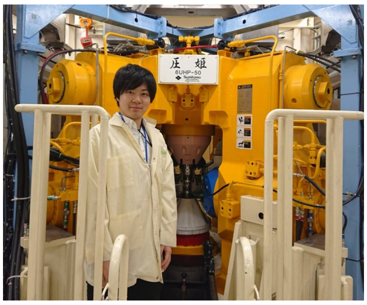


Atsuhime (圧姫) press at J-PARC

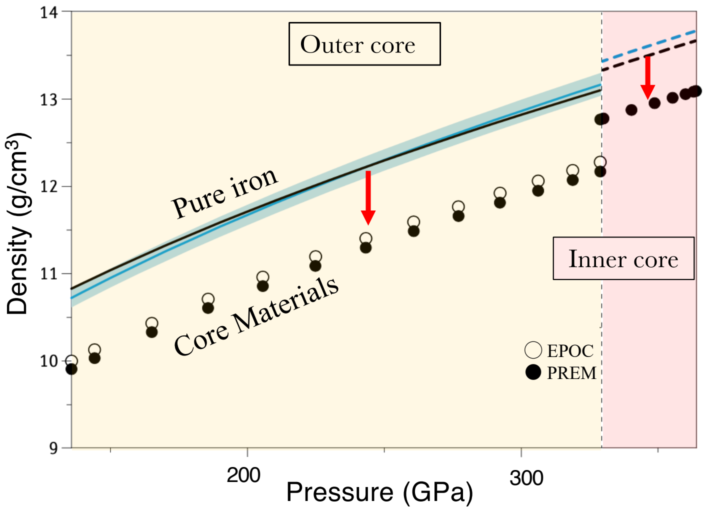
In this presentation, I would like to introduce our recent research obtained using this big press installed at J-PARC, Japan.

Summary of my talk

- ✓ The earth's core is made of iron, but the observed density is lower than that of iron. Light elements reduce the density of iron.
- ✓ Hydrogen is the most likely candidate for light elements in the core. Neutron diffraction under high PT conditions can clarify the mechanism by which hydrogen is incorporated into iron to reduce its density.
- ✓ PLANET beamline for neutron diffraction under high pressure at J-PARC is in international public use.
- ✓ 6-ram multi-anvil press “ATSUHIME (圧姫)” enables neutron diffraction measurements under high pressure and high temperature.
- ✓ Silicon, another candidate of light element, is found to enhance the hydrogen-induced volume expansion of iron.
- ✓ Our results suggest that the amount of hydrogen required for the density deficit needs to be adjusted downwards if Si is contained in the core.

First of all, I would like to show you the summary of my talk.

Density deficit of the Earth's core



after Hirose et al., 2021

- ✓ Outer core: 5 – 10% less dense than pure iron
- ✓ Inner core: 4 – 5% less dense than pure iron
- ⇨ Dissolution of light elements in the core?

H, Si, C, O, S…?

The Earth's core is made of iron. This figure compares pressure dependence on the densities of the pure iron and seismologically determined the core.
You can see considerable density deficit in the outer core and the inter core.
The deficit suggests the dissolution of light elements in the cores.

Hydrogen, a candidate for the light elements in the core

Light elements in the inner core

- Partition coefficients of solid/liquid iron in binary systems:
  Si(~1)>S(~0.8)>H(~0.7)>C(0-0.33)>O(0)

(Hirose et al., 2021; Alfè et al., 2002)

Hydrogen in the core?

- High solubility in iron under *HPHT*
  - Magma Ocean (silicate melt and Fe droplet)
  - Hydrogen supply via the subducting slabs and the core

(Okuchi1997; Tagawa et al., 2022)

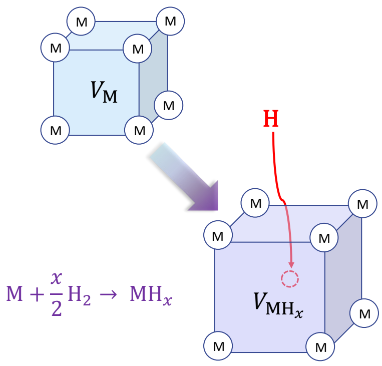
Incorporation of hydrogen reduces the density of Fe?

If the volume of iron does not expand by hydrogen uptake, the density will rather increase.

Among the candidates of light elements in the Earth's core, hydrogen is the most promising candidate based on its geochemical property.
However, it should be noted that the density of iron will rather increase if the volume of iron does not expand by hydrogen uptake.

Volume expansion by hydrogenation of Fe

Hydrogen increases the unit cell of metal by incorporation into the interstitial sites. → Hydrogen-induced volume expansion, v_H



$$v_H = \frac{V_{MH_x} - V_M}{Zx}$$

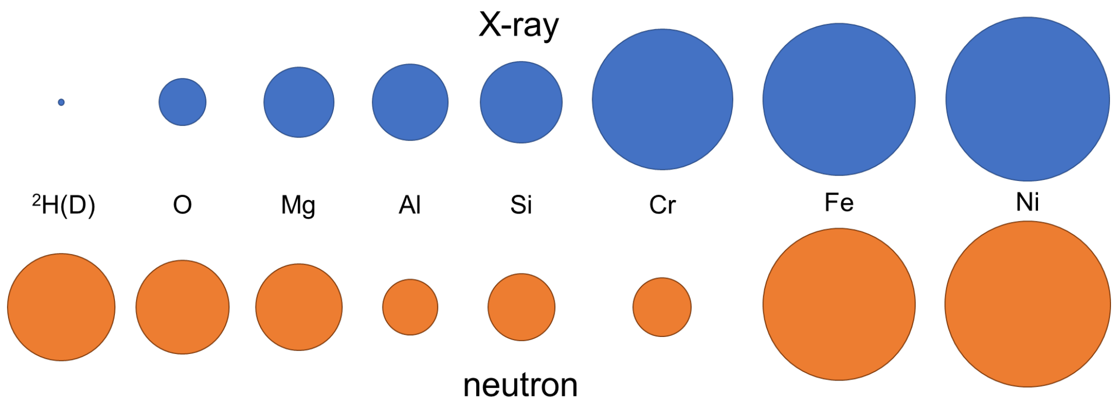
V_{MH_x} : Unit-cell volume of metal hydride
V_M : Unit cell volume of metal
x : Hydrogen atoms in one unit cell
Z : The number of metal atoms in the unit cell

Iron hydride is stable only at high pressure
→ ***In-situ* high-pressure observation is necessary**

cf: H/Fe ~ 5 x10^{-8} at ambient *P*

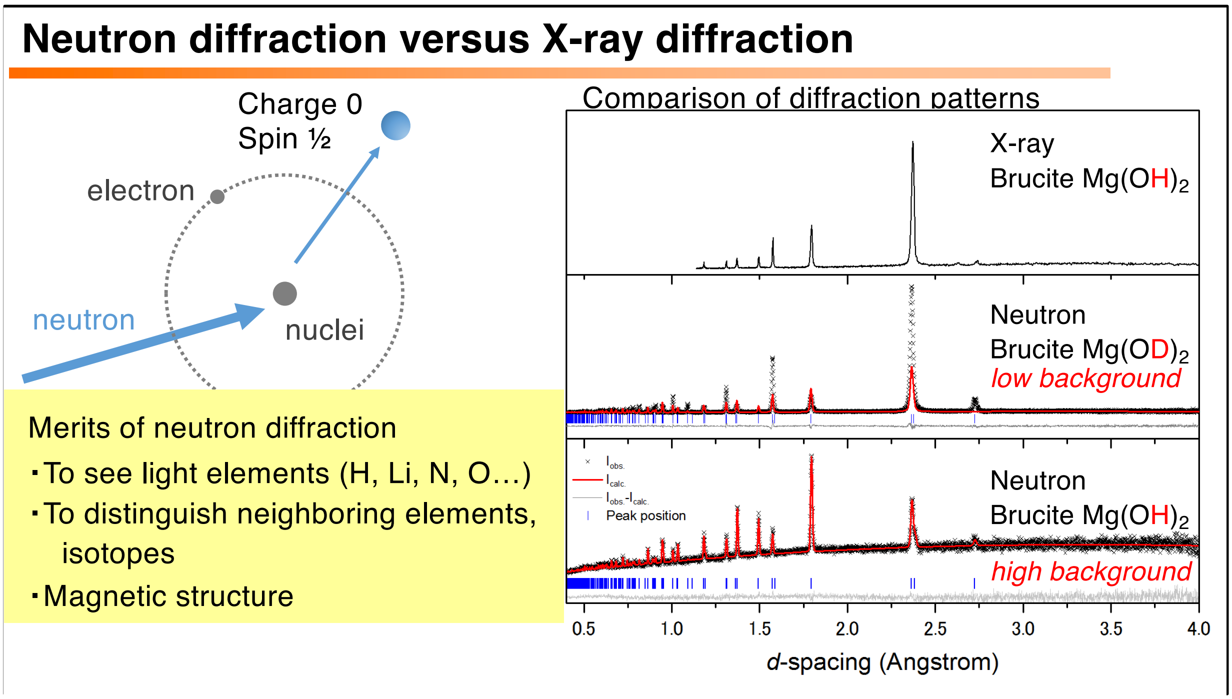
This slide shows the behavior of hydrogen taken into iron lattice.
Here the hydrogen-induced volume expansion is defined as the equation.
To determine the hydrogen-induced volume expansion, we need to conduct in-situ high-pressure observations.

Neutron, a powerful probe for light elements



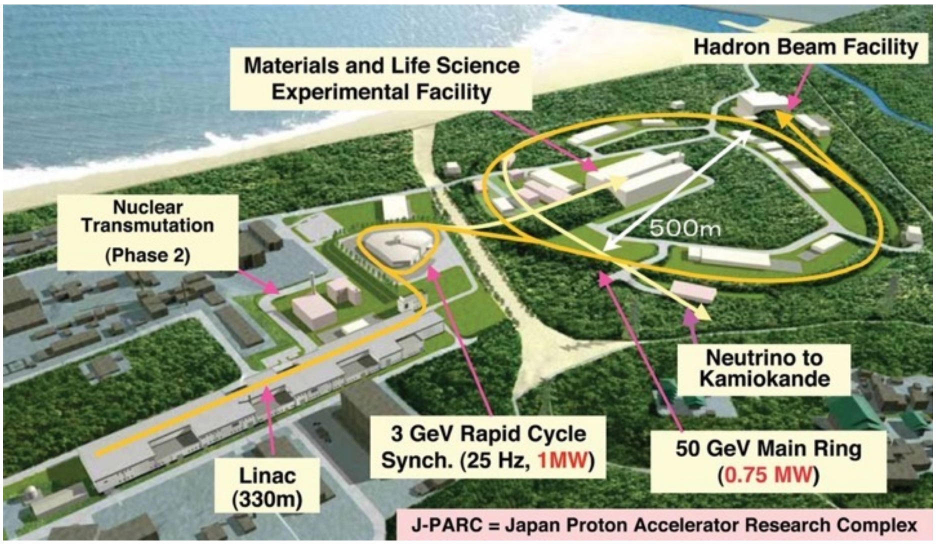
Merits of neutron diffraction
・To see light elements (H, Li, N, O…)
・To distinguish neighboring elements, isotopes

This slides compare scattering cross section of elements both for X-ray and neutron. Neutron has a great advantage to see light elements.



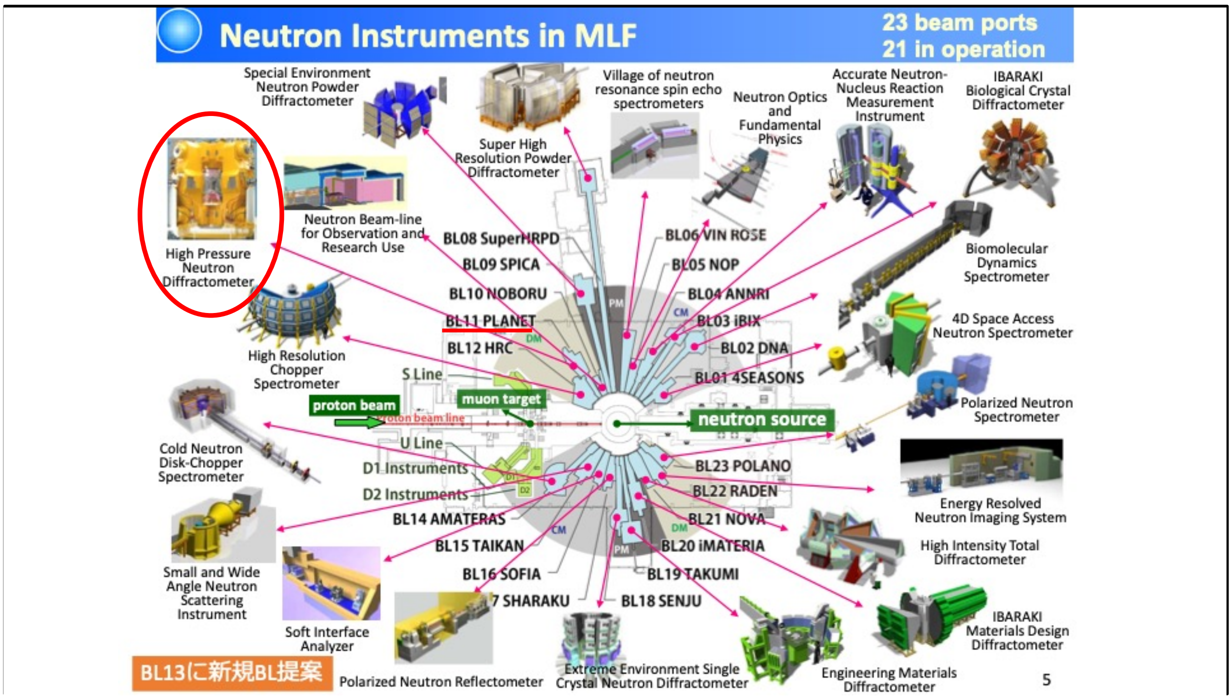
This slide compares neutron diffraction and X-ray diffraction of magnesium hydroxide. Hydrogen generates high background in the diffraction pattern caused by incoherent scattering.
To avoid the high background, we need to use deuterium to measure neutron diffraction of samples containing hydrogen.

J-PARC (Japan Proton Accelerator Research Complex)

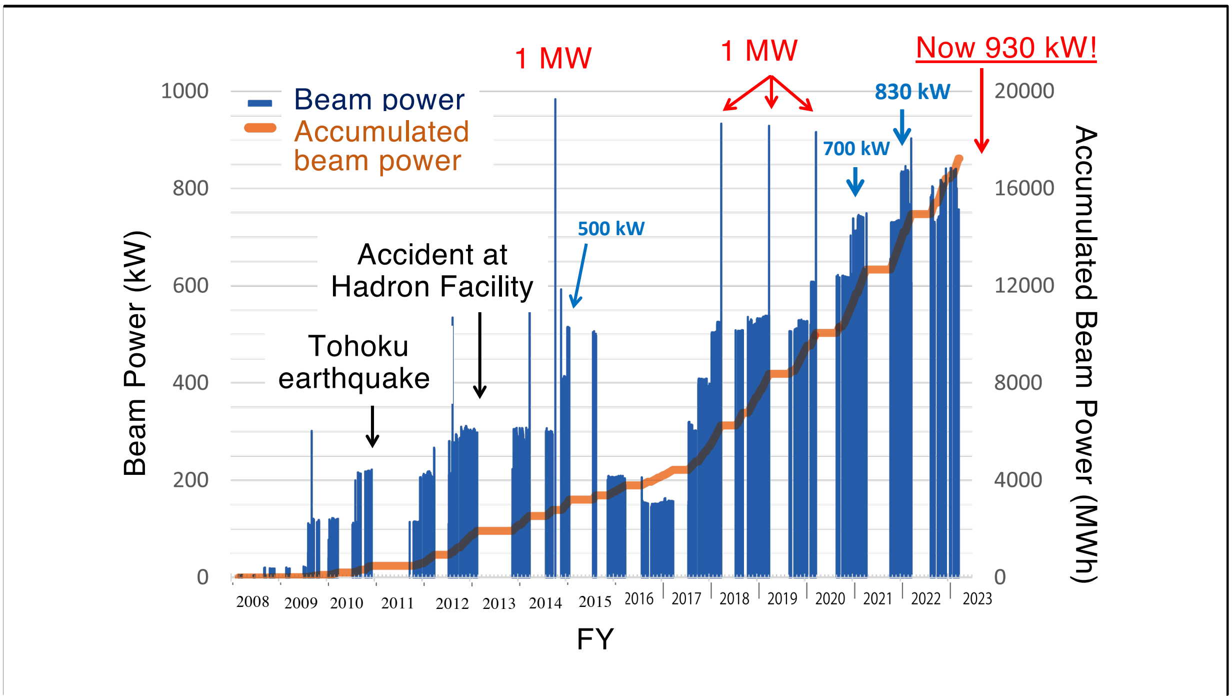


- ✓ About 80 miles (130 km) northeast of Tokyo
- ✓ 23 neutron beamlines, 4 muon beamlines

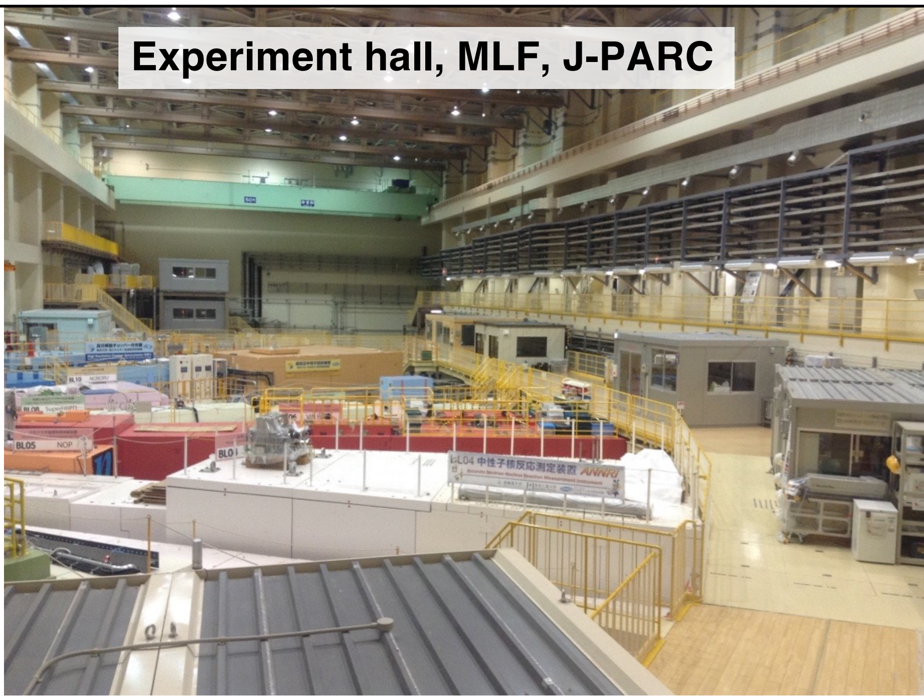
This is an aerial view of the J-PARC facility.



MLF (Material Life Science Facility) in J-PARC has 23 beam ports for neutron and 21 beamlines are in operation.



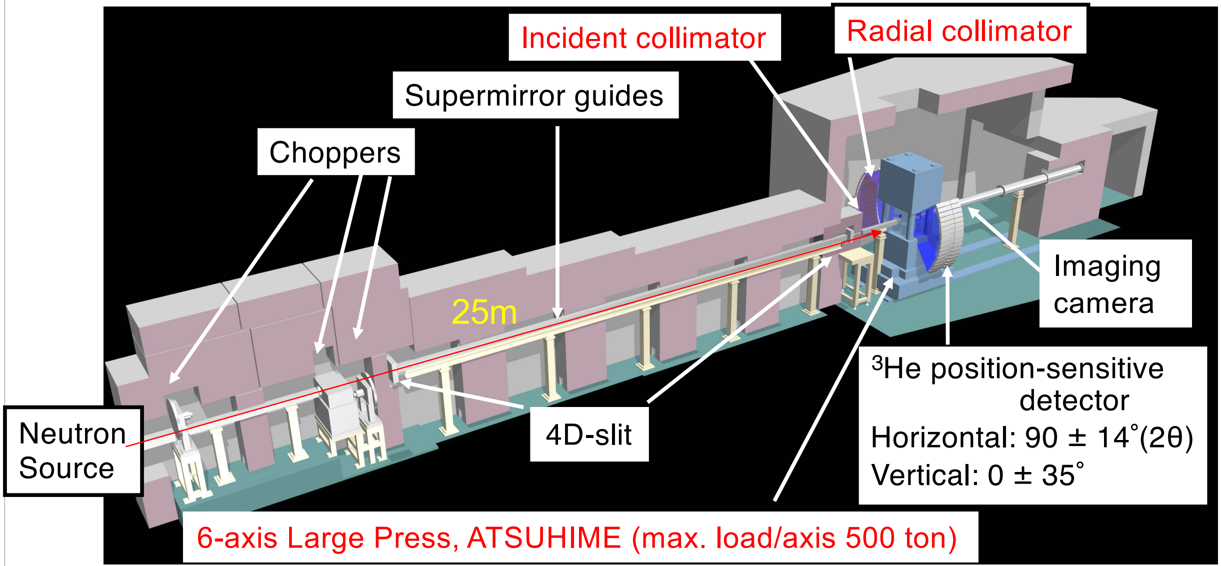
This figure shows beam profile with year.
There are two major shutdowns in 2011 and 2013 caused by the big earthquake and the accident.



This is the photo of the experimental hall.

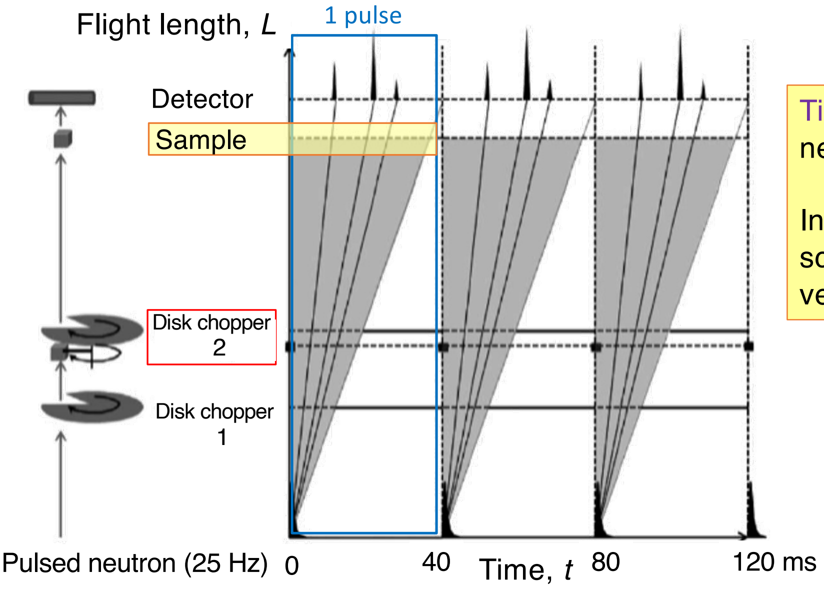

BL-11 PLANET, J-PARC
BL11 PLANET
超高圧中性子回折装置
High Pressure Neutron Diffractometer (PLANET)

BL-11 PLANET (pressure-leading apparatus for neutron diffraction), J-PARC



This is an inside view of PLANET beamline.

BL-11 PLANET (pressure-leading apparatus for neutron diffraction), J-PARC



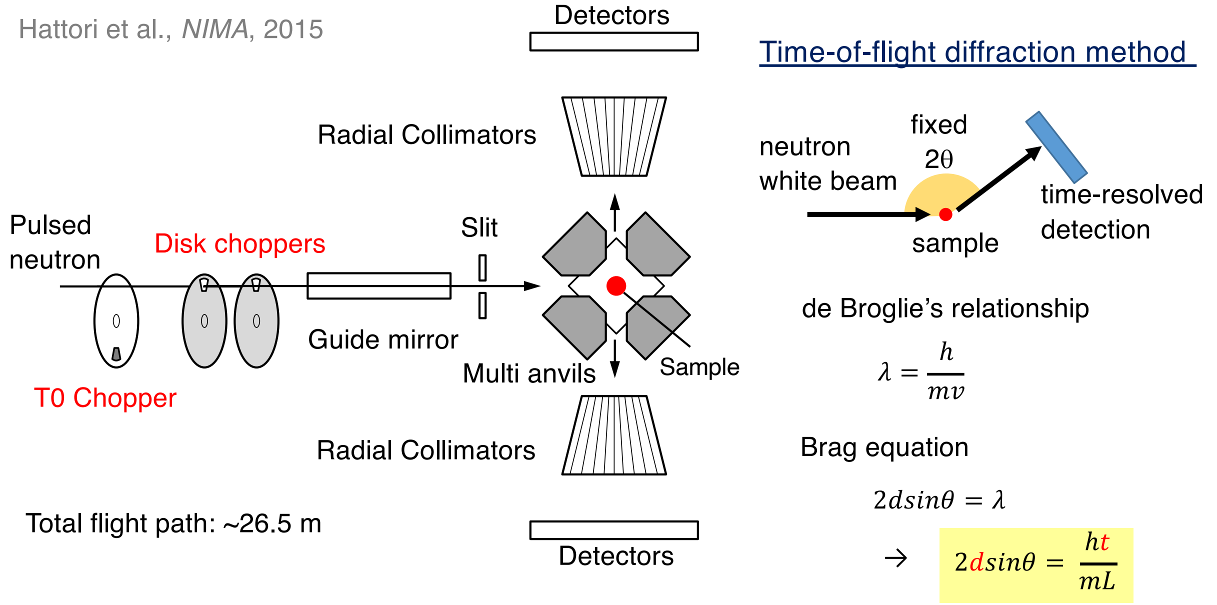
Time of Flight (TOF) neutron diffraction method:

Intensity of elastic scattering changes with the velocity of neutron.

We obtain neutron diffraction patterns with time-of-flight method.
This is similar to the energy dispersive X-ray diffraction measurements.

This photo shows the big press, ATSUHIME, installed at PLANET beamline.

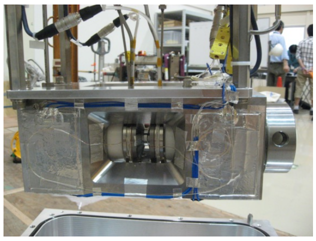
High-pressure neutron diffractometer, PLANET



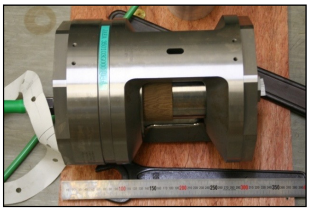
This figure explains the sample geometry in PLANET beamline.
Diffraction angle is fixed at90 degree and the radial collimators determine the sample position to be observed.
We can obtain exclusively the diffraction from the sample without contaminations of surrounding heater, pressure-transmitting medium, gaskets, and so on.

High-pressure instruments used at PLANET beamline

Atsuhime (圧姫) for high P and high T



Mito (水戸) *System* for high P and low T
～ 77 K



Paris-Edinburgh press for high P
～ 40 GPa

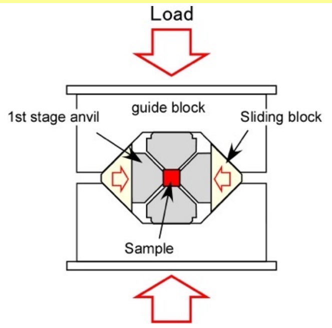
Diamond anvil cell for very high P
～ 100 GPa

Here I display four types high-pressure instruments used in PLANET beamline at MLF, J-PARC.
Each of the instruments has specific pressure and temperature ranges.

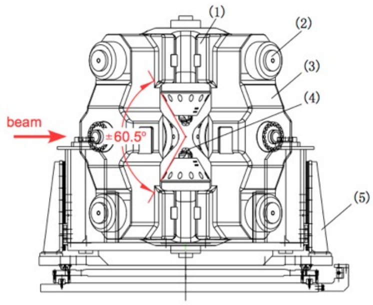
6-rams multi-anvil press “ATSUHIME”

Sano-Furukawa et al., *Rev. Sci. Instrum.*, 2014

- ✓Six independent hydraulic rams compress the cubic space
- ✓No guide blocks enable wide detector coverage. Radial collimators and slits can be placed close to the sample
- ✓Hydrostatic compression is achieved by measuring anvil positions and master-slave control system



DIA-type press: limited window



6-rams press: wide window

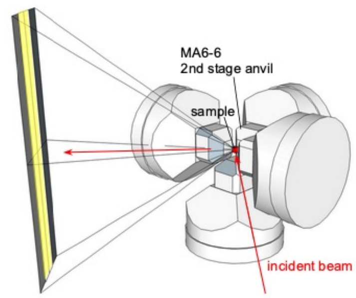
ATSUHIME

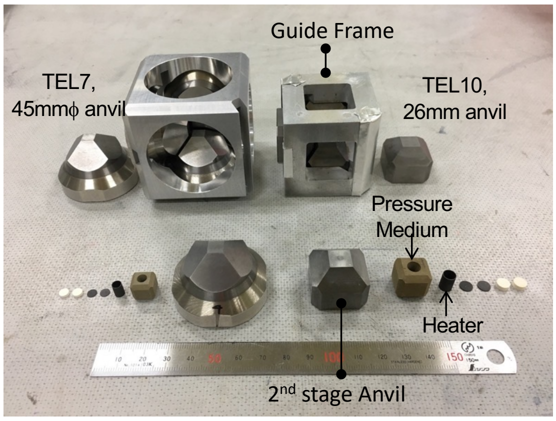
ATSUHIME, the 6-rams multi-anvil press, installed at PLANET beamline has several advantages compared with conventional DIA-type press which are widely used in synchrotron light sources.

6-rams multi-anvil press “ATSUHIME”

- ✓ Anvil gaps remain at 2θ= 90˚, which is compatible with PLANET’s vertical detector.
- ✓ Experiments up to 12 GPa, ~ 1300 K is conducted routinely.

Detector
2 × 0.6 m



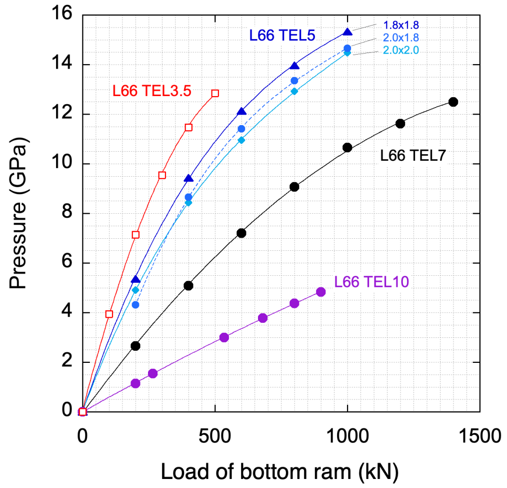


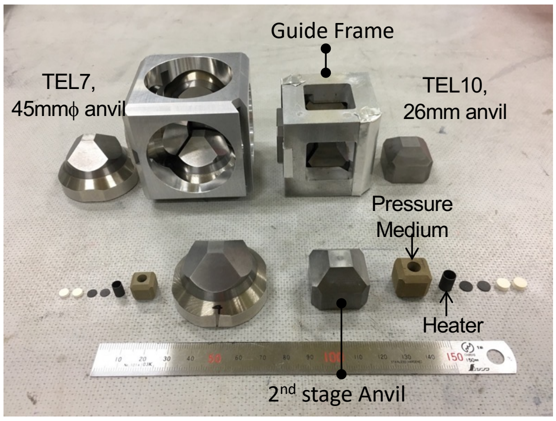
MA6-6 cells

This slide shows the typical (standard) cell assembly for ATHUHIME.
Opening window between the anvil gap

6-rams multi-anvil press "ATSUHIME"

✓ Anvil gaps remain at 2θ= 90˚, which is compatible with PLANET's vertical detector.
✓ Experiments up to 12 GPa, ~ 1300 K is conducted routinely.





MA6-6 cells

The achievable pressure using the MA6-6 cells depends on the truncation edge length (TEL).

Opening window between the anvil gap

First observation of in-situ synthesis of iron hydride

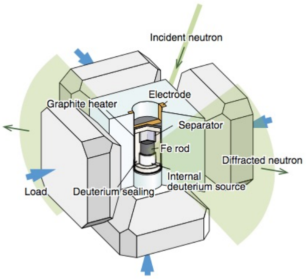
Machida et al., Nature Comm. 2014

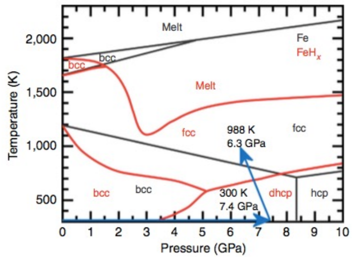
ARTICLE

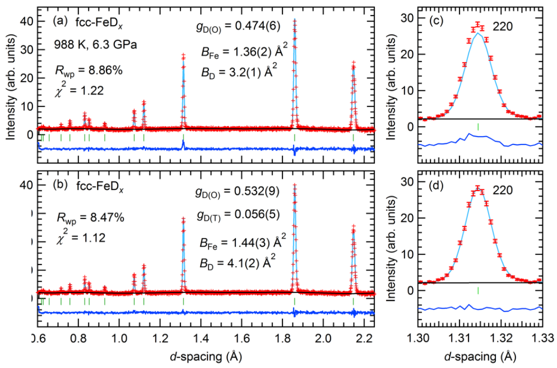
Received 4 Apr 2014 | Accepted 26 Aug 2014 | Published 26 Sep 2014 DOI: 10.1038/ncomms6063 OPEN

Site occupancy of interstitial deuterium atoms in face-centred cubic iron

Akihiko Machida[1], Hiroyuki Saitoh[1], Hidehiko Sugimoto[2], Takanori Hattori[3,4], Asami Sano-Furukawa[3,4], Naruki Endo[1], Yoshinori Katayama[1], Riko Iizuka[5], Toyoto Sato[6], Motoaki Matsuo[6], Shin-ichi Orimo[6,7] & Katsutoshi Aoki[6]





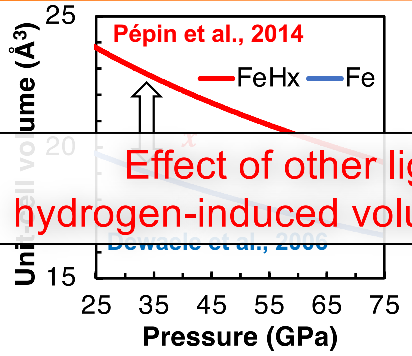


occupies T site in addition to O site in fcc $FeD_{0.64}$.

$\varDelta V/x$ = 2.21(4) Å^3 / atom D at 988 K, 6.3 GPa

The hydrogen occupancy of fcc iron hydride was first published by Machida et al (2014). They found hydrogen occupancy not only in octahedral site but also tetrahedral site.

Determining v_H by neutron diffraction



$$Fe + \frac{x}{2}H_2 \rightarrow FeH_x$$

$$v_{H(D)} = \frac{V_{FeH(D)_x} - V_{Fe}}{Zx}$$

Effect of other light elements on hydrogen-induced volume expansion of Fe?

- fcc-FeD_x (Machida et al., 2014) $\Delta v_D = 2.21(4)$ Å^3
- fcc-FeH_x (Ikuta et al., 2019) $\Delta v_H = 2.22(36)$ Å^3
- fcc-$Fe_{0.91}Ni_{0.10}D_x$ (Shito et al., 2023) $\Delta v_D = 2.45(4)$ Å^3

- hcp-FeD_x (Machida et al., 2019) $\Delta v_D = 2.48(5)$ Å^3
- hcp-$Fe_{0.91}Ni_{0.10}D_x$ (Shito et al., 2023) $\Delta v_D = 3.31(6)$ Å^3

D (^{2}H) is used in neutron diffraction experiments instead of ^{1}H, to avoid high background.

We determine the hydrogen-induced expansion of iron using neutron diffraction.
Neutron diffraction give us occupancy of hydrogen atom in iron.
The table lists the published hydrogen-induced volume expansion for fcc and hcp iron hydrides.
You can see that incorporation of Ni notably increase the value.
We have to investigate the effect of other elements to the hydrogen-induced volume expansion of iron.
This is the motivation of our study.

Target of our research

To determine the hydrogen-induced volume expansion of **hcp-$\mathbf{Fe_{0.95}Si_{0.05}}$** by neutron diffraction and X-ray diffraction under high pressures.

- **hcp** structure is one of the stable structures of pure iron and iron with small amounts of Si at *PT* of inner-core
- **Si** can be a significant light element for the Earth's core
  (Alfè et al., 2002; Fischer et al., 2015; Dauphas et al., 2015)
- *D* (solid/liquid): **Si(~1)**>S(~0.8)>**H(~0.7)**>C(0-0.33)>O(0)

$$v_D = \frac{V_{MD_x} - V_M}{Zx}$$

$M = Fe_{0.95}Si_{0.05}(hcp)$
$v_D = v_H$ (no isotope effect)

We focus on silicon.
Silicon is also a candidate for the light elements incorporated in the Earth's core,
We investigated the effect of silicon to the hydrogen-induced volume expansion of iron under high pressure and high temperature.

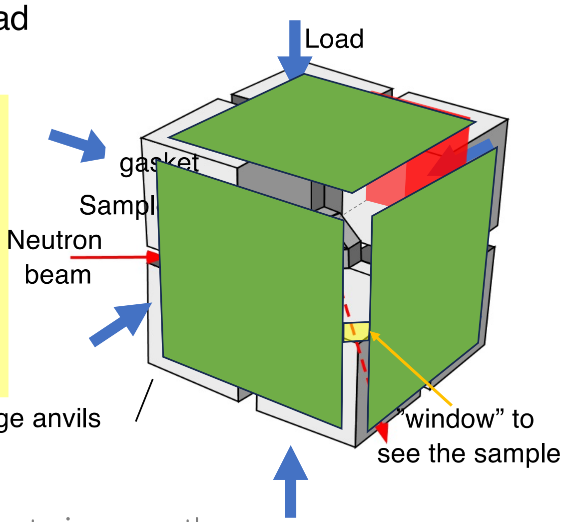
Limitation of MA66 cell and application of MA68 for higher P

- MA66 cell

Sano-Furukawa et al., High Pressure Research, 2021

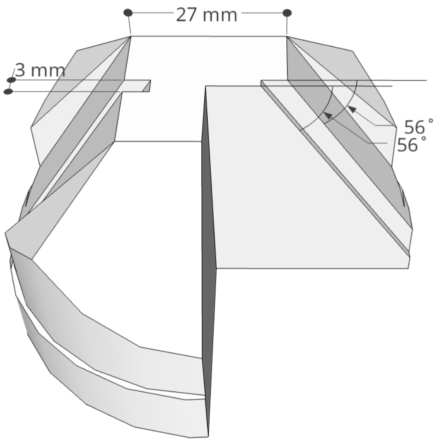
  - ✓ Pressure limitation (with large V sample) ~ 12 GPa with TEL 7
  - ✓ To increase P, need to decrease the TEL and sample
  - ✓ Anvil gaps become narrow at high load

- MA68 cell (Kawai-type cell)
  - ✓ Routinely achievable P ~ 25 GPa
  - ✓ Accessible window is very limited by the 1st and 2nd stage anvils
  - ✓ Modification is needed to increase the opening window



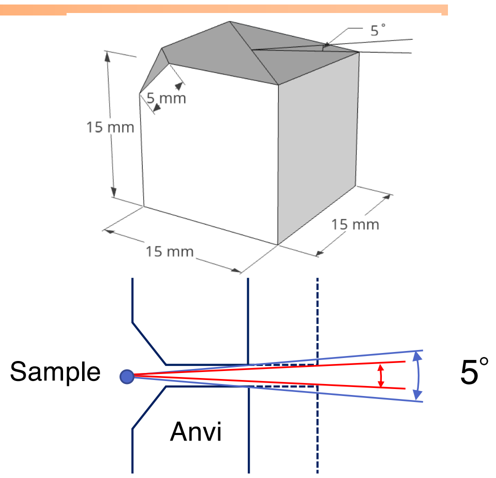
To investigate the chemistry of the core, we have to increase the pressure.
MA66 cell is not enough for generating pressures higher than 10 GPa.
We applied MA68 (Kawai-type) cell for our study.

Limitation of MA66 cell and application of MA68 for higher P



1st stage anvil

- ✓ Taper and slits at 2θ= 90°



2nd stage anvil

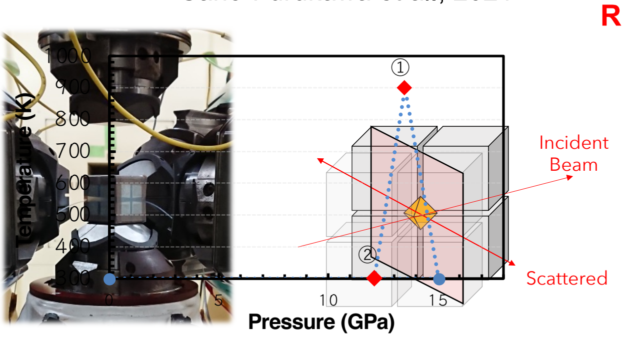
Half tapered with 5°

Sano-Furukawa et al., High Pressure Research, 2021

MA68 (Kawai-type) cell has small opening angle for neutron diffraction.
To increase the signal, we applied 5 degree taper on the two second-stage anvils.

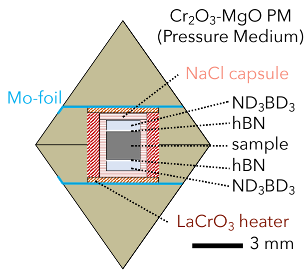
HPHT Neutron diffraction experiments

- Neutron diffraction
  PLANET (BL11), MLF, J-PARC
- Pressure generation
  "ATSUHIME" (Large Volume Press)
  Sano-Furukawa et al. 2014
  MA6-8 for neutron diffraction
  Sano-Furukawa et al., 2021

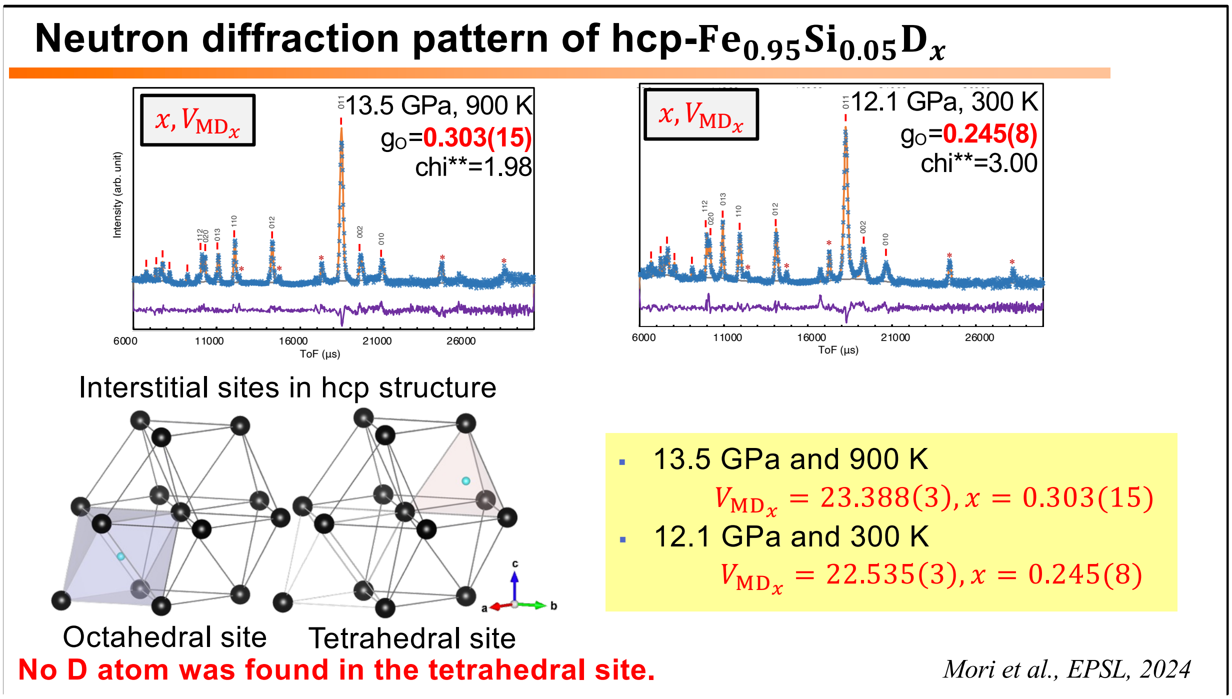


- Starting material
  bcc-$Fe_{0.95}Si_{0.05}$ + ND_3BD_3 (emitting D_2 at high temperature)
- *PT* conditions of obtained profiles
  ① **13.5 GPa, 900 K : 39 hours**
  ② **12.1 GPa, 300 K : 47 hours**

Rietveld refinement→ x, V_{MH_x}



This slide shows the detail of experiments.
We loaded sample (Fe0.95Si0.05 alloy together with ND3BD3 (deuterium-substituted ammonia borane) as a hydrogen source.
First, we applied pressure and then increased temperature to induce the hydrogenation reaction.

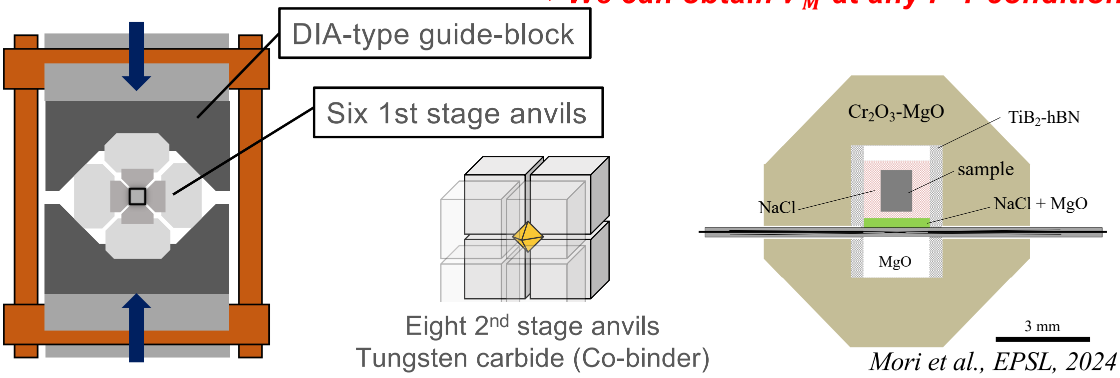


These figures show two neutron diffraction patterns obtained at high pressure conditions.
Rieltveld refinement analysis clarified that occupancy of deuterium (hydrogen) atoms exclusively accommodated in the octahedral sites.

HPHT X-ray diffraction experiments on $Fe_{0.95}Si_{0.05}$

- Synchrotron X-ray diffraction
  BL04B1, SPring-8
- Pressure generation
  "SPEED-Mk.II" (Large Volume Press)
  with DIA-type apparatus
- Starting material
  $Fe_{0.95}Si_{0.05}$ with without H-source
- *PT* conditions
  - **12-22 GPa, 300-800 K**
- Birch Murnaghan Equation of State ***P–T–V_M***

→ ***We can obtain V_M at any P-T condition***

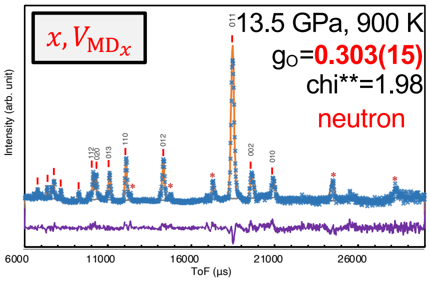


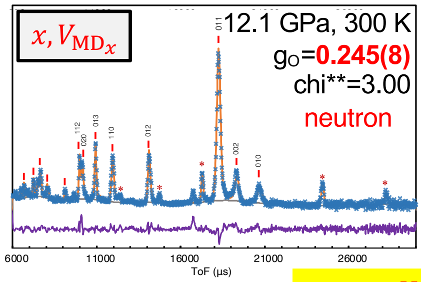
Mori et al., EPSL, 2024

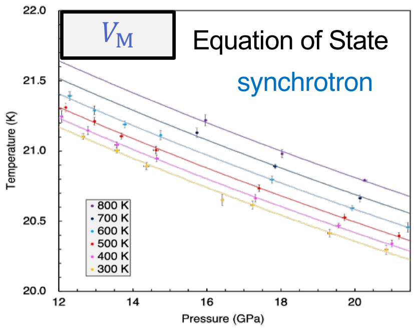
We need to determine the unit cell volume of iron without containing hydrogen.
For this purpose, synchrotron X-ray diffraction at high pressure and high temperature is the best choice because we can obtain the data very quickly and form P-V-T equation of state.

v_D (D-induced volume expansion) of hcp-$Fe_{0.95}Si_{0.05}$

Mori et al., EPSL, 2024







$$v_D = \frac{V_{MD_x} - V_M}{Zx}$$

hcp-$Fe_{0.95}Si_{0.05}$

v_D = **2.92(5)** Å^3 /D-atom at 13.5 GPa and 900 K

v_D = **2.81(2)** Å^3 /D-atom at 12.1 GPa and 300 K

hcp-Fe

v_D = 2.48(5) Å^3 /D-atom at 5 GPa , 573 K +673 K (Machida et al., 2019)

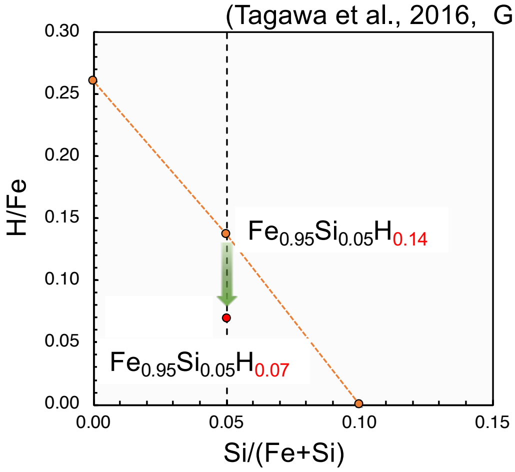
Si increases v_D by ~10-15%

Combining the neutron diffraction and X-ray diffraction data, we obtained hydrogen-induced volume expansion of hcp iron.
It is notable that the values are significantly higher than that of pure iron.

Reconsideration of H concentration in the core

To satisfy the density of inner core at ICB of PREM with Fe-Si-H

hcp-$Fe_{1-x}Si_x$: $Fe_{0.90}Si_{0.10}$ (5.4 wt%)
or
hcp-$Fe_{1-x}H_x$: $FeH_{0.26}$ (0.47 wt%)
(Tagawa et al., 2016, GRL)



Assumptions
- The density of Fe decreases linearly with Si concentration
- T_{ICB} = 5000 K and adapt EOS of hcp-Fe by Fei et al., 2016

hcp-$Fe_{0.95}Si_{0.05}H_x$

✓ If v_H does not change when silicon is incorporated into iron, ***x* = 0.14**

✓ If we apply the v_H obtained in this study, ***x* = 0.07**

H concentration in the core is greatly reduced when the effect of silicon is taken into account.

Mori et al., EPSL, 2024

From the obtained hydrogen-induced volume expansion, we have to revise the hydrogen content estimated from the density deficit if the core contains silicon.

Reconsideration of H concentration in the core

We have to revise the H-content of the outer core with $\mathbf{Fe_{0.88}Si_{0.12}H_x}$

- Tagawa et al. (2016) *GRL*
  - ✓ Compression curve of hcp-$Fe_{0.88}Si_{0.12}H_x$ obtained from X-ray diffraction
  - ✓ H-content was estimated using $v_D = 2.017$ Å^3 obtained from neutron diffraction at **ambient *P*.** ← Quenched hcp-FeD_x at ambient pressure and 100 K. (Antonov et al., 1998)

    ⇨ $\boldsymbol{x = 0.17}$ in the outer core (38 times that of seawater)
- Taking account of the effect of silicon obtained in this study

  If applying $v_D = 2.81(2)$ Å^3
  ⇨ $\boldsymbol{x = 0.13}$ in the outer core (29 times that of seawater)

  If v_D is proportional to Si concentration: $v_D = 3.28(3)$ Å^3 of hcp-$Fe_{0.88}Si_{0.12}$
  ⇨ $\boldsymbol{x = 0.11}$ in the outer core (25 times that of seawater)

Mori et al., EPSL, 2024

From the obtained hydrogen-induced volume expansion, we have to revise the hydrogen content estimated from the density deficit if the core contains silicon.

Acknowledgment

Univ. of Tokyo

Dr. Sho Kakizawa

Dr. Katsutoshi Aoki

Mr. Yuichiro Mori

Mr. Masahiro Takano

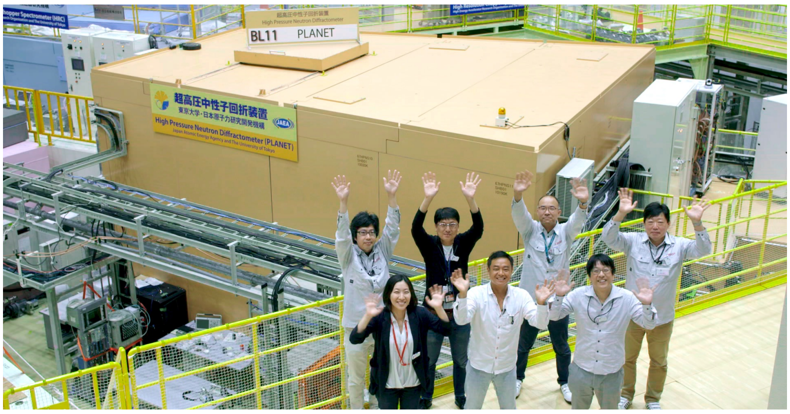
PLANET, J-PARC

Dr. Takanori Hattori

Dr. Asami Sano-Furukawa

Dr. Jun Abe

Dr. Ken-ichi Funakoshi



I am grateful to my collaborators.

Conclusions

- Neutron diffraction experiments under high pressure and high temperature (> 15 GPa, 1200 K) are available at PLANET beamline, J-PARC.
- Hydrogen-induced volume expansion of Fe can be affected by the chemical composition (for example, Ni and Si in Fe)
- We investigated the effect of silicon on the hydrogen-induced volume expansion of iron by combination of neutron diffraction and X-ray diffraction measurements at high pressure and high temperature.
- Hydrogen-induced volume expansion of deuterated hcp-$\mathrm{Fe_{0.95}Si_{0.05}}$ ($v_\mathrm{D} = 2.92(5)$ Å^3 at 13.5 GPa and 900 K; $v_\mathrm{D} = 2.81(2)$ Å^3 at 12.1 GPa and 300 K) are notably larger than $v_\mathrm{D} = 2.48(5)$ Å^3 for hcp pure iron.
- Our results suggest that the amount of hydrogen required for the density deficit needs to be adjusted downwards if silicon is contained in the core.

This slide lists the conclusions of my talk.