Is iron at the Earth's core conditions *hcp*-structured?

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Resumen
El hierro es el componente principal del núcleo terrestre y su estructura y propiedades son de gran importancia para interpretar las observaciones geofísicas y el modelado de dinámica del núcleo. Se argumenta que las líneas de difracción encontradas en el patrón de difracción de rayos-X registrado a alta temperatura y presión por Tateno *et al.*, 2010 e interpretado con la sola presencia de *hcp*-Fe caliente, corresponde en realidad a una parte de la muestra escasamente calentada. Se demuestra que los puntos de difracción observados son, en realidad, debidos a la fase *bcc*-Fe o carburos.
Palabras clave: Estructura del hierro, núcleo de la Tierra, altas presiones y temperaturas.

En las condiciones del núcleo de la Tierra, ¿tiene el hierro una estructura *hcp*?

Abstract
Iron is the main component of the Earth's core and its structure and properties are important for interpretation of geophysical observations and modeling dynamics of the core. We argue that the diffraction lines in the high temperature high pressure X-ray diffraction pattern, presented by Tateno *et al.*, 2010 and interpreted as those of solely hot *hcp*-Fe, correspond indeed to the insufficiently heated part of the sample. We show that observed diffraction spots are either due to *bcc*-Fe or carbides.
Keywords: iron structure, Earth's core, high pressures and temperatures

Summary: Introduction. 1. Results and Discussion 1.1 Effect of laser heating in DAC on appearance of diffraction lines on 2D images. 1.2 Effect of laser heating in DAC on molar volume and *c/a* ratio of *hcp*-Fe. 1.3. Phase composition of the laser-heated samples. 2. Conclusion. 3. Acknowledgments. References.

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Introduction

The Earth's core is the most remote region of our planet. The boundary of the core is at about 2900 km in depth. Not only we do not have samples from the core, but we do not even expect to get any. To date, the most direct observations of the core

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have come from seismological studies using remote-sensing techniques. Due to the complex internal structure of the Earth, seismic investigations require extensive data coverage and appropriate models. Decoding geochemical signature of the core carried by mantle plumes faces similar challenges. Experimental and computational simulations have been hindered by the necessity to approach pressures over 140 GPa and temperatures above 3000 K prevalent in the core. For these reasons, many fundamental issues concerning the Earth's core remain controversial and poorly understood.

Composition of the Earth's core is a geochemical parameter crucial for understanding the evolution and current dynamics of our planet. Since the discovery of the Earth's core about a century ago, the idea of iron being the dominant component of the core gained firm support from cosmochemical and geochemical observations, seismic data, theory of geomagnetism, and high-pressure studies. Cosmochemical data and studies of iron meteorites give evidence that the Earth's core contains significant (5 to 15 %) amounts of nickel. Already in the early 1950s it was recognized that the outer core is less dense than iron or an iron-nickel alloy at corresponding conditions. Current estimates for the density deficit relative to solid iron vary between 6% to 10% for the outer core and 2% to 5% for the inner core (Dubrovinsky *et al.*, 2000; Dubrovinsky *et al.*, 2007; Dewaele *et al.*, 2010). Uncertainties are in part related to the experimental difficulties in measurements of the properties of iron (or iron-nickel alloys) at multimegabar pressure range and high temperatures, but the fundamental problem is the absence of a universal pressure scale that has led to significant discrepancies in the inter-laboratory studies (see, for example, Dubrovinsky *et al.*, 2007). Nevertheless, the main element of the core is iron and its properties at multimegabar pressures and thousands degrees are vital for interpreting mineralogy and geochemistry of the Earth core.

Based on the X-ray diffraction, iron has been reported to adapt several structures at high pressure and temperature: α and δ, body-centered cubic (*bcc*); γ, face-centered cubic (*fcc*); ε, hexagonal close-packed (*hcp*); β, double-*hcp* phase (*dhcp*) or orthorhombic phase. The α-, δ-, and γ-phases at lower pressures are well established and broadly accepted. The β-phase, observed at pressures above 30 GPa and high temperature, is probably metastable or stabilizes due to contaminations. The ε-phase has been proved to be a dominant phase in a wide pressure-temperature range approaching the Earth's core conditions. Theoretical calculations suggest that iron and iron-based alloys at sufficiently high pressures (above 100 GPa) and temperatures, close to the melting point, transform into the *bcc* structured phase (Belonoshko *et al.,* 2003). Moreover, both experimental (Lin *et al.*, 2003) and theoretical (Vočadlo *et al.* 2003) works pointed out towards stabilization of the *bcc*-structured phase due to the elements (particularly, silicon) important for the Earth's inner core chemistry. The *hcp*-*bcc* transformation of the $Fe_{0.9}Ni_{0.1}$ alloy was observed at pressures above 225 GPa and temperatures over 3400 K (Dubrovinsky *et al.*, 2007). Recently Tateno *et al.,* 2010 described breaking through experiments on pure iron at conditions of the Earth's inner core. The authors reported stability of hexagonal close-packed (*hcp*) Fe at pressures up to 377 GPa and 5700 K and a very weak temperature dependence of the ratio of the lattice parameters *c/a* on heating. In view of importance of these results for understanding structure and dynamics of the Earth's core we re-analyze the diffraction data reported by Tateno *et al.,* 2010 and demonstrate that Tateno's *et al.* conclusions regarding stability of *hcp* Fe at multimegabar pressures and temperatures over 5000 K are not sustained by their own data.

1. Results and Discussions

1.1. Effect of laser heating in DAC on appearance of diffraction lines in 2D images

One of the main methodological problems with experiments in laser-heated diamond anvil cells (DACs) is in determining pressure at high temperature. In x-ray diffraction experiments with laser-heated diamond anvil cells (DACs) pressure is usually determined using pressure markers (materials with known thermal equations of state (tEOS) added to the sample) (Dubrovinsky *et al.,* 2007; Ma *et al.,* 2004). Tateno *et al.,* 2010 did not have any pressure marker and used known tEOS of *hcp*-Fe itself (Dubrovinsky *et al.,* 2000). Such an approach could be reasonable, keeping in mind really extreme conditions of the experiments (Tateno *et al.,* 2010), but only in case if a clear evidence of *measuring both the diffraction and temperature from the same hot part of the sample* is provided.

A number of specific features of the diffraction pattern indicate the state of the heated sample: formation of "arcs" or intensive spotting (due to re-crystallization of the sample) of the diffraction lines, as well as their asymmetry and even splitting due to temperature gradients at inhomogeneous heating (in most cases at temperatures above 2500 K) or at misalignment of the X-ray and laser beams. Figure 1 illustrates these indicative features on example of the diffraction patterns of Ni we obtained on its high pressure high temperature (HPHT) study. As seen in the upper panel of Fig. 1, at HPHT conditions the diffraction pattern of Ni is a superposition of diffraction patterns of cold (continues lines) and hot (spots appearing to the right of continues lines) parts of the sample. This superposition is simply due to the fact that some part of the sample irradiated by X-rays is not affected by laser heating. Due to the thermal expansion of the unit cell of Ni at high temperature, the spots representing the hot part of the sample are shifted to the lower 2-theta values. After quenching the unit cell shrinks, so that at room temperature (lower panel) the spots from previously heated (and re-crystallized) part of the sample lie almost exactly on the lines from the cold (not heated) part of the Ni powder.

Fig. 2 shows two 2D X-ray diffraction images presented by Tateno *et al.,* 2010 we could align to each other according to Kikuchi lines. Despite claimed huge difference in temperature (4820 K) the appearance and the texture of continues lines from *hcp*-Fe are the same (some obvious futures are marked by arrows). This observation means that the part of the sample (continues lines of *hcp*-Fe in Tateno *et al.,* 2010) probed by X-ray was not affected by laser-heating. One cannot completely exclude that this is a result of a misalignment of an extremely small sample, the X-ray and laser beams in the extremely difficult experiments.

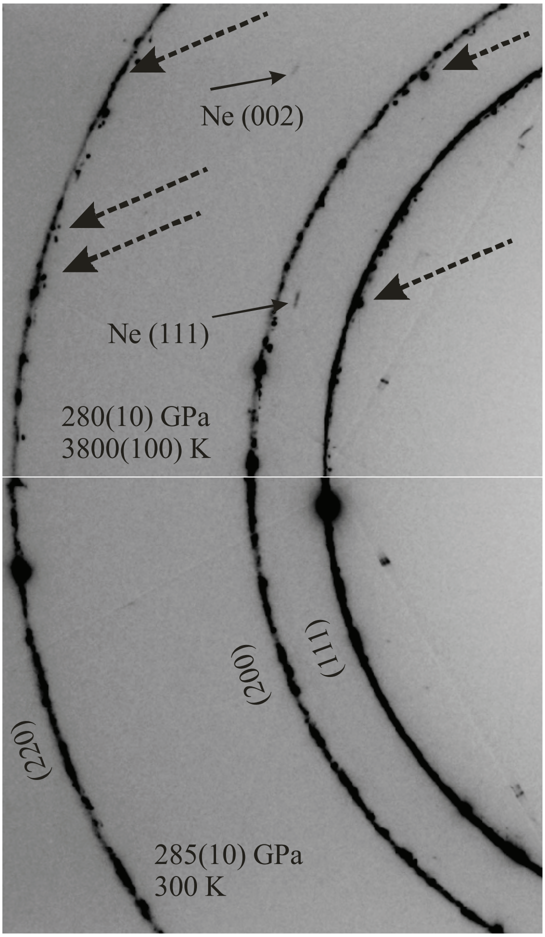

Fig.1. The diffraction pattern of Ni during laser-heating at 280(10) GPa and 3800(100) K (upper panel) and that from the same sample quenched to ambient temperature (300 K) after heating at 285(10) GPa (lower panel). Positions of some spots due to heating at upper panel are highlighted by dashed arrows. As a pressure medium Ne was used, but due to its small amount, comparably low Z, and high pressure, the diffraction lines of Ne are almost invisible.

However, based on our own experience, we suggest that this is rather an intrinsic problem of laser-heating experiments in DACs at very high pressures – due to very thin thermal insulating layer between the diamond anvil and the sample, only a very thin layer of the sample is actually heated, while the rest remains (relatively) cold.

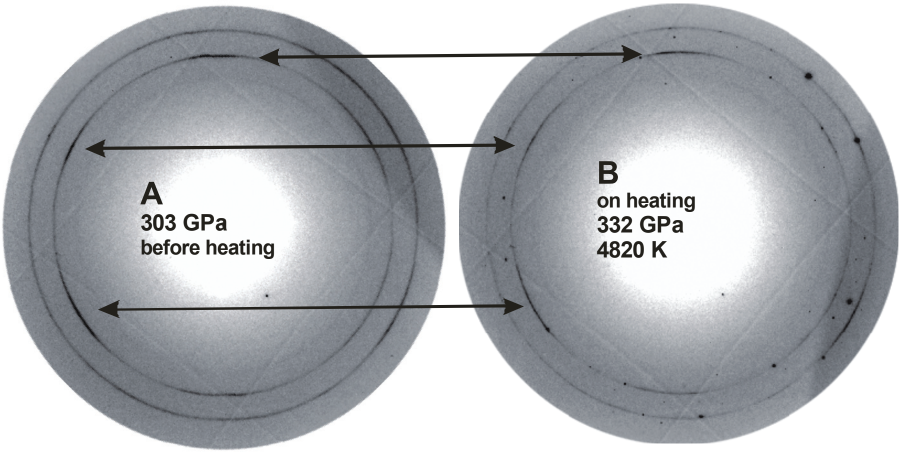

Fig. 2. X-ray diffraction images presented by Tateno *et al.,* 2010 aligned to each other according to Kikuchi lines. Despite claimed huge difference in temperature the appearance and the texture of continues lines from *hcp*-Fe are the same (some obvious futures are marked by arrows).

1.2. Effect of laser heating in DAC on molar volume and *c/a* ratio of *hcp*-Fe

Pressure and temperature affect lattice parameters of *hcp*-Fe, but in different ways – pressure tends to decrease the lattice parameters *c/a* ratio (but very little, almost indistinguishable above 100 GPa), while elevated temperature leads to the increase of the *c/a* ratio (Bubrovinsky *et al.,* 2000; Dewaele *et al.,* 2010; Boehler *et al.,* 2008). Tateno *et al.,* 2010 reported some values of the lattice parameters and the *c/a* ratio obtained in their experiments. Table S2 in Tateno *et al.,* 2010 contains an erroneous value of *c/a* = 1.6019 at 332 GPa and 4820 K that should be 1.5956 instead. When the arithmetic mistake is corrected, Table S2 (Tateno *et al.,* 2010) demonstrates an unprecedented (not observed in previous studies) constancy of the *c/a* ratio over the great temperature interval of 2300 to 4820 K. At the same time the behavior of pressure, as reported by Tateno *et al.,* 2010, is also remarkable. Particularly, Tateno *et al.,* 2010 state that the sample was under pressure of 303 GPa and upon heating to 4820 K the pressure of 332 GPa developed. According to the tEOS of *hcp*-Fe, reported in our previous paper (Dubrovisnky *et al.,* 2000) and used by Tateno *et al.,* 2010, it means that the molar volume (4.144 cm^3/mole) of the sample did not change during heating. Applying similar reasoning, for the sample compressed to 321 GPa its heating to 5520 K at constant volume should result in pressure of 358 GPa, and Tateno *et al.,* 2010 indeed give a value of 356 GPa (*i.e.* within uncertainty it is the same pressure that we calculated for the unchanged volume). Such a "constant volume" and "constant *c/a*" behavior of *hcp*-Fe suggests that vast majority of the sample was not heated to the declared temperatures while the diffraction data were collected, and the observed "constant volume" of the sample (at ambient or relatively low temperatures) was incorrectly used in the *hcp*-Fe tEOS with improper high temperatures.

1.3. Phase composition of the laser-heated samples

According to the phase analysis conducted by Tateno *et al.,* 2010 samples heated at pressures up to 377 GPa and 5700 K contain *hcp*-Fe, high-pressure phase of SiO_2 (used as a thermal insulator), and iron carbide. Fig. 3 shows simulated in GSAS the X-ray diffraction profile of a mixture of *hcp*-Fe, Fe_3C, and Fe_7C_3 in proportion 100:1:1. Lattice parameters of *hcp*-Fe (a=2.1528 Å, c=3.4351 Å, at P=332 GPa and T=4820 K) and Fe_3C (a=3.843 Å, b=4.411 Å, c=5.713 Å at P=332 GPa and T=4410 K) are taken from Tateno *et al.,* 2010. Lattice parameters of Fe_7C_3 for the same pressure are estimated based on works by Nakajima *et al.*, 2009. While Tateno *et al.,* 2010 reported the appearance of several spots in the diffraction patterns upon heating at high pressures and explained them either by crystal growth of *hcp*-Fe, or by formation of Fe_3C (or by crystallization of pyrite-type SiO_2), the Fig. 3 shows that (a) Fe_3C has in fact many more diffraction lines than the number of lines observed and indexed by Tateno *et al.,* 2010 and, thus, the identification of Fe_3C in Tateno *et al.,* 2010 is ambiguous; (b) a number of lines of Fe_3C and Fe_7C_3 are overlapping that means that Fe_7C_3 can not be ruled out; (c) Fe_7C_3 has lines coinciding with (100) and (101) lines of *hcp*-Fe and this could be a reason for appearing spots on corresponding *hcp*-Fe lines; and (d) the (002) line of *hcp*-Fe, if present, could not be confused with any one of Fe_3C or Fe_7C_3. Note, that positions of the diffraction lines of *fcc*-Fe with the same molar volume as that of *hcp*-Fe (~4.15 cm^3/mole) reported by Tateno *et al.,* 2010 for 332 GPa and 4820 K would coincide with the diffraction lines of iron carbides, and in this sense the presence of fcc-Fe cannot be unambiguously excluded.

As we stated above, the (002) line of *hcp*-Fe, if present, would not coincide with any lines of Fe_3C or Fe_7C_3. According to Tateno *et al.,* 2010, this line, as appeared in their diffraction patters, is distinctly different from other lines of iron – the "(002)" appears only as spots and only upon heating (Fig. 2). The position of this "(002)" spotty line does not agree well with positions of other, (100) and (101), continues lines (as appeared in the 2D images, Fig. 2) of *hcp*-Fe. For example, for the only high-P,T diffraction pattern presented by Tateno *et al.,* 2010, the value of the c lattice parameter calculated from the (100) and (101) reflections is 3.4351 Å, while the one obtained from the "(002)" peak is 3.4404 Å that is higher than any other c values reported in Tateno *et al.,* 2010 (note, that Tateno *et al.,* 2010 did not use at all the "(002)" line for calculating lattice parameters reported in Table S2). At the same time, if one assumes that spots are coming from the hot part of the sample (*i.e.* at 4820 K measured spectroradiometrically and 303 GPa as determined from continues diffraction lines of *hcp*-Fe), the expected value of the (110) reflection of *bcc*-Fe would be 1.71-1.72 Å (the range is due to possible 0-2% difference in volumes of *hcp*- and *bcc*-phases of iron (Dubrovinsky *et al.,* 2007) at these conditions) that coincides with the reflection assigned by Tateno *et al.,* 2010 (1) as (002) of *hcp*-Fe. The quantitative full-profile treatment of the spot-rich part of the pattern confirms this analysis (Fig. 4).

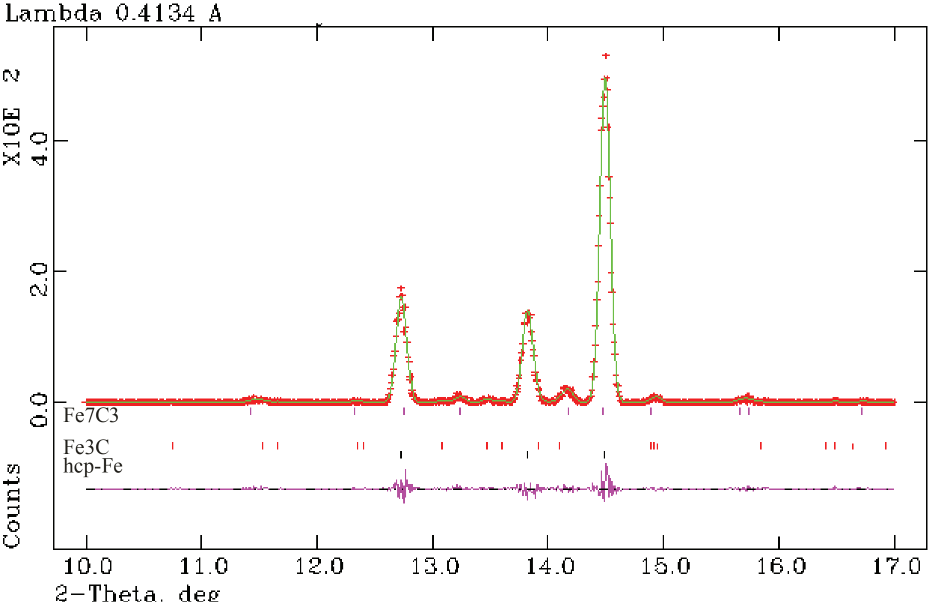

Fig. 3. Simulated in GSAS the X-ray diffraction profile of a mixture of *hcp*-Fe (bottom tick-marks), Fe$_3$C (middle tick-marks), and Fe$_7$C$_3$ (upper tick-marks) in proportion 100:1:1.

2. Conclusions

In summary, from the data published by Tateno *et al.,* 2010 we can draw the following conclusions:

- Major part of the sample (continues lines of *hcp*-Fe at 2D X-ray images) probed by X-rays has the same texture before and after laser heating and, thus, was not affected by laser-heating at reported temperatures and pressures;
- Heated portion of the sample intensively reacted with carbon forming carbide(s), as reported previously (Prakapenka *et al.,* 2003);

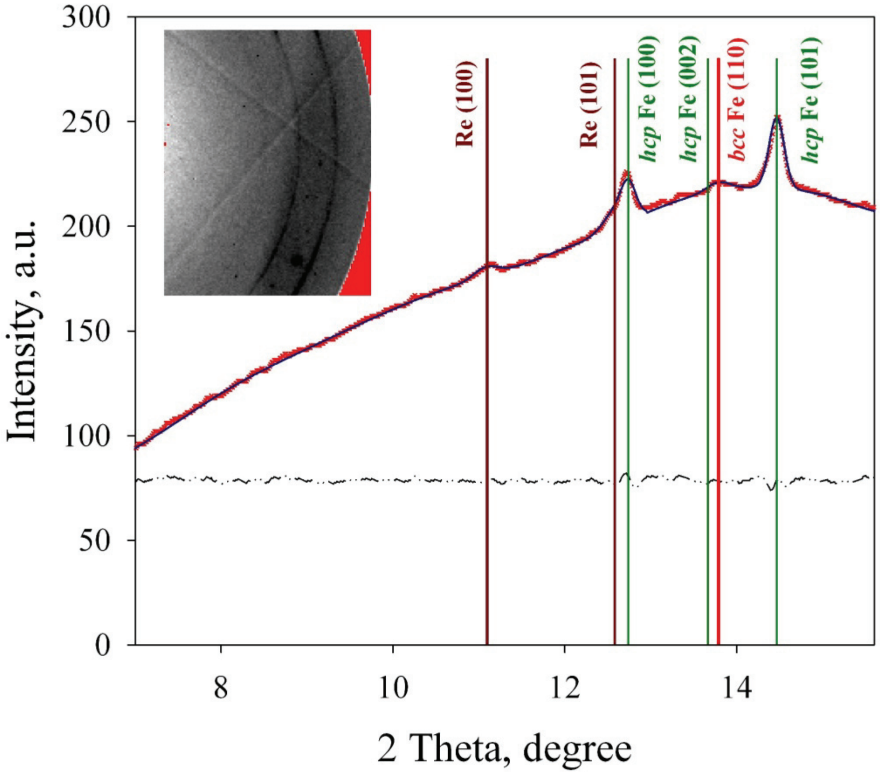

Fig. 4. The GSAS plot of the diffraction pattern of the sample treated, according to Tateno *et al.,* 2010, at "332 GPa and 4820 K" (red crosses). The simulated model biased diffraction pattern is shown as a solid blue line. Residuals are shown by dot-dashed black line in the bottom. The integrated area of the corresponding 2D diffraction pattern from Tateno *et al.,* 2010 is shown in the insert (see also Fig. 2).

- Formation of *bcc*-iron and iron carbides is sufficient to explain all features of the presented diffraction patterns, although complexity of the diffraction patterns and limited reciprocal space may preclude their unambiguous interpretation.

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