



High-pressure polymorphism of Fe₂P and its implications for meteorites and Earth's core

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[1] Minerals with composition (Fe,Ni)₂P, are rare, though important accessory phases in iron and chondritic meteorites. The occurrence of these minerals in meteorites is believed to originate either from the equilibrium condensation of protoplanetary materials in solar nebulae or from the later accretion and condensation processes in the cores of parent bodies. Fe-Ni phosphides are considered a possible candidate for a minor phase present in the Earth's core, and at least partially responsible for the observed density deficit with respect to pure iron. We report results of high-pressure high-temperature X-ray diffraction experiments with synthetic barringerite (Fe₂P) up to 40 GPa and 1400 K. A new phase transition to the Co₂Si-type structure has been found at 8.0 GPa, upon heating. The high-pressure phase can be metastably quenched to ambient conditions at room temperature, and then, if heated again, transforms back to barringerite, providing an important constraint on the thermodynamic history of meteorite.

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1. Introduction

[2] Fe-Ni-P minerals, e.g. nickelporphide, schreibersite, barringerite, as well as analogous P-rich sulfides are often found in meteorites, such as Ollague (Imilac) pallasite [Buseck, 1969], Onello [Britvin *et al.*, 2002], Yamato-793274 [Koberl *et al.*, 1991], and CM chondrites [Nazarov *et al.*, 1997]. Equilibrium protoplanetary material condensation modeling [Pataev and Wood, 2000] suggests that these phases may have formed in the solar nebulae, but there is a strong argument that they might also have experienced later alterations, in the parent bodies or after delivery to Earth [Ivanova *et al.*, 2005]. Understanding the thermodynamic properties and pressure-temperature phase relations of these minerals is essential in consideration of

the alteration hypothesis, and can provide important insights and constraints into the chemistry and physics of one of the most primitive environments in the Universe. Convincing evidence exists, based on comparison of the silicate Earth model and natural chondritic abundances of elements, that phosphorus is present in Earth's core [McDonough and Sun, 1995; McDonough, 2003].

[3] In meteoritic samples, the (Fe,Ni)₂P grains exhibit a range of Ni:Fe atomic ratios, varying from 0.5 to over 1.5 [Nazarov *et al.*, 1998]. There are two known polymorphs of (Fe,Ni)₂P, both found in meteorites. The more common is hexagonal barringerite with the C22 structure type and space group *P*-62*m*, the same as synthetic Fe₂P. To our knowledge, besides an early compression study on a synthetic powder sample to 10 GPa [Fujiwara *et al.*, 1981], and several low temperature moderate-pressure studies aimed at revealing the effects of pressure on Curie temperature [Abliz *et al.*, 2006; Fujiwara *et al.*, 1982], nothing is known about the high-pressure behavior of barringerite. An early high-pressure quench study [Senateur *et al.*, 1976] indicated that a second, orthorhombic polymorph of Fe₂P, with C23 (Co₂Si) type structure may be stable or metastable at ambient conditions. A recent study of samples from the Onello meteorite described an orthorhombic phase, named allabogdanite, with C23 structure type and space group *Pnma* [Britvin *et al.*, 2002]. The relation between these two polymorphs in the Fe-Ni-P system is not yet completely understood, but a transformation between the same two structure types is known from another binary phosphide system, Co₂P. In Co₂P the stable, ambient β -phase has the orthorhombic C23-type structure, and upon heating to 1428 K transforms to the hexagonal, C22-type α -phase through a reconstructive mechanism, involving bond breaking and re-formation [Ellner and Mittemeijer, 2001]. The α -Co₂P is stable at high temperature, and can be metastably retrieved at ambient conditions by rapid quenching. By analogy to Co₂P, the following conclusions have been inferred for the (Fe,Ni)₂P system: (1) barringerite is a high-temperature polymorph of (Fe,Ni)₂P, and (2) ordering associated with significant Ni content or small Co content is the most likely reason for stabilization of the allabogdanite structure [Britvin *et al.*, 2002; Buseck, 1969]. Here, we report results that change this interpretation.

2. Experiments

[4] In order to bring definite answers to the interpretation of the stability of the two polymorphs in pure Fe₂P system

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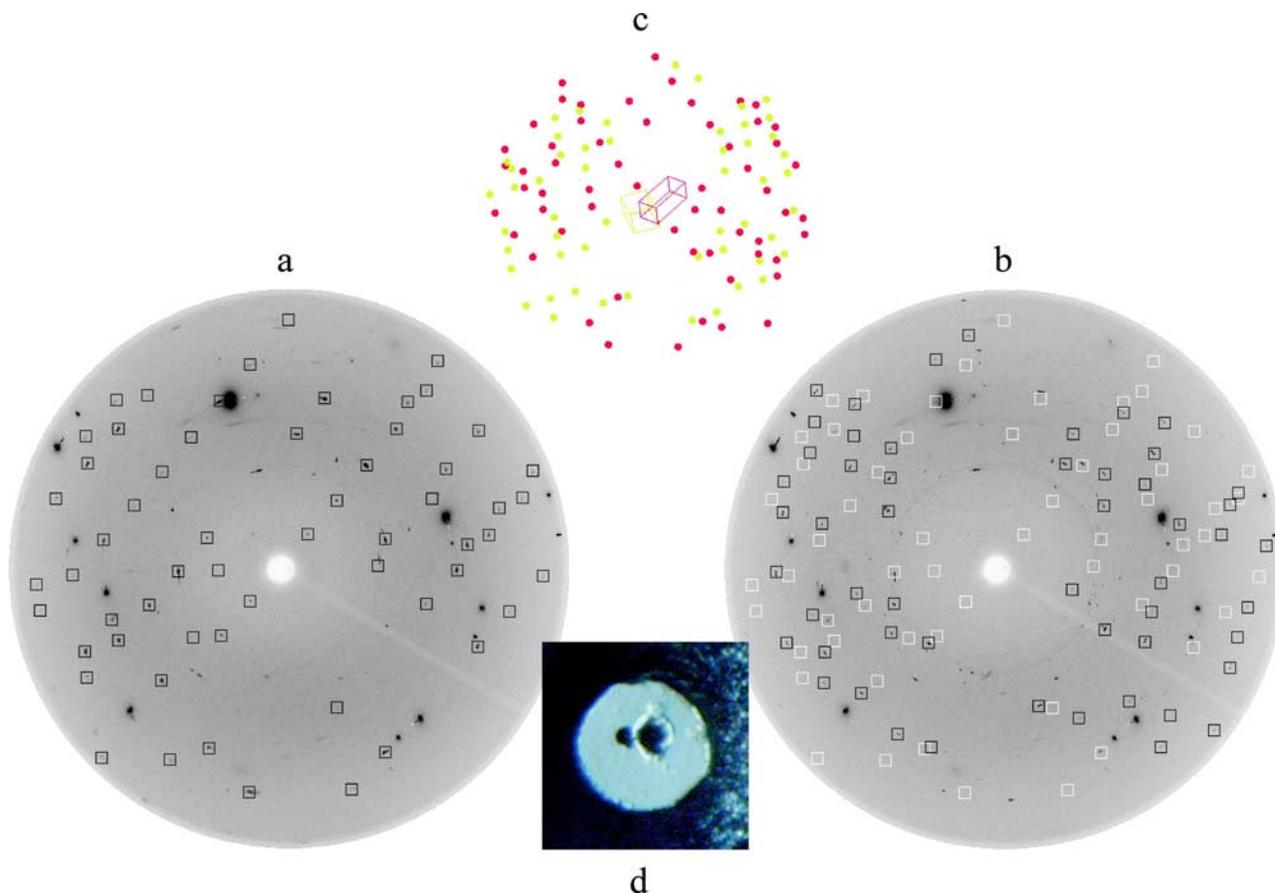


Figure 1. SXD diffraction patterns of Fe₂P. (a) The C22 type phase at 33 GPa before heating, (b) the C23 type phase at 33 GPa after heating. Grey squares mark locations of peaks of the C22 phase before heating, (c) projection of the two reciprocal spaces of hexagonal phase crystal (red/dark) and orthorhombic crystal (green/light) along the hexagonal $1\ 0\ 0$ direction, (d) two crystals of the hexagonal phase in a diamond anvil cell at 20 GPa.

we performed synchrotron single-crystal X-ray diffraction (SXD) experiments at high pressure and temperature. The starting material was obtained through high-temperature synthesis in evacuated silica tube from stoichiometric mixture of elements, which resulted in a coarse-grained mixture of Fe₂P and FeP (part of Fe was lost due to reaction with the SiO₂ tube walls). Nevertheless, it was possible to hand-pick several micrograins of approximately $10 \times 10 \times 5$ mm size, which were identified using SXD analysis as single crystals of Fe₂P. Comparison of unit cell parameters obtained from the single crystal sample ($a = 5.8764(3)$ Å, $c = 3.4493(1)$ Å) with the unit-cell-stoichiometry dependence [Carlsson *et al.*, 1973] confirms that our starting material is close to ideal Fe_{2.0}P_{1.0} composition. In the first compression experiment two single crystals were loaded into a diamond anvil cell (DAC) with 16:4:1 MeOH:EtOH:H₂O pressure medium and ruby pressure standard (Figure 1d). The samples were compressed in small, 3 GPa pressure steps, with SXD data collected at each step. Up to 30 GPa there was no sign of excessive uniaxial strain (auxiliary material Figure S1).¹ At 33 GPa significant broadening of single crystal peaks was observed, and one of the crystals was moderately heated

with a diode-pumped fiber laser, operating at a wavelength of $1.064\ \mu\text{m}$ [Prakapenka *et al.*, 2008] to an approximate temperature of 1400 K, as estimated from the black body radiation. An SXD pattern collected after the heating revealed that the heated sample retained the single crystal character, but the positions of the diffraction peaks were quite different than before (Figures 1a and 1b). In contrast, the diffraction pattern of the unheated crystal remained unchanged. Three-dimensional reconstruction of reciprocal space and peak indexing revealed that the heated crystal transformed to an orthorhombic structure with unit cell $a = 5.3814(6)$ Å, $b = 3.447(3)$ Å, $c = 6.422(2)$ Å (at 33 GPa) and space group $Pnma$. The new structure was easily identified as isostructural with β -Co₂P. Comparison of the orientation matrices of the hexagonal and orthorhombic crystals revealed no obvious crystallographic relation (Figure 1c, auxiliary material Table S2), thus we conclude that the transition occurs through a reconstructive mechanism and re-crystallization. The new phase was further pressurized to 40 GPa with laser annealing at each pressure increase, to determine the equation of state (EOS). No further transformation or crystal orientation changes were found. After reaching 40 GPa a decompression experiment was conducted, without heating. The new, C23-type phase could be metastably quenched to ambient conditions without signs of excessive uniaxial

¹Auxiliary materials are available in the HTML. doi:10.1029/2008GL033867.

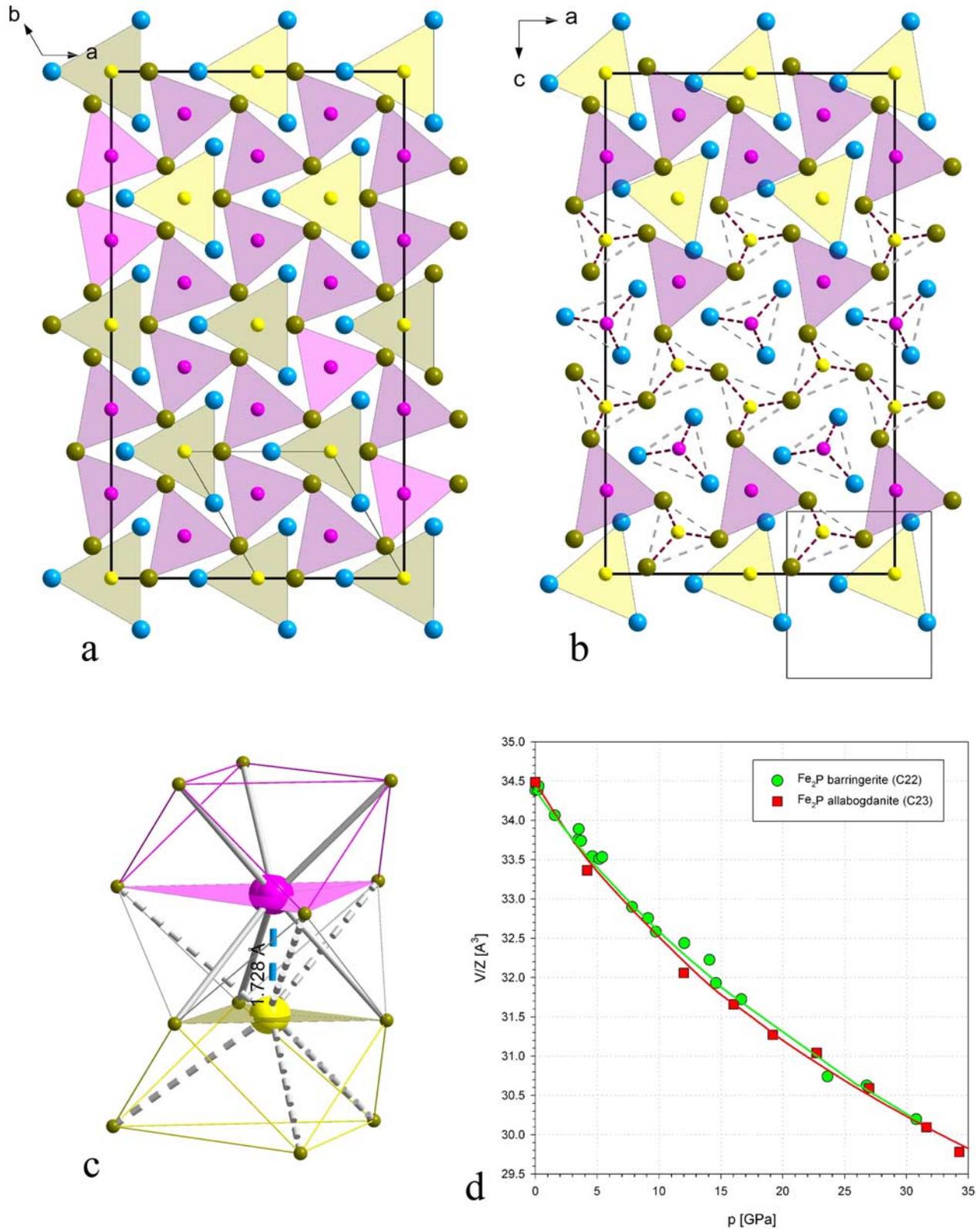


Figure 2. Mechanism of the phase transition in Fe_2P . (a) and (b) The crystal structures of the hexagonal and orthorhombic phases, respectively. The triangles depict the equatorial triangle of the P coordination polyhedra. Yellow triangles are located at fractional atomic coordinate 0.5 along the viewing direction, whereas purple triangles are at coordinate 0. In Figure 2b the dashed triangles show the P atoms that changed location (moved along the viewing direction) during the transition. (c) The coordination polyhedron and the two possible P sites between which the transition occurs. (d) Equation of state of the hexagonal (green) and orthorhombic (red) phases of Fe_2P . The vertical axis represents unit cell volume divided by the Z number.

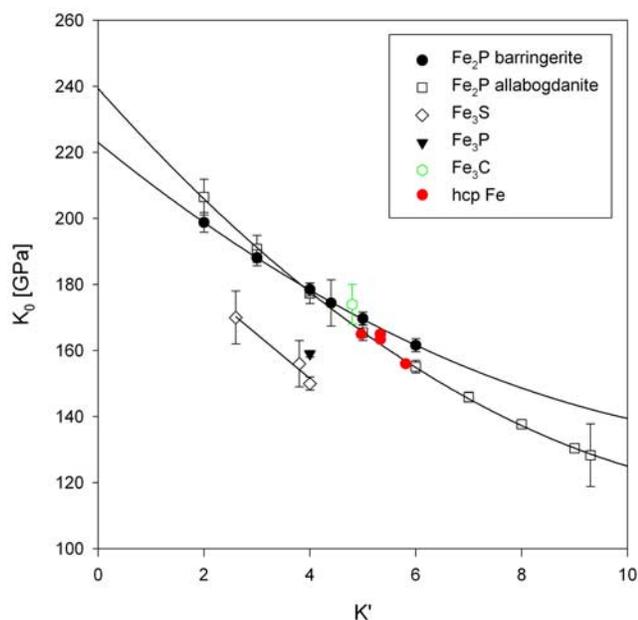


Figure 3. EOS parameters for main candidates for light-element-containing component of the Earth's core. In EOS calculations there is an intrinsic correlation between the bulk modulus K_0 and its pressure derivative K' , which can be visualized by plotting the values of K_0 obtained for different fixed values of K' . The bulk modulus of both of Fe₂P phases is $\sim 18\%$ higher than that of Fe₃S [Seagle *et al.*, 2006] and Fe₃P [Scott *et al.*, 2007] and is comparable with hcp Fe [Dewaele *et al.*, 2006; Mao *et al.*, 1990] and Fe₃C [Li *et al.*, 2002]. The higher value of bulk modulus means that compared to the other candidate phases with lower K_0 , a much smaller content of Fe₂P would need to be present in the core to account for the observed density deficit.

strain (auxiliary material Figure S2). After completely releasing pressure, the sample was heated again to about 1400 K, and subsequent SXD analysis revealed that it transformed back to the original hexagonal barringerite single-crystal, but again, without an obvious relation of the orientation matrices (auxiliary material Table S2.). Since in the first experiment, the pressure at which the orthorhombic phase becomes stable was not constrained, we conducted a second experiment with a polycrystalline sample (containing hexagonal Fe₂P with a small amount of FeP impurity) and NaCl pressure medium. This time the sample was pressurized in smaller, 1 GPa steps, and heated to ~ 1400 K at each step. Conversion to the C23 structure was observed at 8.0 GPa. Since the experiments conducted with both single crystal and polycrystalline samples, as well as with different pressure media produced the same transformation sequence, we rule out chemical, non-hydrostaticity or sample-orientation effects as possible causes of the transformation.

3. Results and Discussion

[5] The two polymorphs have a very similar compressibility, as shown in Figure 2d. The bulk moduli of the C22 and C23 phases, determined using the 3-rd order Birch Murnaghan EOS are 174(7) GPa and 177(3) GPa, respec-

tively (at $K' = 4.0$, auxiliary material Table S1 and Figure 3). The ambient pressure density of the orthorhombic phase is marginally lower than that of the hexagonal phase, which explains the ambient stability of the latter. During compression at pressure of about 5 GPa the two $V(p)/Z$ curves cross, and the orthorhombic phase assumes a higher density, which is consistent with the observed pressure at which the transition occurs.

[6] The fact that at ambient temperature both phases can be compressed and decompressed by as much as 20 GPa past the transition pressure without inducing the transition constitutes a remarkable example of metastability. Our observation of the C23 phase in pure Fe end-member demonstrates that the presence of Ni is not necessary for the orthorhombic structure to be metastable at ambient pressure. While it is possible that Ni may have a stabilizing effect on the C23 structure, it seems unlikely, as (1) C23 phase has never been observed in pure Ni₂P, and (2) based on the comparison of ionic radii of Fe and Ni one would expect the pressure of C22- \rightarrow C23 transition to be higher in the Ni-end member. In order to understand the origin of metastability of the two phases of Fe₂P it is necessary to take a close look at the relation between their crystal structures. A common supercell can be conveniently defined for the purpose of such comparison, as shown in Figures 2a and 2b. Both structures share basically the same, pseudo-hexagonal arrangement of Fe atoms, but differ in the organization of the P substructure. P atoms are located in voids coordinated by 9 Fe atoms. If viewed along the hexagonal c direction, for every two neighboring, face-sharing voids only every other one is occupied. A conversion between the two structure types can be accomplished though diffusion of half of the P atoms along the c -hexagonal direction from the sites occupied in the C22 structure, to empty voids. The P atoms have to move by ~ 1.7 Å to the neighboring void (Figure 2c), with the transformation preserving the topology of the Fe lattice, which undergoes a relatively minor distortion to accommodate the new coordination scheme. While such transformation is topologically very simple, and the resulting structures most likely differ very little in total energy, breaking of the three Fe-P bonds, needed for the P atoms to move to the new voids requires substantial kinetic energy to overcome the activation barrier.

[7] There is a significant similarity of the metastability and polymorphism in Fe₂P to the high-pressure polymorphism of silica phases. The octahedral high-pressure polymorph of SiO₂, stishovite, was shown to undergo first a structural distortion to the CaCl₂ structure [Kingma *et al.*, 1995] (at 50 GPa), and then a transformation to the α -PbO₂ structure [Murakami *et al.*, 2003] (at 121 GPa and high temperature), which involves diffusion of every other Si cation along the octahedral edge-sharing chains into previously unoccupied octahedral voids [Dera *et al.*, 2002]. Interestingly, similar to Fe₂P, the high-pressure α -PbO₂-type polymorph of silica (seifertite) can be metastably quenched to ambient conditions. SiO₂ seifertite is also found in meteoritic samples, and its occurrence serves as a useful proxy of the pressure-temperature history of meteorites. It should be emphasized that the remarkable metastability of both hexagonal as well as orthorhombic Fe₂P provides an indicator of thermodynamic history of meteor-

ites, which is even more convenient than SiO₂, since the Fe₂P phases do not amorphize, but instead undergo a single-crystal-to-single-crystal transition. Occurrence of allabogdanite clearly indicates one of two possible scenarios: (1) the phase was formed at elevated pressure (above 8.0 GPa) and high temperature and after formation, it has never experienced heating above 1400 K at low pressure, or (2) Fe₂P was initially formed as barringerite at moderate pressure and high temperature, and then transformed to allabogdanite most likely during a shock event on the parent body. In the second scenario any high-temperature ambient-pressure alteration after the impact can be clearly ruled out. Presence of hexagonal barringerite, on the other hand, indicates that the peak pressure and temperature of impact shock did not exceed 8.0 GPa and 1400 K.

[8] The outer core of the Earth is believed to contain less than 1 wt. % of phosphorus [Stewart and Schmidt, 2007; Stewart et al., 2007], which is certainly less than the content required to stabilize the Fe₂P structure. However, the estimate of the combined content of the light elements in the core (~5 wt. %) [Wood et al., 2006], the ability of the C23 structure to accommodate multi-component solid solutions involving all top candidates for the light element core component [Chandra et al., 1980; Jernberg et al., 1984; Stewart and Schmidt, 2007], and the recent evidence of heterogeneity of the outer core density [Soldati et al., 2003] all make the possibility of Fe₂P presence in the core more plausible. With the bulk modulus higher and the ambient density lower than that of Fe₃P and Fe₃S (Figure 3) much less Fe₂P would need to be present in the core to account for the observed density deficit.

[9] The C23 structure type is more common among binary and ternary systems than the C22 type, with examples including many silicides, germanides, and phosphides (often containing cations relevant for the deep Earth, such as Fe, Ni, Ti, Mn or Co), but relatively few sulfides. Since more compounds can accommodate the allabogdanite structure than the barringerite structure, it can be expected that the structural compatibility of Fe₂P for alloying with other siderophile elements at high pressure and temperature should increase with respect to the ambient compatibility. However, with the limited pressure range covered in our experiments, it remains to be verified whether the C23 structure remains stable to the outer core pressure and temperature conditions.

[10] In addition to sulfur and phosphorus, silicon is considered one of the key candidates for the light-element core constituent [Lin et al., 2003, 2002]. It has been demonstrated that quite a large amount (up to 35% atomic ratio) of phosphorus in the diiron phosphide structure can be substituted by silicon [Jernberg et al., 1984]. Interestingly, introduction of Si into the Fe₂P structure opens a possibility of purely temperature-induced C22→C23 phase transition [Jernberg et al., 1984]. While Earth science researchers start to address the issues of interplay between different light elements in ternary systems between Fe, S and Si [Sherman, 1997] and Fe, S and P [Stewart and Schmidt, 2007], we are still very far from understanding the relevant multi-component phase diagrams. In particular, by analogy to the Co₂P-Co₂Si system, a solid solution between (Ni,Fe)₂(P,S) and (Fe,Ni)₂Si is possible, providing ways for

formation of new compounds that could be stable at Earth's core conditions.

4. Methods

[11] X-ray diffraction data were collected at the bending magnet station 13BMD of GSECARS facility, at the Advanced Photon Source, ANL. The monochromatic incident beam wavelength was 0.3344 Å. The incident beam was focused using a pair of Kirkpatrick Baez mirrors to a focal spot of approximately 0.008 by 0.015 mm. A MAR345 image plate detector, placed approximately 350 mm from the sample was used to record the diffraction images. The sample was rotated during the exposure within a range of $\omega = \pm 20^\circ$. Typical exposure time was 30s/degree. The data was processed using GSE-ADA software [Dera, 2007]. The pressure inside the DAC was measured using the ruby fluorescence method [Mao et al., 1986].

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