# Revision 1

1	New pressure-induced phase transition to Co <sub>2</sub> Si-type Fe <sub>2</sub> P
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14	ABSTRACT
15	We found a new phase transition in $Fe_2P$ from $Co_2P$ -type (C23) to $Co_2Si$ -type (C37) structure
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the Earth's inner core.

27 Keywords: iron phosphides, Fe<sub>2</sub>P, high pressure, core, light element

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### INTRODUCTION

30 Planetary cores, not only of our planet but also other planets, likely include light elements in 31 addition to iron and nickel (McDonough 2014). The equation of state (EoS) of liquid Fe, the 32 most recently determined in a diamond-anvil cell (DAC) by Kuwayama et al. (2020), 33 demonstrates that the Earth's outer core is less dense by 7.5-7.6% than the liquid pure Fe. 34 suggesting the presence of substantial amounts of light impurity elements (e.g., Birch 1952; 35 Hirose et al. 2013). The inner core is also less dense than pure Fe by 4–5% (Fei et al. 2016) when 36 inner core boundary is at ~5400 K (Hirose et al. 2013). Phosphorous (P) should be one of core 37 impurity elements since iron meteorites contain up to 1.8 wt% P (Buchwald 1975). Indeed, the 38 silicate Earth is depleted in P (~90 ppm) relative to chondrites (0.1–0.2 wt%) (McDonough 2014; 39 Wasson and Kallemeyn 1988), indicating that most of P is stored in the metallic core.

40 Chondrites and iron meteorites include nickel-bearing iron phosphides such as (Fe,Ni)<sub>3</sub>P 41 schreibersite and (Fe,Ni)<sub>2</sub>P barringerite/allabogdanite (low-/high-pressure polymorphs) (Britvin 42 et al. 2002; Buchwald 1975). In the Fe-P system, Fe<sub>3</sub>P is the most Fe-rich phosphide at 1 bar and 43 forms eutectic relation with Fe (Zaitsev et al. 1995). Experimental studies reported the Fe<sub>3</sub>P is 44 stable to at least 111 GPa (Stewart and Schmidt 2007; Lai et al. 2020). On the other hand, 45 theoretical calculations predicted that  $Fe + Fe_2P$  or  $Fe_4P + Fe_2P$  is stable relative to  $Fe_3P$  under 46 Earth's inner core conditions (Zhao et al. 2017; Sagatov et al. 2020). Indeed, recent experiments 47 have demonstrated that Fe<sub>3</sub>S decomposes into Fe + Fe<sub>2</sub>S above 250 GPa (Ozawa et al. 2013; 48 Tateno et al. 2019a). Since the Fe-S and Fe-P systems are known to exhibit similar phase 49 relations (e.g., Stewart and Schmidt 2007),  $Fe_2P$  may be important iron phosphides in planetary 50 cores.

51 The elastic property and phase relations in Fe<sub>2</sub>P were previously reported by experiments to 52 40 GPa and 1400 K (Dera et al. 2008). Stable Fe<sub>2</sub>P crystal is barringerite at 1 bar (hexagonal, 53 *P-62m*, C22) and changes to allabogdanite (orthorhombic, cotunnite-type *Pnma*, C23) above 8 54 GPa. Stable structures at higher pressures were predicted by theory, but results have been 55 controversial. Wu et al. (2010) calculated that C23 Fe<sub>2</sub>P transforms into a trigonal structure with 56 space group P-3m above 153 GPa, but they did not consider the  $Co_2Si$ -type (C37) structure. 57 While first-principles swarm structure predictions by Zhao et al. (2017) reported a wide stability 58 of orthorhombic Co<sub>2</sub>Si-type (C37) Pnma structure from ~10 to 400 GPa, the more recent 59 calculations by Sagatov et al. (2020) demonstrated that C23 Fe<sub>2</sub>P is stable up to 400 GPa and 60 4000 K. On the other hand, theoretical and experimental studies showed that Fe<sub>2</sub>S forms the C37 61 structure under core conditions above 190 GPa (Bazhanova et al. 2017; Tateno et al. 2019a).

In order to clarify high-pressure phase relations in Fe<sub>2</sub>P, here we examine phase equilibria in
Fe<sub>2</sub>P up to 83 GPa at high temperatures based on in-situ X-ray diffraction (XRD) measurements.
Results demonstrate that the C23 phase undergoes a transition into the C37 structure above 42
GPa with about 2% volume reduction. We also obtain the EoS of C37 Fe<sub>2</sub>P. These results suggest
the possible presence of C37-type (Fe,Ni)<sub>2</sub>(Si,S,P) in metallic iron cores of planets.

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### **METHODS**

69 High-pressure and -temperature (*P-T*) experiments were performed by using laser-heated 70 DAC techniques at beamline BL10XU, SPring-8 synchrotron facility (Hirao et al. 2020). A 71 symmetric DAC used a couple of diamond anvils with flat 300  $\mu$ m or beveled 200  $\mu$ m culet. 72 Starting material was fine powder of Fe<sub>2</sub>P (99.5 % purity, Sigma-Aldrich Co.) that was shaped 73 into a foil. It was packed into a sample chamber in a pre-indented rhenium gasket, together with 74 thermal insulation layers of KCl (99.99% purity, Kojundo Chemical Lab. Co. Ltd). The initial 75 sample size was ~10  $\mu$ m in thickness and ~70–100  $\mu$ m in diameter, depending on the culet size

of diamond anvils. After loading, a whole DAC was dried in a vacuum oven at 393 K for at least 2 hr to eliminate moisture in the sample chamber, and then the sample was squeezed. After compression to a target pressure at room temperature, we performed heating from both sides with Yb<sup>3+</sup>-doped YAG fiber lasers. Heating spot size was 20–30  $\mu$ m. Sample temperature was measured by a spectro-radiometric method. Pressure was determined from the volume of KCl with its thermal EoS (Tateno et al. 2019b). Temperature of KCl layers was estimated by following Campbell et al. (2009).

83 Angle-dispersive XRD patterns were collected on a flat panel detector (PerkinElmer 84 XRD0822) (Fig. 1). A monochromatic X-ray beam with energy of  $\sim 30$  KeV was used. The 85 wavelength of the X-ray beam, the distance between sample and the detector, and their alignment 86 were calibrated by using a CeO<sub>2</sub> standard. The calibrated wavelength was 0.4138 Å (runs #1, 2) 87 and 0.4141 Å (runs #3, 4). The incident X-ray beam size was ~8 µm in full-width at half 88 maximum. The variations in temperature within such 6  $\mu$ m area at the hot spot were less than 89  $\pm 10\%$ . Collected XRD patterns were analyzed using the IPAnalyzer and PDIndexer programs 90 (Seto et al. 2010).

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### RESULTS

93 New pressure-induced phase transition in Fe<sub>2</sub>P

We performed four separate sets of high *P-T* experiments up to 83 GPa in pressure and 2330
K in temperature (Fig. 2, Table S1 in the Supplemental Information). In order to avoid kinetic
hindering of phase transition, heating was made for at least 10 min at a given temperature above
1300 K.

In run #1, broad diffraction peaks from the hexagonal C22 phase of the starting material were
observed at 33 GPa before heating (Fig. 1). Upon heating, the XRD pattern changed to that of the
orthorhombic C23 Co<sub>2</sub>P-type structure at 1650 K, whose unit-cell parameters are in good

101 agreement with those reported previously (Dera et al. 2008). The C23 phase was observed up to 102 39 GPa and 1340 K in subsequent compression/heating cycles. When we further compressed and 103 reheated this sample to 1650 K at 52 GPa, several new peaks were found, while 210 and 103 104 peaks from the C23 phase disappeared (Fig. 1f). The overall XRD pattern was assigned with the 105 Co<sub>2</sub>Si-type (C37) structure (Fig. 1h). A direct transformation from the C22 starting material to 106 C37 was observed in runs #2 and #4. We confirmed the stability of the C37 phase up to 83 GPa.

The coexistence of C23 and C37 phases was observed in run #3. The relative peak intensities
of the C23 and C37 phases did not change during heating to 1380 K at 44 GPa for 35 min (Fig.
S1 in the Supplementary Information). This sample transformed completely to single phase C37
during heating at 49 GPa. The back transformation to C23 was found upon decompression and
reheating at 39 GPa. These observations tightly constrain the phase transition boundary between
C23 and C37 (Fig. 2). The stability of the C23 phase was confirmed down to 12 GPa and 1300
K.

114 The C23 and C37 structures of Fe<sub>2</sub>P exhibited the same symmetry, but atomic arrangements and lattice parameters are distinct. The P atom is coordinated to nine and ten Fe atoms in C23 115 116 and C37, respectively (Geller 1955, Rundqvist 1960). Upon C23 to C37 transition, the 117 orthorhombic unit-cell is shortened along a-axis by 5.8% but elongated by 0.9% and 3.4% along 118 b- and c-axes, respectively (Fig. S2 in the Supplementary Information). The c/a axial ratio of 119 C37 Fe<sub>2</sub>P was found to be 1.34-1.41, much larger than 1.16-1.21 of the C23 phase. They are 120 similar to 1.44 for C37 Co<sub>2</sub>Si (Geller 1955) and 1.16 for C23 Co<sub>2</sub>P (Rundqvist 1960) at ambient 121 condition. The c/a of C37 Fe<sub>2</sub>P is also similar to 1.35–1.40 of C37 Fe<sub>2</sub>S reported at 180–293 GPa 122 (Tateno et al. 2019).

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### 124 Equation of state for C37 Fe<sub>2</sub>P

125 Pressure-volume (P-V) data were collected for C23 and C37 Fe<sub>2</sub>P at 0-42 GPa and 42-81 126 GPa, respectively (Table S2 in the Supplementary Information). We used 19–24 diffraction lines 127 to obtain the volume of C37 phase expect at 41.8 GPa where only 11 peaks were employed 128 because of the coexistence of the C23 and C37 phases. Volumes were measured at 300 K each 129 time after heating to high temperatures, which minimizes non-hydrostatic stress on a sample. It 130 has been reported that the KCl pressure medium with thermal annealing results in small 131 deviatoric stress on a sample (Tateno et al. 2019b). Indeed, it is supported by relatively sharp 132 XRD peaks from the sample (Fig. 1). The present *P*-*V* data for the C23 phase are consistent with its EoS reported by Dera et al. (2008); the deviations of our data from their EoS are within 0.6% 133 134 (Fig. 3). The *P*-*V* data of C37 Fe<sub>2</sub>P were fitted by the 2nd-ordered Birch-Murnaghan EoS, giving  $V_0 = 133.0(8)$  Å<sup>3</sup> and bulk modulus  $K_0 = 193.6(78)$  GPa at zero pressure when its pressure 135 136 derivative  $K_0$  is fixed at 4. Such  $K_0$  of the C37 phase is larger than 174 GPa for C23 (Dera et al. 137 2008).

The volume reduction upon C23 to C37 transition is calculated to be 2.3% at 42 GPa from
their EoSs, which agrees with 1.7% volume difference between coexisting C23 and C37 at 42
GPa and 300 K in run #3 (Fig. 3). Similar isosymmetric phase transition from C23 to C37 in
PbF<sub>2</sub> involves ~2% volume reduction at ~10 GPa (Haines et al. 1998).

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### DISCUSSION

Iron phosphides have affinities with iron sulfides at high pressure; for instance,  $Fe_3P$  and Fe<sub>3</sub>S have identical crystal structure (Fei et al. 2000) and form a solid solution  $Fe_3(P,S)$  above 23 GPa (Stewart and Schmidt 2007). The recent XRD measurements by Tateno et al. (2019a) demonstrated that Fe<sub>2</sub>S adopts the C37 structure, same as that for Fe<sub>2</sub>P shown above, in a pressure range from ~190 GPa to at least 306 GPa at 3000 K. It is most likely that C37-type Fe<sub>2</sub>P and Fe<sub>2</sub>S form continuous solid solution at that pressure range. Furthermore, hexagonal Fe<sub>2</sub>Si

phase also occurs at 1 bar and high temperature (note that C37 is the Co<sub>2</sub>Si-type structure).
While Fe<sub>2</sub>Si is not stable above 14 GPa (Fischer et al. 2013), C37-type Ni<sub>2</sub>Si was observed to 75
GPa and predicted to be stable to 400 GPa (Errandonea et al. 2008).

153 In addition,  $Fe_2S$  is the most Fe-rich sulfide above ~250 GPa, where  $Fe_3S$  decomposes into 154 Fe + C37 Fe<sub>2</sub>S (Tateno et al. 2019a; Ozawa et al. 2013). Similarly it is possible that C37 Fe<sub>2</sub>P, 155 rather than  $Fe_3P$ , is the most Fe-rich phosphide at that pressure range as has been predicted by 156 theoretical calculations (Zhao et al. 2017; Sagatov et al. 2020). Previous XRD measurements on 157 Fe<sub>3</sub>P up to 111 GPa reported the occurrence of the peaks from hcp-Fe after heating above 70 158 GPa (Lai et al. 2020), which may indicate a decomposition of Fe<sub>3</sub>P. Indeed, hcp Fe + C37 Fe<sub>3</sub>P 159 assemblage has a smaller volume than Fe<sub>3</sub>P (Lai et al. 2020) at any pressure range, and the 160 volume difference increases with increasing pressure, suggesting that the hcp  $Fe + C37 Fe_2P$ 161 assemblage is stabilized with respect to Fe<sub>3</sub>P under core pressures. These indicate that C37-type 162 (Fe,Ni)<sub>2</sub>(S,Si,P) could form with wide solid solution and be the most Fe-rich compound not only 163 in the Fe-S binary system but in wider compositional space including Ni, Si, and P.

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### **IMPLICATIONS**

166 While the abundance of phosphorous has been estimated to be 0.2 wt% in the core 167 (McDonough 2014), iron meteorites contain up to 1.8 wt% P, which may be the upper bound for 168 its concentration in the Earth's core. Here we estimate how the 1.8 wt% P contributes to the 169 density deficit in the outer core. The density of C37 Fe<sub>2</sub>P was calculated using the present 300 K 170 EoS and the thermal expansion of hcp Fe (Fei et al. 2016) (Fig. S3 in the Supplementary 171 Information). The thermal expansion coefficient of hcp-Fe (Fei et al. 2016) is similar to that of 172 Fe<sub>3</sub>S at 1 bar (Thompson et al. 2020). Theoretical calculations also showed that the effects of 173 light elements on thermal expansion are almost negligible at inner core conditions (Li et al. 174 2018). We therefore assume the thermal expansion for C37 Fe<sub>2</sub>P the same as that of hcp Fe. The

density of C37 Fe<sub>2</sub>P is estimated to be  $9.67 \pm 0.12$  g/cm<sup>3</sup> at 136 GPa and 4000 K of topmost core 175 176 conditions. It is 13.5% lower than that of hcp Fe and thus suggests density reduction of 0.41%177 per 1 at% P, indicating that the 7.5–7.6% density deficit of the outer relative to liquid Fe 178 (Kuwayama et al. 2020) may be explained by 18.4 at% (11.2 wt%) P in liquid Fe. The maximum 179 P content in the liquid core based on cosmochemical estimates (1.8 wt%) only accounts for 17% 180 of the observed density deficit. The estimation based on the density difference between solids 181 might be an underestimate. Recent work on the EoS for liquid Fe-P based on sound velocity 182 measurements (Kinoshita et al. 2020) reported slightly smaller effect of P on the density of liquid 183 Fe.

At 329 GPa and 5000 K relevant to the topmost inner core conditions, the density of C37 Fe<sub>2</sub>P is calculated to be  $11.86 \pm 0.18$  g/cm<sup>3</sup>. The observed density of 12.76 g/cm<sup>3</sup> (Dziewonski and Anderson 1981) is elucidated by mixing 62% hcp Fe and 38% C37 Fe<sub>2</sub>P. Indeed, it requires 8.5 wt% P in the inner core, which is unlikely unless phosphorous in the Earth's core is concentrated in its solid part.

The present study imply that C37-type (Fe,Ni)<sub>2</sub>(S,Si,P) forms with wide solid solution and is the most Fe-rich compound in the multi-component Fe-Ni-S-Si-P system. It could constitute planetary metallic iron cores, although it is not dense enough to be a main constituent of the Earth's inner core.

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- 285

## 286 Figure captions

**FIGURE 1.** XRD patterns in run #1 collected (a-c) at ~33 GPa exhibiting the C22 phase before

**288** heating and C23 upon and after heating, (e-g) at ~46 GPa demonstrating metastable C23 before

heating, C37 upon and after heating. Calculated XRD patterns are given for (d) C23 and (h) C37
structures. Asterisks, unknown peaks.

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FIGURE 2. Phase diagram of Fe<sub>2</sub>P. The stabilities of C23 and C37 Fe<sub>2</sub>P are shown by blue and
magenta, respectively. Both coexisted near the phase boundary. The C22-C23 boundary from
Dera et al. (2008).

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- **FIGURE 3.** Compression curves of C23 (blue) and C37 Fe<sub>2</sub>P (magenta) at 300 K. Filled circles,
- this study; blue open diamonds, Dera et al. (2008). Curves are based on the EoSs for C23 (Dera
- **298** et al. 2008) and C37 (this study).





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# 20 30 40 50 60 70 Pressure (GPa)

