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1 **Melting experiments on the Fe–C binary system up to 255 GPa:**

2 **Constraints on the carbon content in the Earth's core**

3

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17

18 **ABSTRACT**

19 Phase relations, including the eutectic liquid composition in the Fe–C binary
20 system, remain unclear under the core pressure range, which makes estimating the
21 carbon budget in the Earth’s core difficult. To explore this issue, we have conducted
22 melting and subsolidus experiments on Fe-C alloys in a diamond-anvil cell up to 255
23 GPa. Textural and compositional characterizations of quenched samples show that
24 carbon concentration in the eutectic liquid slightly decreases with increasing pressure
25 and is about 3 wt.% at the inner core boundary (ICB) pressure. The solubility of carbon
26 in solid Fe is found to be almost constant at ~1.0 wt.%. *In situ* X-ray diffraction data
27 indicate that Fe forms eutectic melting with Fe₃C to 203 GPa and with Fe₇C₃ at 255
28 GPa.

29 Previous studies on liquid Fe-C alloys suggested that the density of the outer core is
30 explained by liquid Fe containing 1.8 to 4.2 wt.% C. If the liquid core includes <3 wt.%
31 C as a single light element, hexagonal close-packed (hcp) Fe crystallizes at the ICB.
32 However, the carbon content in such solid Fe is ≤1 wt.%, less than that required to
33 account for the inner core density deficit from pure iron. When the outer core includes
34 ≥3 wt.% C, it forms Fe₇C₃ at the ICB, whose density is too small for the inner core.
35 Carbon is therefore not a primary light element in the core. Nevertheless, the outer core
36 liquid can be Fe-C-Si, Fe-C-S, or Fe-C-H. Such core liquid crystallizes solid Fe with
37 light elements including less than 1 wt.% C, which may explain the density and the
38 sound velocities observed in the inner core.

39

40 *Keywords:* core; iron alloy; carbon; eutectic liquid; high pressure

41

42 1. Introduction

43 Carbon has been believed to be one of feasible light elements contained in planetary
44 cores because of its high abundance in the solar system and strong affinity to molten
45 iron (Benz and Elliott, 1961; Anders and Grevesse, 1989; Wood, 1993). Recent first-
46 principles calculations predicted that the incorporation of a small amount of carbon in
47 hcp Fe is compatible with the density and sound velocities observed in the Earth's inner
48 core (Li et al., 2018).

49 In order to reveal the abundance of carbon in the core, it is important to understand
50 the Fe–C phase diagram at high pressure, in particular at 330 GPa, which corresponds to
51 the conditions at the ICB. Wood (1993) first thermodynamically calculated the phase
52 relations in the Fe–C system up to 136 GPa and predicted that the Earth's core could
53 contain ~4 wt.% C. Nakajima et al. (2009) experimentally determined the melting phase
54 relationships in the Fe-rich portion of the Fe–C system up to 29 GPa and demonstrated
55 that Fe₇C₃ appears as a liquidus phase. Using an *in situ* X-radiographic imaging
56 technique, Lord et al. (2009) found that carbon concentration in the eutectic liquid in the
57 Fe–C binary system decreases substantially with increasing pressure to 70 GPa. The
58 thermodynamic modeling by Fei and Brosh (2014) based on multi-anvil experiments up
59 to 25 GPa predicted that the Fe–C eutectic liquid composition includes 2.2 wt.% C at
60 330 GPa. More recently Morard et al. (2017a) reported the change in carbon
61 concentration in the eutectic liquid in the Fe–Fe₃C binary up to 107 GPa and estimated
62 it to be 2.6 wt.% C at the core–mantle boundary (CMB). However, they obtained liquid
63 compositions from X-ray diffraction (XRD) patterns with the Rietveld method, which
64 includes great uncertainty. So far, melting experiments on the Fe–C system have not
65 been carried out under the core pressure range (>136 GPa). Moreover, the solubility of

66 carbon in solid iron also remains unknown above 25 GPa (Chabot et al., 2008; Walker
67 et al., 2013; Fei and Brosh, 2014).

68 It is also important to verify the change in liquidus phase in the Fe–C system. It has
69 been suggested that the liquidus field of Fe_7C_3 expands with respect to that of Fe_3C and
70 eutectic melting occurs between Fe and Fe_7C_3 above 120 GPa (Lord et al., 2009; Fei
71 and Brosh, 2014). Furthermore, the recent experiments by Liu et al. (2016) showed the
72 decomposition of Fe_3C into Fe + Fe_7C_3 above 145 GPa, but it contradicts the formation
73 of Fe_3C at >300 GPa and >5000 K reported by Tateno et al. (2010). Fe_7C_3 has been
74 regarded as a possible constituent in the inner core because it provides a good match for
75 both compressional (V_P) and shear velocities (V_S) (or Poisson's ratio) of the inner core
76 under relevant conditions (Nakajima et al., 2009; Mookherjee et al., 2011; Chen et al.,
77 2014; Prescher et al., 2015). The calculations by Li et al. (2016), however, demonstrated
78 that the density of Fe_7C_3 is too small for the inner core.

79 Recent progress in melting experiments in a diamond-anvil cell (DAC) combined
80 with a focused ion beam (FIB) technique has enabled us to determine the eutectic liquid
81 composition to the core pressure range (Ozawa et al., 2016; Mori et al., 2017; Hirose et
82 al., 2017). In this study, we have conducted both subsolidus and melting experiments on
83 Fe-C alloys up to 255 GPa in order to determine the change in melting phase relations
84 with increasing pressure, in particular 1) the stability of Fe_7C_3 at liquidus, 2) carbon
85 concentration in eutectic liquid, and 3) the solubility of carbon in solid iron. Based on
86 these results, we discuss the possible carbon content in the Earth's core and the
87 mineralogy of the inner core.

88

89 **2. Experimental methods**

90 High-pressure and -temperature (P - T) conditions were generated in a laser-heated
91 DAC using double-, single-beveled, and flat diamond anvils with 60, 90, 150, and 300
92 μm culet size. Starting materials were foils of Fe containing 1.9 wt.% C and 4.0 wt.% C,
93 which are homogeneous mixtures of fine-grained Fe and Fe_3C synthesized by an ultra-
94 rapid quenching method (Morard et al., 2011, 2017a). Rhenium gaskets were pre-
95 indented to about 40 μm thickness before laser drilling or spark erosion of sample holes
96 with 30–100 μm diameters. Sample pellets were loaded between two pieces of about 10
97 μm thick dry Al_2O_3 , which served as a pressure-transmitting medium and a thermal
98 insulator from the diamond anvils. After loading, the whole DAC was dried in a
99 vacuum oven at 423 K for more than 12 hrs, and subsequently a sample chamber was
100 flushed with dry argon and squeezed in an argon atmosphere.

101 After compression to a desired pressure, the sample was heated from both sides
102 with a couple of 100-W single-mode Yb fiber lasers. We used beam-shaping optics,
103 which converts a Gaussian beam to one with a flat energy distribution and thus reduces
104 radial temperature gradient in the sample. A laser-heated spot was up to ~ 20 μm across.
105 One-dimensional temperature distributions on the surface of the sample were obtained
106 using a spectro-radiometric method (Ohishi et al., 2008). Heating duration was limited
107 to about 5 s in order to avoid fluctuations in temperature, which would otherwise cause
108 complex melting textures. The experimental temperature reported in this study is that at
109 the solid/liquid boundary, which is obtained by combining the measured radial
110 temperature distribution with the melting texture observed in a sample's cross section
111 (Fig. 1) (see Ozawa et al., 2016 for details). We polished the sample using an FIB from
112 both sides little by little (~ 1 μm for each step) in order to have a cross section at the
113 center of a liquid pool. The sample was thinned to about 3 μm thickness at the end. The

114 uncertainty in temperature is $\pm 5\%$ according to Mori et al. (2017), which includes
115 uncertainties in the width of the liquid pool as well as those derived from the facts that
116 we calculated temperature from integrated light not only from the sample surface but
117 also from the pressure medium and that spatial resolution of the temperature profile was
118 2 to 3 μm .

119 Pressure at room temperature was obtained based on the Raman shift of a diamond
120 anvil (Akahama and Kawamura, 2004). It was then corrected for a contribution of
121 thermal pressure. According to Andraut et al. (1998), when purely isochoric heating is
122 made, the thermal pressure is written as $\Delta P = \alpha K_T T$, in which α is thermal expansivity
123 and K_T is isothermal bulk modulus. Assuming the thermal parameters for liquid Fe-C
124 same as those for pure iron, we employ $\alpha K_T = 9 \text{ MPa/K}$ (Ichikawa et al., 2014) for runs
125 performed above 83 GPa. Andraut et al. (1998) demonstrated that 90% of such
126 isochoric thermal pressure contributes to an experimental pressure increase at the core
127 pressure range. For runs #1, #2, and #5 conducted at relatively low pressures, the lower
128 αK_T value of 4 MPa/K and 60% of the theoretical value were applied (Morard et al.,
129 2011; Andraut et al., 1998). The overall errors in pressure should be less than $\pm 10\%$ in
130 the present experiments including the uncertainty in thermal pressure estimate, as
131 argued in Mori et al. (2017). Indeed, we found 191 GPa at 2300 K in run #7 based on
132 the volume and equation of state (EoS) of Fe_3C (Sata et al., 2010), which is consistent
133 with 194 GPa calculated with the thermal pressure correction.

134 Synchrotron XRD measurements were carried out *in situ* at high P - T in runs #7
135 and #8 at BL10XU, SPring-8 (Ohishi et al., 2008) using an X-ray beam with an energy
136 of $\sim 30 \text{ keV}$. Angle-dispersive XRD spectra were collected on a flat panel detector
137 (Perkin Elmer) with typical exposure time of 200 ms. A monochromatic incident X-ray

138 beam was collimated to 2 μm (FWHM). Visible fluorescent light induced by X-rays in a
139 diamond was used to precisely align the laser-heated spot with the X-ray beam. Two-
140 dimensional XRD images were integrated to produce a conventional one-dimensional
141 diffraction profile using the IPAnalyzer software (Seto et al., 2010).

142 Recovered samples from our DAC experiments were cross-sectioned using a Ga^+
143 focused ion beam (FIB) instrument (FEI VersaTM3D DualBeamTM). During FIB
144 sectioning, sample was monitored by scanning electron microscopy using back-
145 scattered electrons to precisely section the center of a heated spot. The sample cross
146 sections were then examined by a field-emission-type scanning electron microscope
147 (FE-SEM) and energy dispersive X-ray spectrometry (EDS) with a silicon drift detector.
148 The section was then mounted on a Cu grid and further thinned to approximately 3 μm
149 thickness for further analysis with a field-emission-type electron probe microanalyzer
150 (FE-EPMA, JXA-8530F, JEOL) in order to determine chemical compositions. Since Fe-
151 C samples are good electric conductors, no coating material was necessary for EPMA
152 analysis with an accelerating voltage of 10 kV and a beam current of 15 nA. A focused
153 electron beam for spot analyses was less than 50 nm in size. We used both Fe_3C and
154 Fe_7C_3 as standards that were synthesized at 5 GPa/1473 K and applied the ZAF
155 correction (Nakajima et al., 2009). Corundum (for Al and O) and pure iron (for Fe) were
156 also used for standards. The X-ray counting time for peak/background was 20s/10s.
157 LDE2 (C), TAP (Al), LIFH (Fe), and LDE1H (O) were analyzing crystals.

158 Very minor amounts of aluminum and oxygen were found when analyzing the
159 sample, most likely due to a signal from a neighboring/underlying Al_2O_3 insulation
160 layer. We estimated the carbon concentrations in quenched liquid and solid metals after
161 subtracting Al_2O_3 from raw analyses. In addition, we analyzed two samples (runs #2 &

162 #6) by EPMA with a liquid nitrogen cold finger (JXA-8530FPlus HyperProbe Electron
163 Probe Microanalyzer) at both 10 kV and 15 kV accelerating voltage (Table S1). The
164 results demonstrate that the carbon contents obtained with and without the cold finger
165 are similar to each other. We repeated the analyses of the Fe₃C standard twenty times
166 and found that the carbon concentration changed only by ±0.1766 atm%. While
167 chemical compositions were calculated by using both the 'standard' ZAF correction and
168 the phi-rho-z type procedure, the results are consistent with each other (see Table S1).

169

170 **3. Results**

171 *3.1. Carbon contents in eutectic liquid and coexisting solid iron*

172 We have conducted eight separate DAC runs for melting experiments in a pressure
173 range from 23 GPa to 255 GPa (Table 1). Figs. 1 and 2 show typical melting textures on
174 recovered samples. There is a chemically homogeneous part at the center of a laser-
175 heating spot, which is non-stoichiometric in composition and should represent a
176 quenched liquid. The liquidus phase (solid phase in contact with liquid) is found at both
177 sides of the liquid. The outermost low-temperature area remained subsolidus. We
178 observed iron carbide (Fe₃C or Fe₇C₃) or metallic iron (or both) as liquidus phase(s). In
179 runs #2, #4, #5, and #8, both iron carbide and iron were present, suggesting that the
180 quenched liquid in these runs may represent a eutectic liquid in the Fe–C binary system.
181 Carbon diffusivity in liquid iron was estimated to be about 10⁻⁸ m²/s under the present
182 *P-T* conditions (Helffrich, 2014), indicating that 1 s is long enough for carbon to diffuse
183 in the present liquid pool that was less than 20 μm across (Figs. 1 and 2). Since
184 melting/crystallization at the liquid/solid boundary occurs almost instantaneously,
185 chemical homogeneity in the liquid assures that chemical equilibrium was attained in

186 the present heating duration of about 5 s. The Fe-C liquids obtained in the core pressure
187 range included about 1 wt.% oxygen in addition to carbon (Table 1), which might have
188 affected phase relations in the Fe-C binary system.

189 We determined the carbon concentration in quenched liquid up to 255 GPa, the
190 conditions corresponding to the middle of the outer core, more than twice the pressure
191 compared to previous experimental studies (e.g., Lord et al., 2009; Fei and Brosh, 2014;
192 Morard et al., 2017a). Fig. 3 demonstrates the carbon concentrations in liquids as a
193 function of pressure, which constrains the change in eutectic liquid composition,
194 considering that they indicate the lower and upper bounds for the carbon content in
195 eutectic liquid at each pressure when coexisting with iron and iron carbides,
196 respectively. These data show a small reduction in carbon content in the eutectic liquid
197 with increasing pressure above 23 GPa. Our results are not consistent with the
198 continuous reduction that was thermodynamically predicted by Fei and Brosh (2014)
199 and experimentally reported by Lord et al. (2009) (Fig. 3). The difference from Lord et
200 al. (2009) may be attributed to the difference in analytical method: Lord and others
201 employed an X-radiographic imaging technique for chemical analysis, while we based
202 our measurements on electron microprobe analyses.

203 We also obtained the carbon concentrations in solid iron coexisting with Fe-C
204 liquid as a function of pressure (Fig. 4). Liquid Fe-C coexists with face-centered cubic
205 (fcc) iron at relatively low pressure range, in which carbon atoms occupy the octahedral
206 interstitial sites (Fei and Brosh, 2014). Previous studies reported that the maximum
207 solubility of carbon in fcc-Fe is <2.1 wt.% at 1 bar and predicted that it decreases at
208 higher pressures (Walker et al., 2013; Fei and Brosh, 2014). Our results show about 1.0
209 wt.% in fcc-Fe from 23 to 54 GPa, in good agreement with such predictions. Above 138

210 GPa in the present experiments, hcp Fe should have crystallized from Fe-C liquid and
211 again included 1.0 wt.% or less C. The effect of pressure on the solubility of carbon in
212 hcp Fe was not observed.

213

214 3.2. Eutectic temperature in the Fe–C system

215 The temperature at the solid/liquid boundary gives the upper bound for eutectic
216 temperature. These temperatures are plotted as a function of pressure in Fig. 5a, which
217 constrains the eutectic melting curve to mid-outer core pressures. We fit the Simon-
218 Glatzel equation to the data (Simon and Glatzel, 1929):

$$219 \quad T_m = T_{mref} \left(\frac{P - P_{ref}}{a} + 1 \right)^{1/c} \quad (1)$$

220 where T_m is eutectic temperature, and both a and c are fitting parameters. $T_{mref} = 1513$
221 K at $P_{ref} = 5$ GPa is employed as a reference eutectic temperature from previous data
222 obtained using a large-volume press (Fei and Brosh, 2014). The best fitted parameters
223 are $a = 8.4 \pm 3.3$ GPa and $c = 4.1 \pm 0.5$. The obtained eutectic melting curve shown in
224 Fig. 5a is consistent with those of previous studies by Liu et al. (2016) and Morard et al.
225 (2017a) within experimental uncertainties. Fig. 5b compares the eutectic melting curves
226 of iron alloys. Under the core pressure range, the Fe–C system exhibits a eutectic
227 temperature lower than those of Fe (Anzellini et al., 2013), Fe–FeSi (Fischer et al.,
228 2013), and Fe–FeO (Morard et al., 2017a). And, the Fe–C eutectic melting temperature
229 is higher than that in Fe–Fe₃S below ~250 GPa, but is lower at higher pressures
230 including the ICB pressure (Mori et al., 2017).

231

232 3.3. Liquidus field of Fe₇C₃

233 In runs #7 and #8 using the Fe-4.0 wt.%C starting material, the sample was
234 initially compressed at room temperature to 176 GPa and 226 GPa, respectively (Fig.
235 6). Broad XRD peaks from hcp Fe and Fe₃C were observed before heating in both runs.
236 The peaks from both phases became sharper and spotty upon heating to 2300 K in run
237 #7, in which more than 10 peaks were indexed to Fe₃C cementite (Sata et al., 2010), and
238 only Fe₃C phase was observed from the sample in the XRD pattern during melting at
239 203 GPa and 3350 K. In addition, we confirmed with an FE-EPMA that the quenched
240 liquid was surrounded by Fe₃C in the recovered sample (Fig. 7a). These indicate that Fe
241 forms eutectic melting with Fe₃C at 203 GPa.

242 In the case of run #8, the diffraction peaks from hcp Fe and Fe₃C became sharper
243 and spotty upon heating. We then observed the appearance of the peaks that are
244 assigned to Fe₇C₃ (orthorhombic, *Pbca*) (Prescher et al., 2015) after we melted the
245 sample by increasing temperature to 3570 K at 255 GPa. After quenching this sample,
246 we confirmed with the FE-EPMA that the liquid was in contact with both Fe and Fe₇C₃,
247 whereas the subsolidus part was composed of Fe and Fe₃C (Fig. 7b). These show that
248 eutectic melting occurs between Fe and Fe₇C₃ at 255 GPa. This observation is not
249 consistent with Liu et al. (2016), who argued that Fe₃C dissociates into Fe + Fe₇C₃ at
250 subsolidus above 145 GPa when using Fe₃C as a sample. Liu and others based their
251 conclusions purely on the change in XRD patterns, and they may have collected them
252 above eutectic temperature.

253

254 4. Discussion

255 4.1. Phase diagram of Fe–C system at ICB

256 The eutectic liquid composition (Fig. 3) and eutectic melting curve obtained in this
 257 study (Fig. 5) indicate that eutectic melting occurs in Fe–Fe₃C at Fe + 3.5 wt.% C at
 258 135 GPa and 3000 K. And, these data determined up to 255 GPa suggest that the
 259 eutectic liquid includes about 3 wt.% C at 330 GPa and 3750 K.

260 We model the liquidus curve for the Fe-rich side of the eutectic to 330 GPa (Fig.
 261 8). Considering an ideal solution, a molar ratio of Fe in liquid at T is given by:

$$262 \quad \chi_{\text{Fe liq}} = \exp \left\{ \frac{\bar{G}_{\text{Fe sol}}^0 - \bar{G}_{\text{Fe liq}}^0}{RT} \right\} = \exp \left\{ - \int_{T_{m \text{ Fe}}}^T \frac{\bar{H}_{\text{Fe sol}}^0 - \bar{H}_{\text{Fe liq}}^0}{RT^2} dT \right\} \quad (2)$$

263 where $\bar{G}_{\text{Fe } i}^0$ and $\bar{H}_{\text{Fe } i}^0$ are standard Gibbs free energy and the enthalpy of phase i ,
 264 respectively, $T_{m \text{ Fe}}$ is the melting temperature of pure Fe, and R is gas constant. When
 265 we assume that an enthalpy change upon fusion, $\bar{H}_{\text{Fe liq}}^0 - \bar{H}_{\text{Fe sol}}^0$, is independent from
 266 temperature, Eq. (2) is written as:

$$267 \quad \chi_{\text{Fe liq}} = \exp \left\{ \left(\frac{\bar{H}_{\text{Fe liq}}^0 - \bar{H}_{\text{Fe sol}}^0}{RT_{m \text{ Fe}}} \right) \times \left(1 - \frac{T_{m \text{ Fe}}}{T} \right) \right\} = \exp \left\{ A \times \left(1 - \frac{T_{m \text{ Fe}}}{T} \right) \right\} \quad (3)$$

268 Here A is constant and calculated from $T_{m \text{ Fe}}$ (Anzellini et al., 2013), eutectic
 269 temperature, and eutectic composition (Figs. 3 and 5) at a given pressure (see also Mori
 270 et al., 2017).

271

272 4.2. Fe-C core liquid?

273 Melting phase relations in the Fe–C system constrain the carbon budget in the
 274 Earth's core and the mineralogy of the solid inner core. The maximum carbon content in
 275 the outer core has been estimated from the core density deficit. Recent experimental and
 276 computational studies on the density of liquid Fe–C alloys indicate 1.8 to 4.2 wt.% C in
 277 the liquid core at the ICB (Badro et al., 2014; Nakajima et al., 2015; Morard et al.,
 278 2017b), although earlier estimates based on the EoS of solid Fe₃C suggested higher

279 carbon concentration (7.7–9.2 wt.% C) (Sata et al., 2010). Since the eutectic point is
280 located at about 3 wt.% C at 330 GPa (Fig. 8), if the Fe-C outer core includes less than
281 3 wt.% C, it crystallizes hcp Fe with ≤ 1 wt.% C at the ICB (Fig. 4). In this case,
282 however, the difference in carbon concentration between the liquid and solid core is too
283 small to explain the density jump (4.5 to 6.5%) across the ICB (Shearer and Masters,
284 1990; Masters and Gubbins, 2003). Moreover, assuming a linear density change
285 between pure Fe (Sakamaki et al., 2016), Fe₃C (Sata et al., 2010), and Fe₇C₃ (Prescher
286 et al., 2015), hcp Fe with 1.0 wt.% C is found to be only 1.3% lighter than pure iron,
287 which is not enough to account for the inner core density deficit of 4–6% (Brown and
288 McQueen, 1986; Shearer and Masters, 1990; Masters and Gubbins, 2003; Dewaele et
289 al., 2006; Komabayashi and Fei, 2010). This is supported by the recent calculations by
290 Li et al. (2018). Less than 3 wt.% C as a single light element in the core is therefore
291 unlikely.

292 Next we consider the case that the liquid core contains more than 3 wt.% C as the
293 sole light component, from which Fe₇C₃ crystallizes at the ICB (Fig. 8). It has been
294 suggested that both V_P and V_S —in particular the slow V_S (high Poisson’s ratio)—of the
295 inner core could be reconciled with non-magnetic Fe₇C₃ (Mookherjee et al., 2011; Chen
296 et al., 2014; Prescher et al., 2015). If the inner core is composed of solid Fe₇C₃, the
297 liquid outer core should include 5.4–6.7 wt.% C according to Badro et al. (2014) or 5.2–
298 6.0 wt.% C based on Nakajima et al. (2015), considering that the outer core should be
299 4.5–6.5% less dense than solid Fe₇C₃ (Chen et al., 2014). More than 5 wt.% C in liquid
300 iron, however, leads to a bulk sound velocity and a density much higher and lower than
301 those observed for the outer core, respectively (Badro et al., 2014; Nakajima et al.,
302 2015; Morard et al., 2017b) and is thus unlikely. The computational study by Li et al.

303 (2016) also showed that the density of Fe_7C_3 is too low to be a major constituent of the
304 inner core.

305 These suggest that carbon cannot be a predominant light element in the outer core.
306 It is indeed consistent with Wood et al. (2013), who proposed that the maximum carbon
307 content in the core is 1.0 wt.%, which was deduced from the carbon isotopic signature
308 in silicate Earth and the silicate-metal fractionation factors. It has also been argued that
309 the outer core velocity is explained by the incorporation of a small amount of carbon
310 that is not enough to account for its density deficit from pure iron (Badro et al., 2014;
311 Nakajima et al., 2015).

312

313 *4.3. Fe-C-X core liquid?*

314 Furthermore, we consider the Fe-C-X (X = Si, S, O, or H) ternary systems to seek
315 possible ranges of outer core composition, from which hcp Fe crystallizes (Figs. 9a-d).
316 The eutectic liquid composition in each Fe-X binary system has been estimated to be Fe
317 with 3 wt.% C (this study), 1.5 wt.% Si (Ozawa et al., 2016), 5 wt.% S (Mori et al.,
318 2017), and >10 wt.% O (Morard et al., 2017a) at 330 GPa. The hydrogen concentration
319 in the Fe-H eutectic liquid is unclear, but it would be around 1 wt.% H according to
320 Fukai (1992) and Shibasaki et al. (2014). The ternary eutectic points in these systems
321 are not exactly known, but the recent melting experiments performed by Tateno et al.
322 (2018) have demonstrated that the Fe-Si-S ternary eutectic point is located 1) near the
323 tie line between the Fe-FeSi and Fe-Fe₃S binary eutectic points and 2) close to the Fe-
324 Fe₃S binary join because the eutectic temperature in Fe-Fe₃S is much lower than that in
325 Fe-FeSi. The present data show that the eutectic temperature in the Fe-C binary system
326 is low compared to those in other systems (Fe-Si, Fe-S, and Fe-O) at 330 GPa (Fig. 5).

327 On the basis of these observations, [Figs. 9a–d](#) illustrate the liquidus phase relations
328 (showing a compositional range from which a specific solid phase first crystallizes) in
329 the Fe–C–X ternary systems at the ICB, with each ternary eutectic point located
330 relatively close to the Fe–C binary eutectic point except for the Fe–C–H system.

331 Previous experiments and calculations have estimated the maximum amount of
332 each light element in the liquid core to explain the outer core density deficit. Estimates
333 based on liquid iron alloys show 4.6–6.4 wt.% Si (Morard et al., 2013; Badro et al
334 2014), 5.8–14.0 wt.% S (Morard et al., 2013; Badro et al., 2014; Umemoto et al., 2014;
335 Kawaguchi et al., 2017), 5.5 wt.% O (Badro et al., 2014), and 1.0 wt.% H (Umemoto
336 and Hirose, 2015) at the ICB, which are again less than those obtained by the earlier
337 study on the EoSs of solid FeSi, FeS, and Fe_{0.95}O (Sata et al., 2010). These give the
338 possible compositional range of Fe–C–X ternary outer core liquid in [Figs. 9a–d](#) (green
339 area).

340 We find that hcp Fe crystallizes from possible liquid core compositions in all of the
341 Fe–C–Si, Fe–C–S, Fe–C–O, and Fe–C–H systems. The recent calculations by Li et al.
342 (2018) proposed that all of the density, V_P , and V_S of the solid inner core are explained
343 by hcp Fe₃₀C₁Si₁ (Fe + 0.7 wt.% C + 1.6 wt.% Si). Such inner core composition is
344 feasible, considering that the maximum solubilities of silicon and sulfur in hcp Fe when
345 coexisting with liquid alloys are ≤ 1.5 wt.% Si and 4 wt.% S at the ICB, respectively
346 (Ozawa et al., 2016; Mori et al., 2017). Hcp Fe + 1 wt.% C + 4.0 wt.% S also could
347 account for the inner core density (Sakai et al., 2012). Hydrogen is known to be soluble
348 in solid Fe (Fukai, 1992; Shibazaki et al., 2012; Terasaki et al., 2012), suggesting that
349 the hcp Fe–C–H inner core is also feasible. On the other hand, solid Fe crystallizing from
350 liquid Fe–C–O contains ≤ 1 wt.% carbon and a negligible amount of oxygen (Ozawa et

351 al., 2010), which does not account for the inner core density deficit (Li et al., 2018).
352 Therefore, while carbon is not a predominant light element in the core, the outer core
353 liquid can be Fe-C-Si, Fe-C-S, or Fe-C-H.

354

355 **5. Conclusion**

356 We have conducted melting experiments on the Fe–C binary system up to 255 GPa
357 by using a laser-heated DAC. The carbon concentration in eutectic liquid and the
358 solubility of carbon in solid iron were determined based on textual and chemical
359 characterizations for samples recovered from the DAC. Results show that 1) the carbon
360 content in eutectic liquid slightly decreases with increasing pressure from 4.3 wt.% C at
361 ambient pressure to 3.6 wt.% C at 255 GPa, 2) eutectic melting occurs between Fe and
362 Fe₃C to 203 GPa and between Fe and Fe₇C₃ at 255 GPa, and 3) the maximum solubility
363 of carbon in solid iron is almost constant (≤ 1 wt.%) up to 255 GPa. The eutectic liquid
364 in the Fe–C binary system includes about 3 wt.% C at 330 GPa.

365 If carbon is the sole light element in the core and the outer core includes <3 wt.%
366 C, hcp Fe crystallizes at the ICB but includes only less than 1 wt.% C, which does not
367 explain the inner core density deficit. If the liquid core contains more than 3 wt.% C, it
368 forms Fe₇C₃ at the ICB, whose density is too low for the inner core. These indicate that
369 carbon is not a primary light element in the core. On the other hand, the outer core can
370 be liquid Fe-C-Si, Fe-C-S, or Fe-C-H. It crystallizes hcp Fe including light elements
371 with less than 1 wt.% C, which may explain the density and the sound velocities
372 observed in the inner core.

373

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384

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572

573 **Figure captions**

574

575 **Fig. 1.** (a) Temperature profile and (b) composite X-ray maps for oxygen (red), carbon
576 (purple), iron (green), and aluminum (light blue) for run #3 performed at 138 GPa (see
577 [Fig. S1](#) for raw radiation spectra). Homogeneous quenched liquid is found at the center
578 (hot part) surrounded by solid layers of iron. A measured temperature profile is
579 combined in (a), which provides temperature at the liquid/solid boundary.

580

581 **Fig. 2.** Typical melting texture of a quenched sample and composite X-ray maps for
582 oxygen, carbon, aluminum, and iron for run #5 at 40 GPa. SIM, scanning ion
583 microscope image; SL, secondary electron image; Comp, backscattered image.
584 Homogeneous quenched liquid is found at the center surrounded by solid layers of Fe
585 and Fe₃C.

586

587 **Fig. 3.** Carbon concentrations in liquids obtained in this study. Liquid compositions are
588 shown by triangles (blue) when coexisting with solid Fe, inverse triangles (purple) when
589 in contact with Fe₃C, squares (red) when both solid Fe and Fe₃C were found, and a
590 diamond (orange) when solid Fe and Fe₇C₃ were formed. The triangles and inverse
591 triangles give lower and upper bounds for carbon concentration in eutectic liquid,
592 respectively. Open and cross symbols represent eutectic compositions reported by
593 previous studies (Chabot et al., 2008; Lord et al., 2009; Fei and Brosh, 2014; Morard et
594 al., 2017a). Green curve shows the change in eutectic liquid composition with
595 increasing pressure.

596

597 **Fig. 4.** Carbon contents in solid iron found in this study. Closed symbols are the same as
598 in Fig. 3. Previous reports on the maximum solubility of carbon in solid iron are shown
599 by open symbols (Walker et al., 2013; Fei and Brosh, 2014).

600

601 **Fig. 5.** (a) Fe–Fe₃C (or Fe–Fe₇C₃ above 255 GPa) eutectic melting curve (orange)
602 obtained in this study (closed symbols). It agrees well with the previously determined
603 Fe–C melting curves by Morard et al. (2017a) (blue) and Liu et al. (2015) (green). Black
604 dotted curve represents the solidus of Fe₃C composition reported by Liu et al. (2016).
605 Purple dashed curve shows the melting temperature of pure Fe (Anzellini et al., 2013).
606 (b) Eutectic melting curve of the Fe–C system obtained in this study compared with
607 those of the Fe–Fe₃S (Mori et al., 2017), Fe–FeO (Morard et al., 2017a), and Fe–FeSi
608 (Fischer et al., 2013) binary systems.

609

610 **Fig. 6.** XRD patterns of Fe + 4.0 wt.% C obtained before and after heating (no melting),
611 and during and after melting (a) at 203 GPa in run #7 and (b) 255 GPa in run #8. The
612 unit-cell parameters and volumes of Fe₃C and Fe₇C₃ are $a = 3.95(1) \text{ \AA}$, $b = 4.54(1) \text{ \AA}$, c
613 $= 5.95(1) \text{ \AA}$, and $V = 106.9(4) \text{ \AA}^3$ for Fe₃C, and $a = 10.40(1) \text{ \AA}$, $b = 3.96(1) \text{ \AA}$, $c =$
614 $12.06(1) \text{ \AA}$, and $V = 496.4(3) \text{ \AA}^3$ for Fe₇C₃.

615

616 **Fig. 7.** Quenched textures and composite X-ray maps for carbon, oxygen, and iron at (a)
617 203 GPa (run #7) and (b) 255 GPa (run #8). While liquid was surrounded by Fe₃C in
618 the sample quenched at 203 GPa, it was in contact with Fe₇C₃ and Fe at 255 GPa (the
619 subsolidus part was composed of Fe₃C and Fe).

620

621 **Fig. 8.** Phase diagrams for the iron-rich portion of the Fe–C binary system at 54, 138,
622 203, and 255 GPa from the present experiments and at ICB conditions (330 GPa) by
623 extrapolation. Red and blue (and gray) curves represent Fe–Fe₃C and Fe–Fe₇C₃
624 eutectic, respectively.

625

626 **Fig. 9.** Likely liquidus phase relations in the Fe–C–X ternary systems at 330 GPa. Red
627 circles represent the eutectic compositions in the Fe–C (this study), Fe–Si (Ozawa et al.,
628 2016), Fe–S (Mori et al., 2017), Fe–O (Morard et al., 2017a), and Fe–H binary systems
629 (Fukai, 1992). Green regions show the range of possible composition of the outer core
630 that explains its density based on studies on liquid iron alloys (Morard et al., 2013;
631 Badro et al., 2014; Umemoto et al., 2014; Umemoto and Hirose, 2015; Nakajima et al.,
632 2015; Kawaguchi et al., 2017).

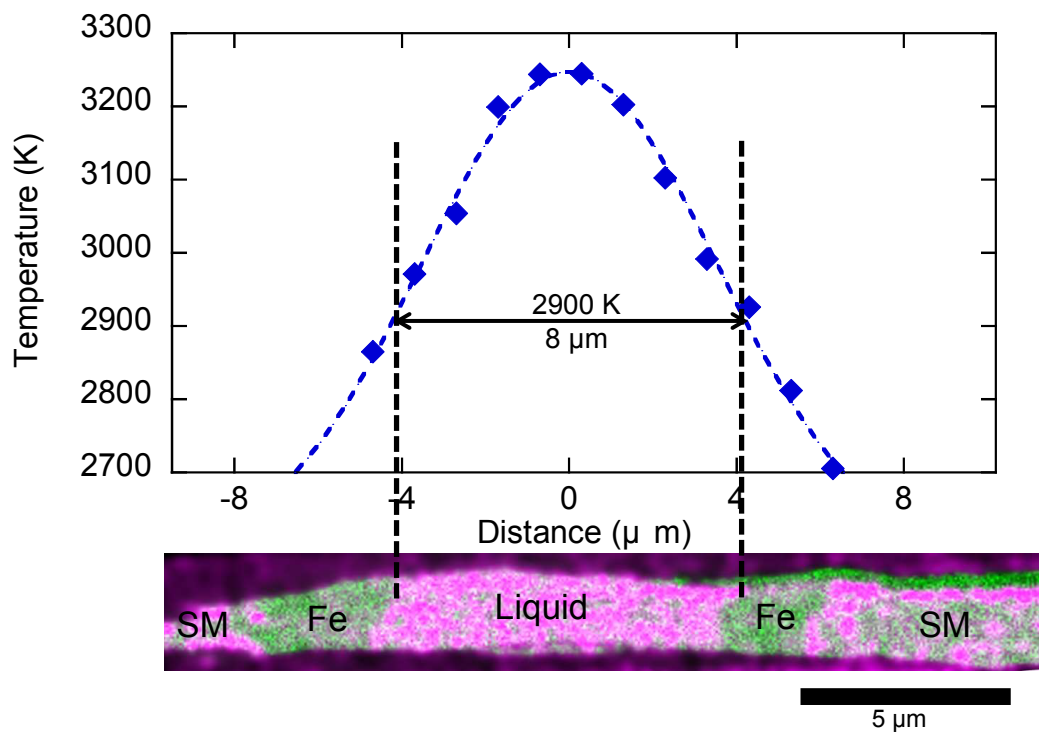
Table 1

Experimental results in the Fe-C binary system

Run#	Starting material	P (GPa)	eutectic T (K)	Phases present	Liquid		Solid iron			
					C (wt%)	Fe (wt%)	O (wt%)	C (wt%)	Fe (wt%)	O (wt%)
1	Fe-1.9 wt%C	23(2)	1950(100)	Liq + Fe	4.04(30)	96.30(30)	0.16(5)	0.85(24)	99.08(16)	0.07(11)
2	Fe-1.9 wt%C	54(5)	2550(130)	Liq + Fe + Fe ₃ C	4.45(32)	95.70(30)	0.34(30)	1.00(45)	98.89(51)	0.11(7)
3	Fe-1.9 wt%C	138(14)	2900(150)	Liq + Fe	3.95(22)	94.84(21)	1.70(17)	0.68(48)	99.38(29)	0.05(11)
4	Fe-1.9 wt%C	211(21)	3230(160)	Liq + Fe + Fe ₃ C	4.19(20)	95.23(30)	0.95(30)	1.04(22)	98.96(24)	not detected
5	Fe-4.0 wt%C	40(4)	2300(120)	Liq + Fe + Fe ₃ C	3.83(24)	96.50(23)	0.17(22)	0.64(4)	99.49(20)	not detected
6	Fe-4.0 wt%C	83(8)	2640(130)	Liq + Fe ₃ C	3.90(23)	95.72(12)	0.88(8)	-	-	-
7	Fe-4.0 wt%C	203(20)	3350(170)	Liq + Fe ₃ C	3.92(9)	95.39(22)	1.19(21)	-	-	-
8	Fe-4.0 wt%C	255(25)	3570(180)	Liq + Fe + Fe ₇ C ₃	3.60(21)	96.84(49)	1.06(50)	0.61(34)	99.43(31)	not detected

Numbers in parentheses are standard deviation uncertainties in the last digit(s).

(a)



(b)

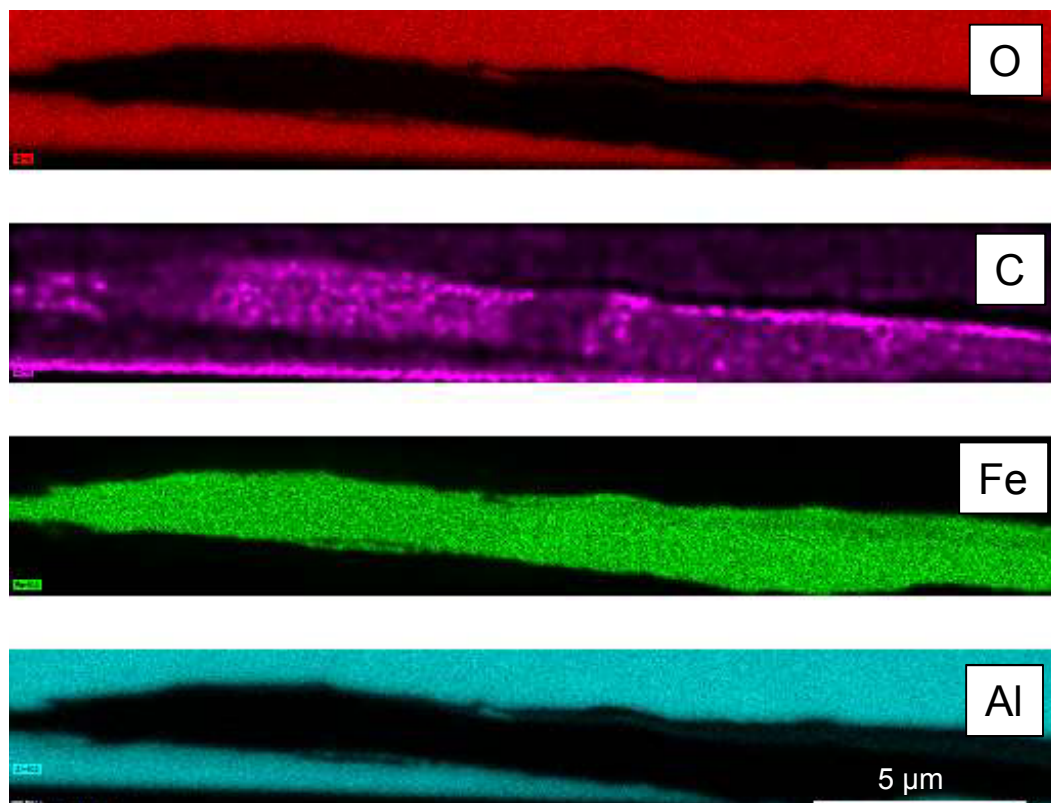


Fig. 1

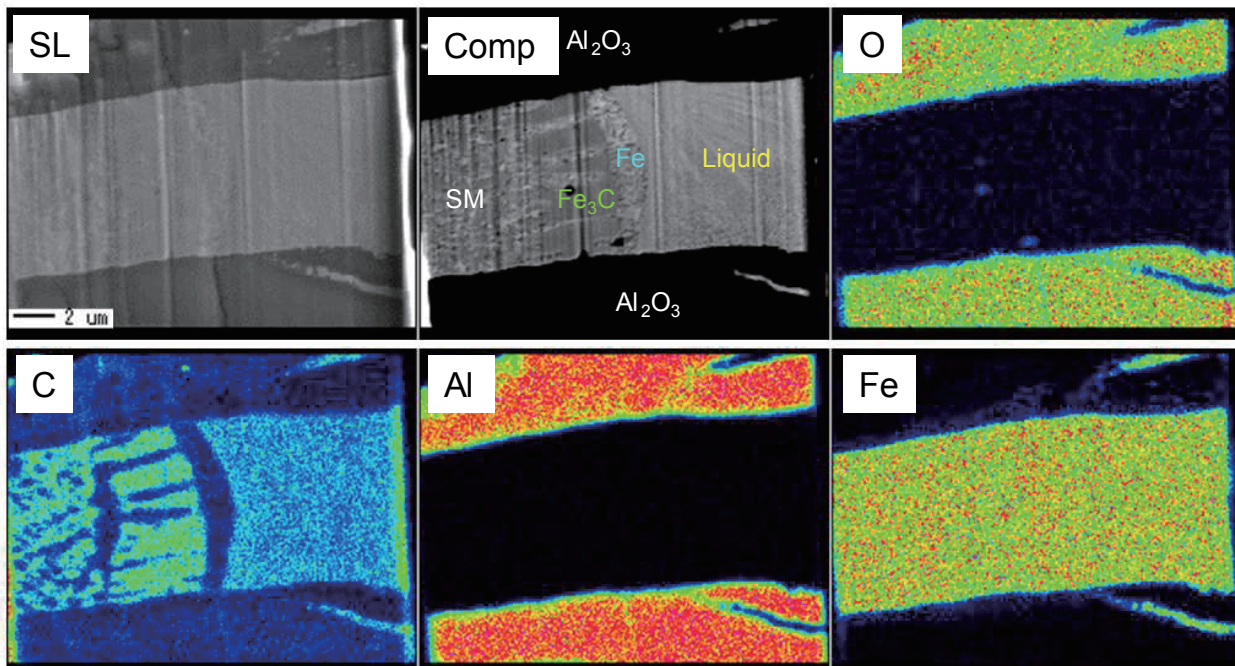
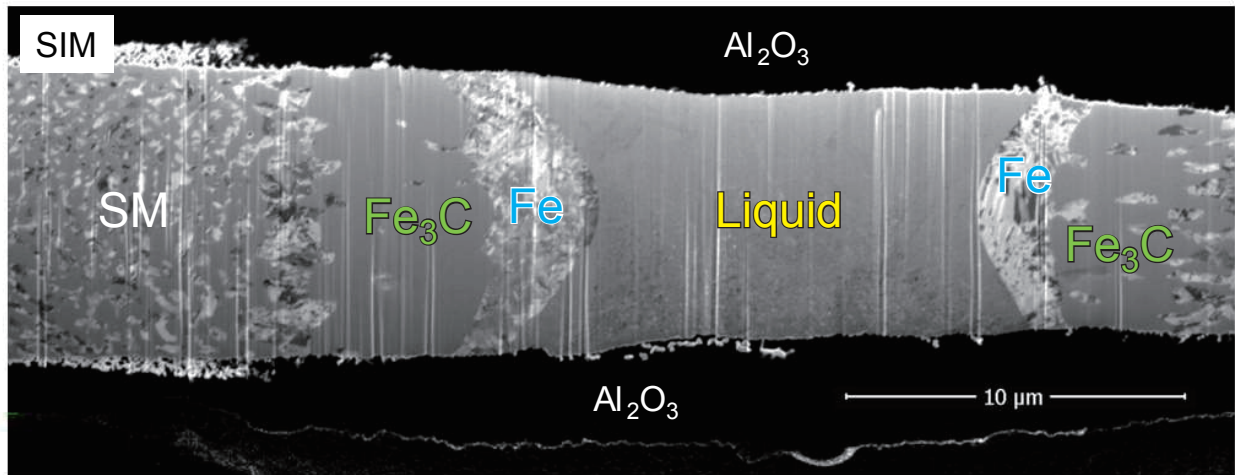


Fig. 2

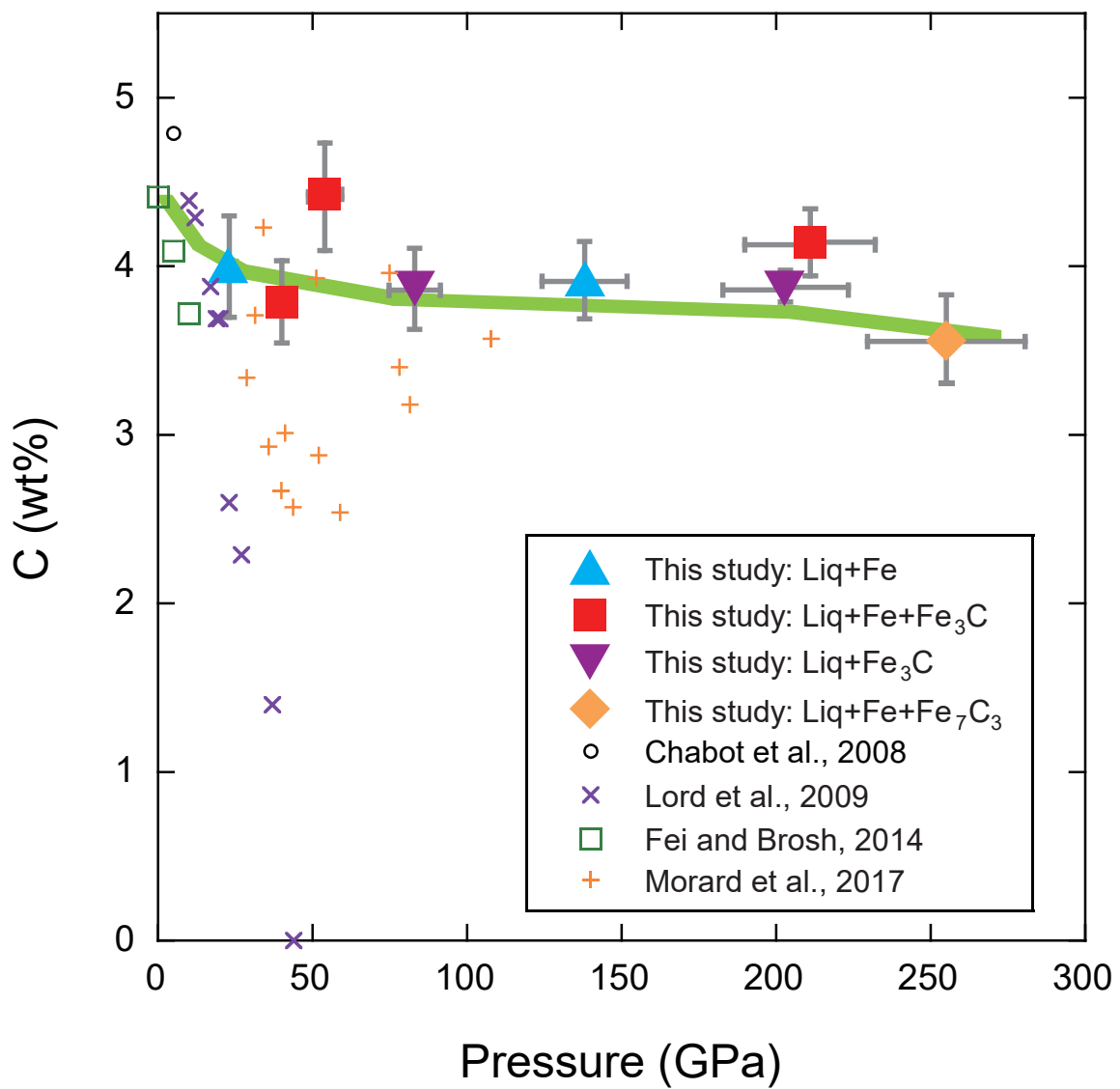


Fig. 3

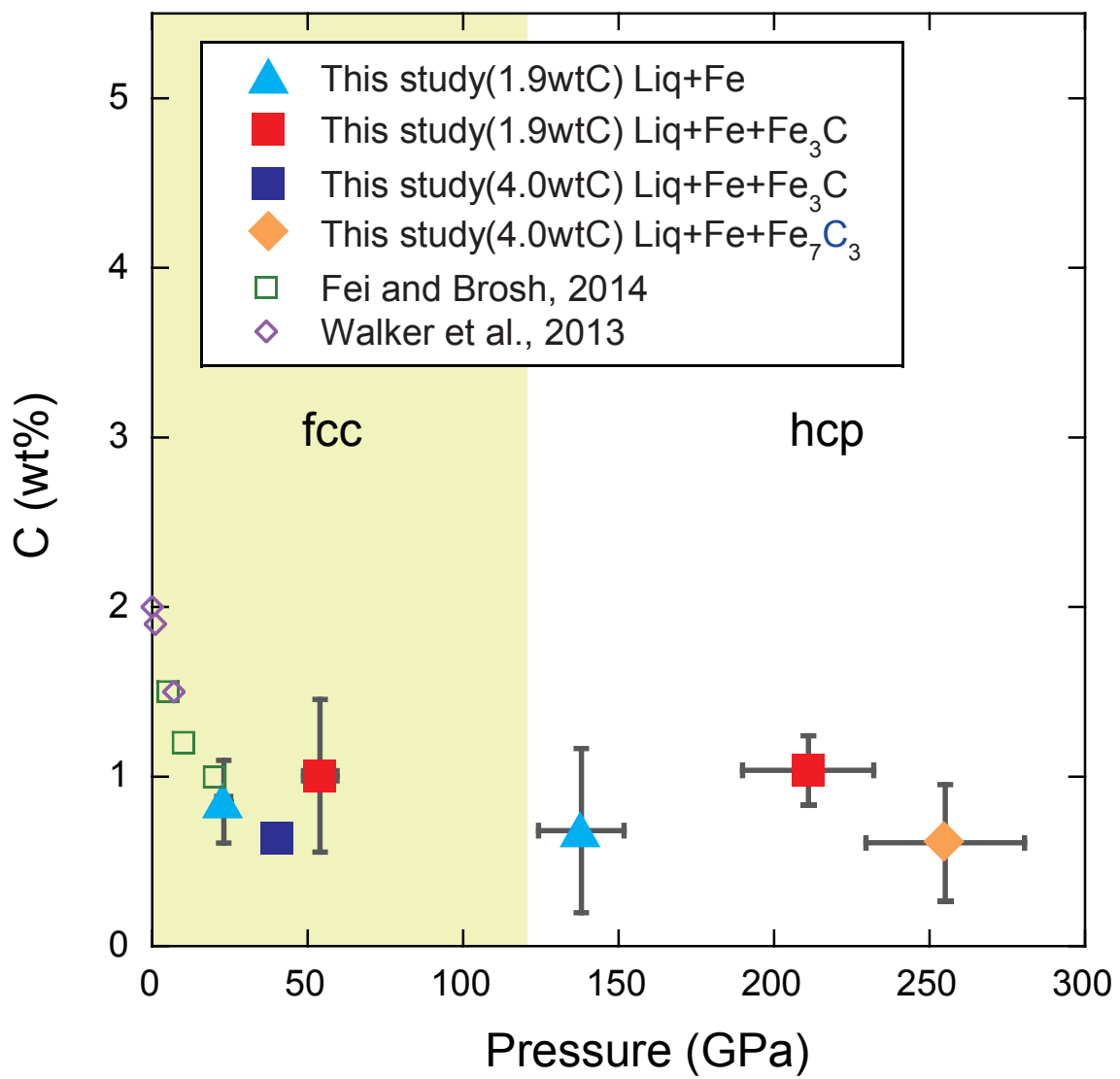


Fig. 4

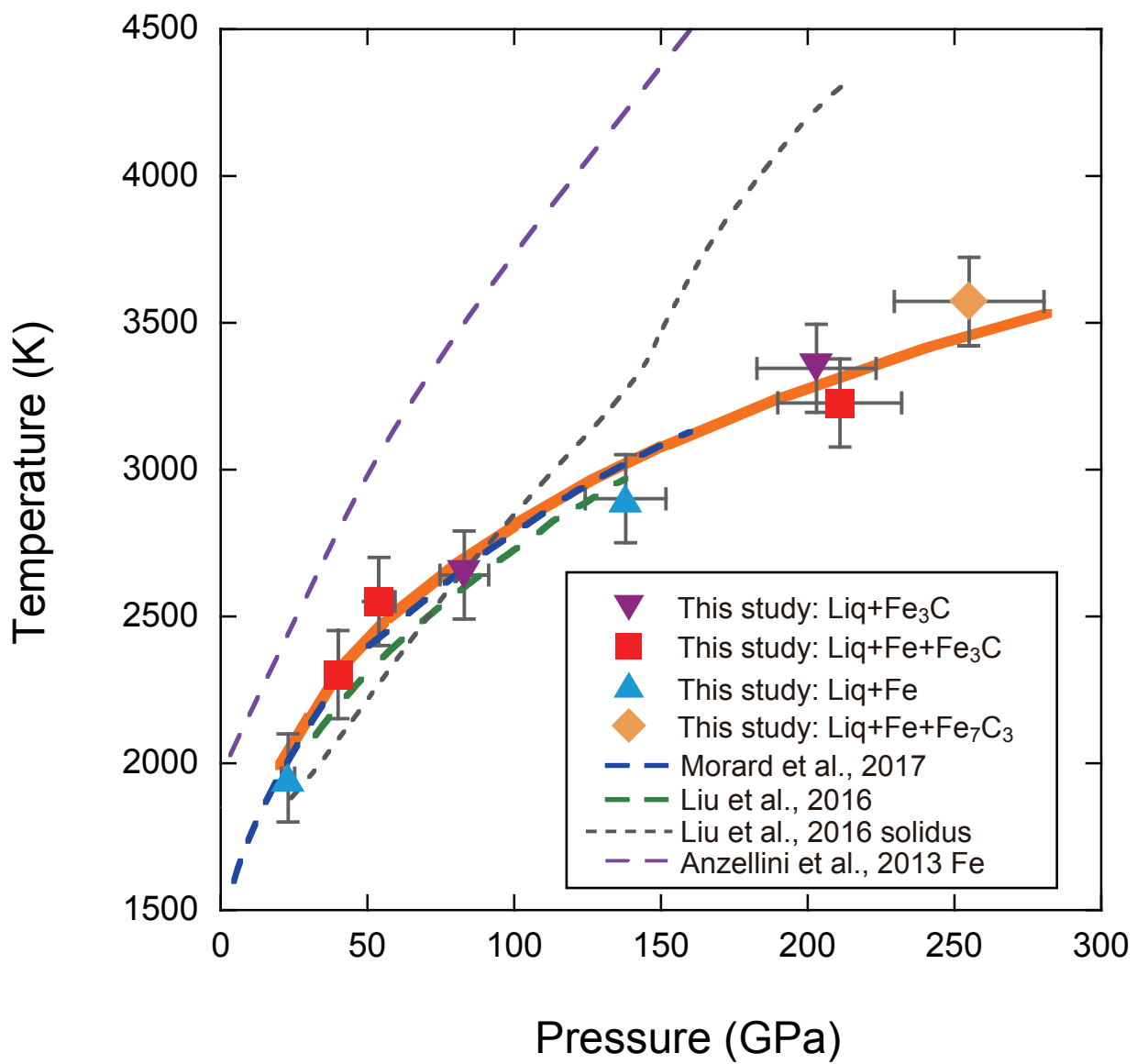


Fig. 5 (a)

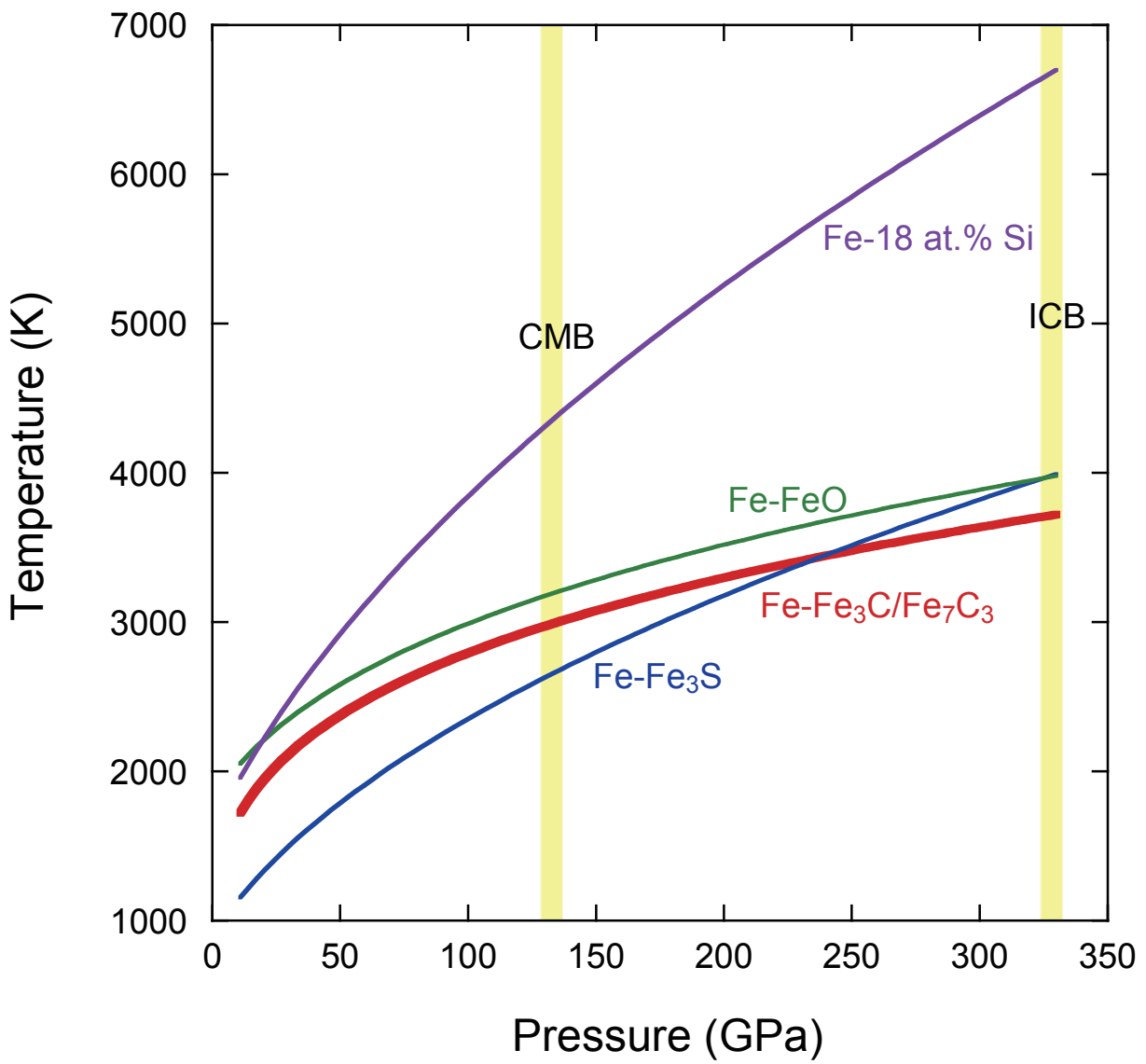


Fig. 5 (b)

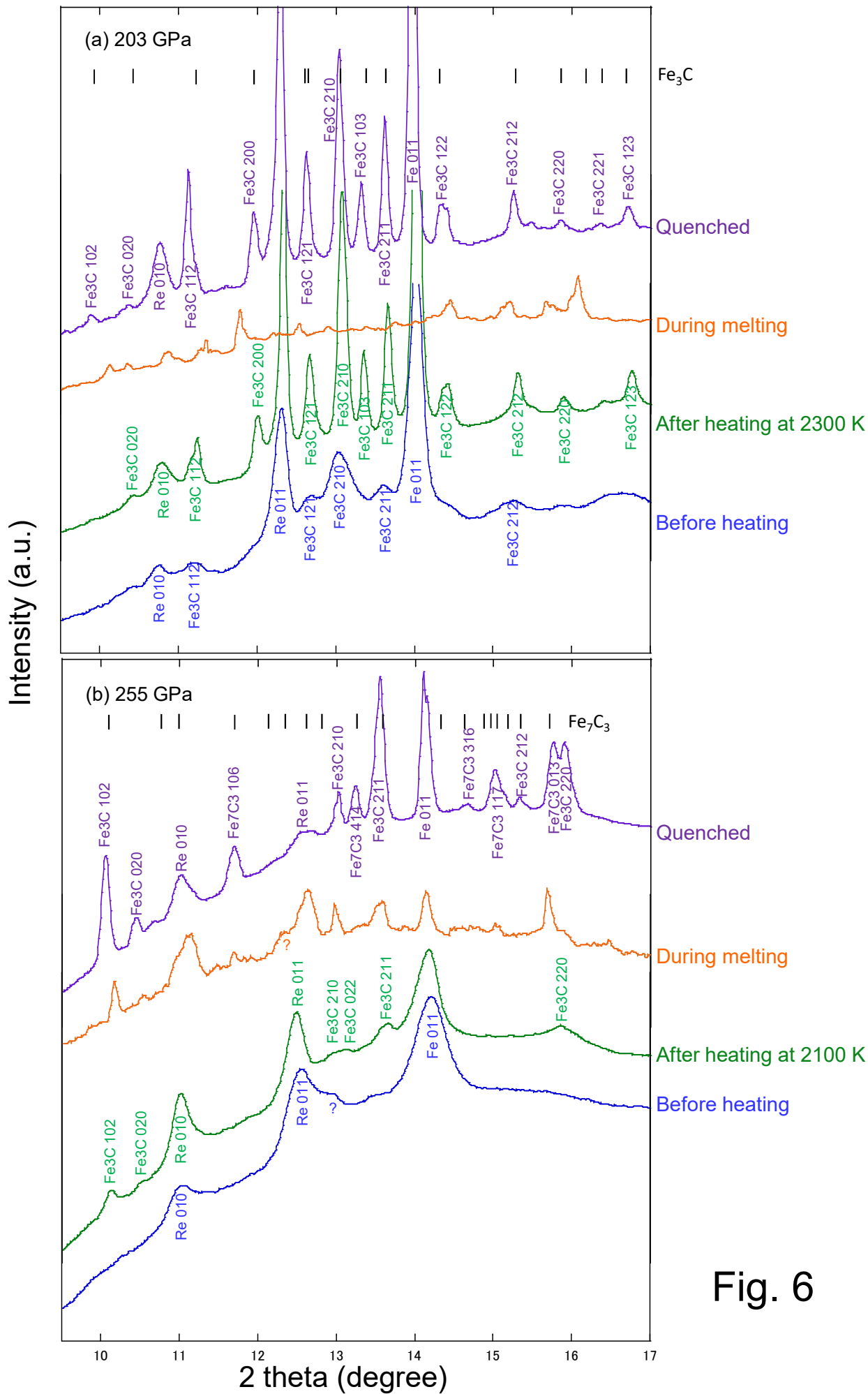
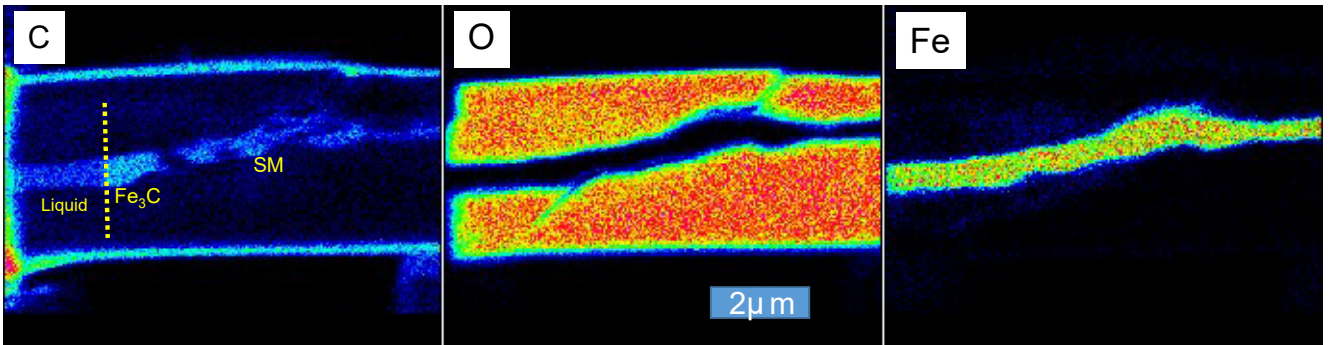
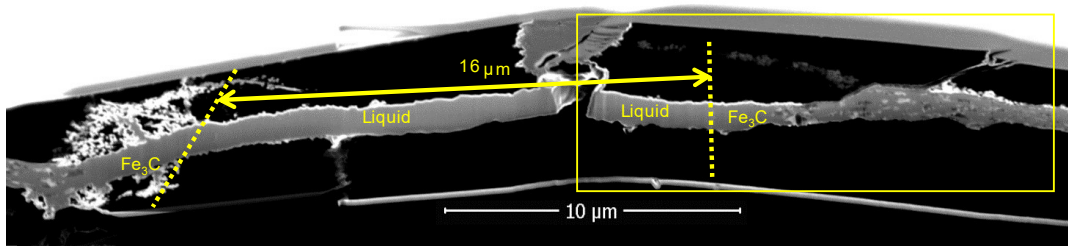


Fig. 6

(a)



(b)

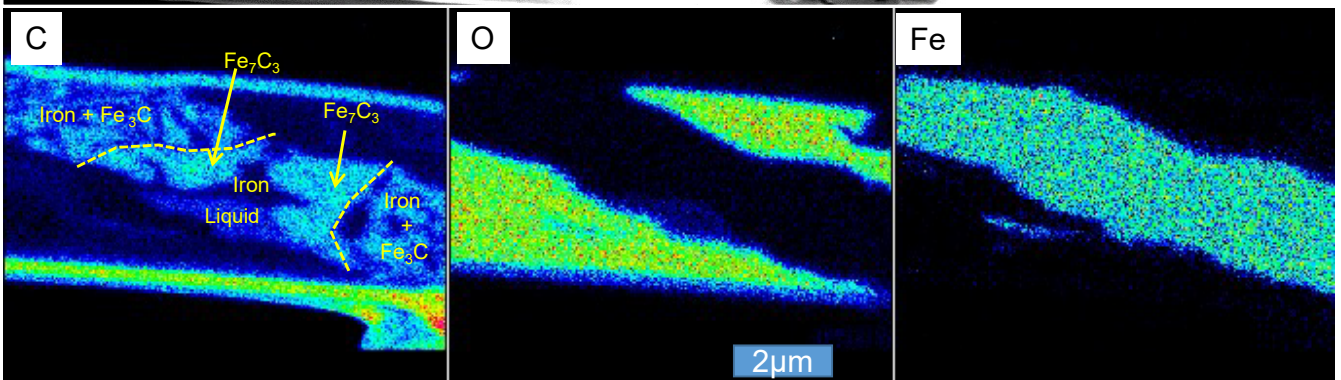
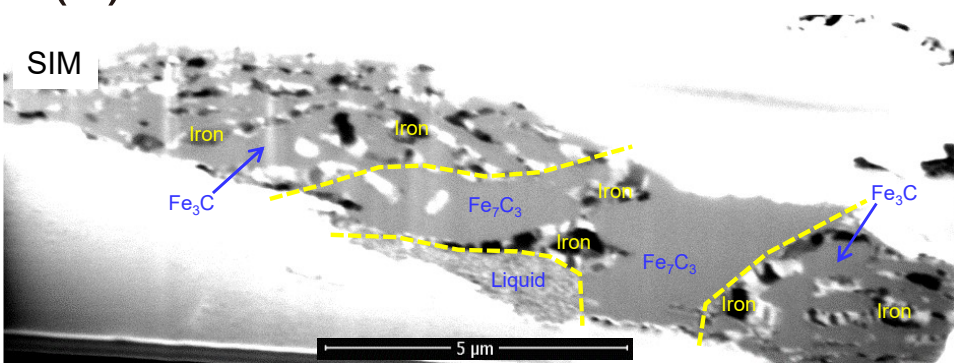


Fig. 7

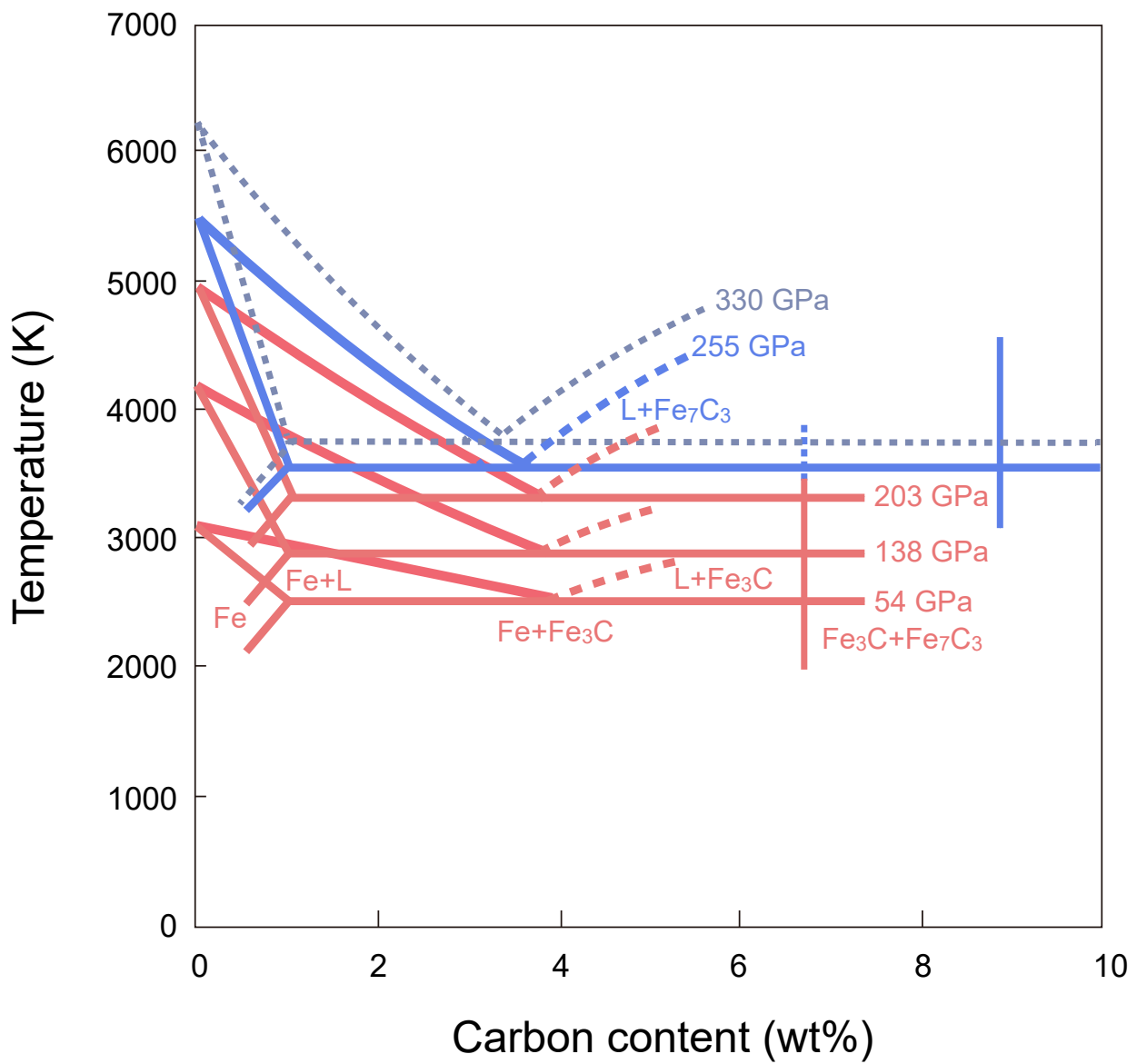


Fig. 8

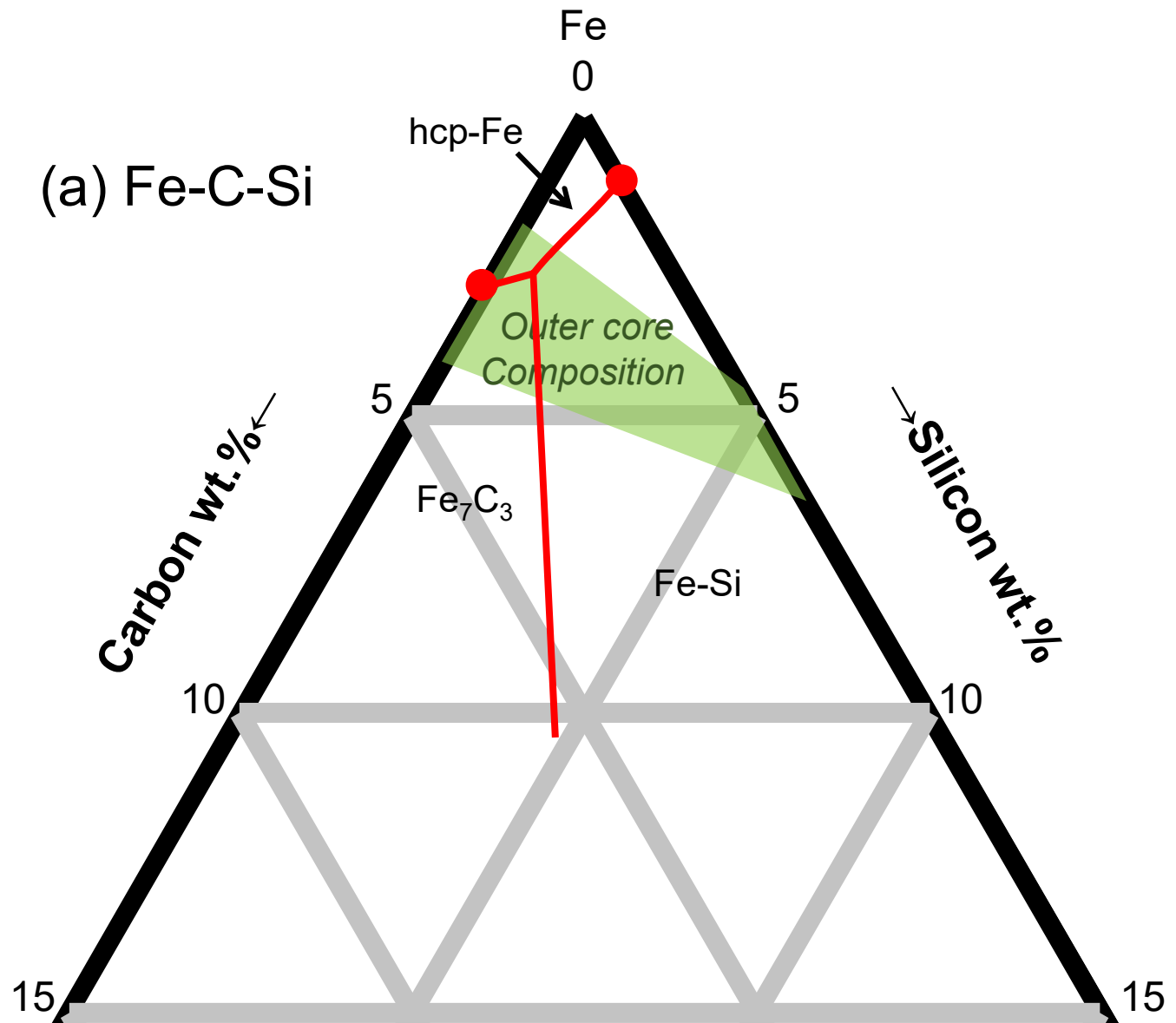


Fig. 9 (a)

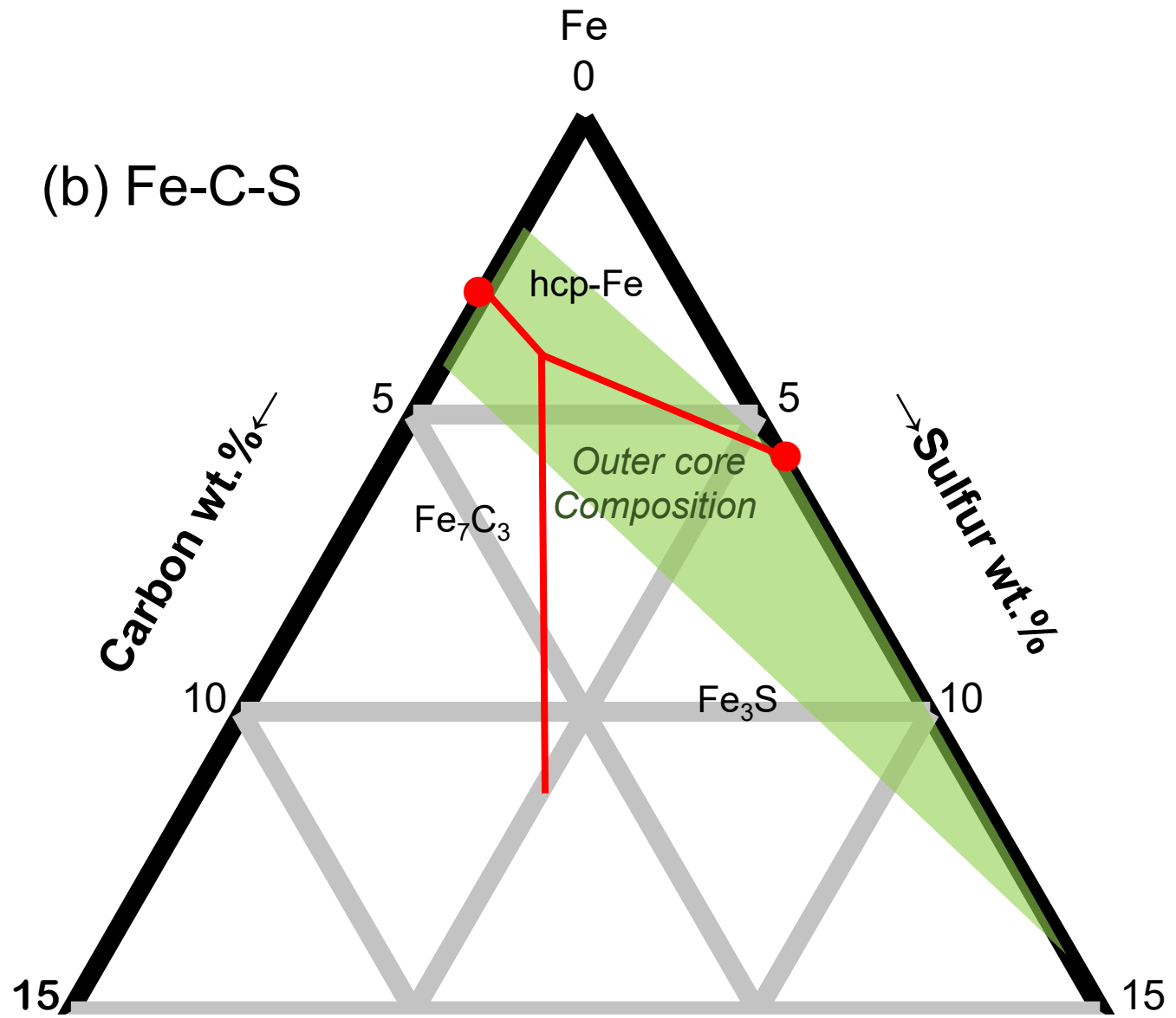


Fig. 9 (b)

(c) Fe-C-O

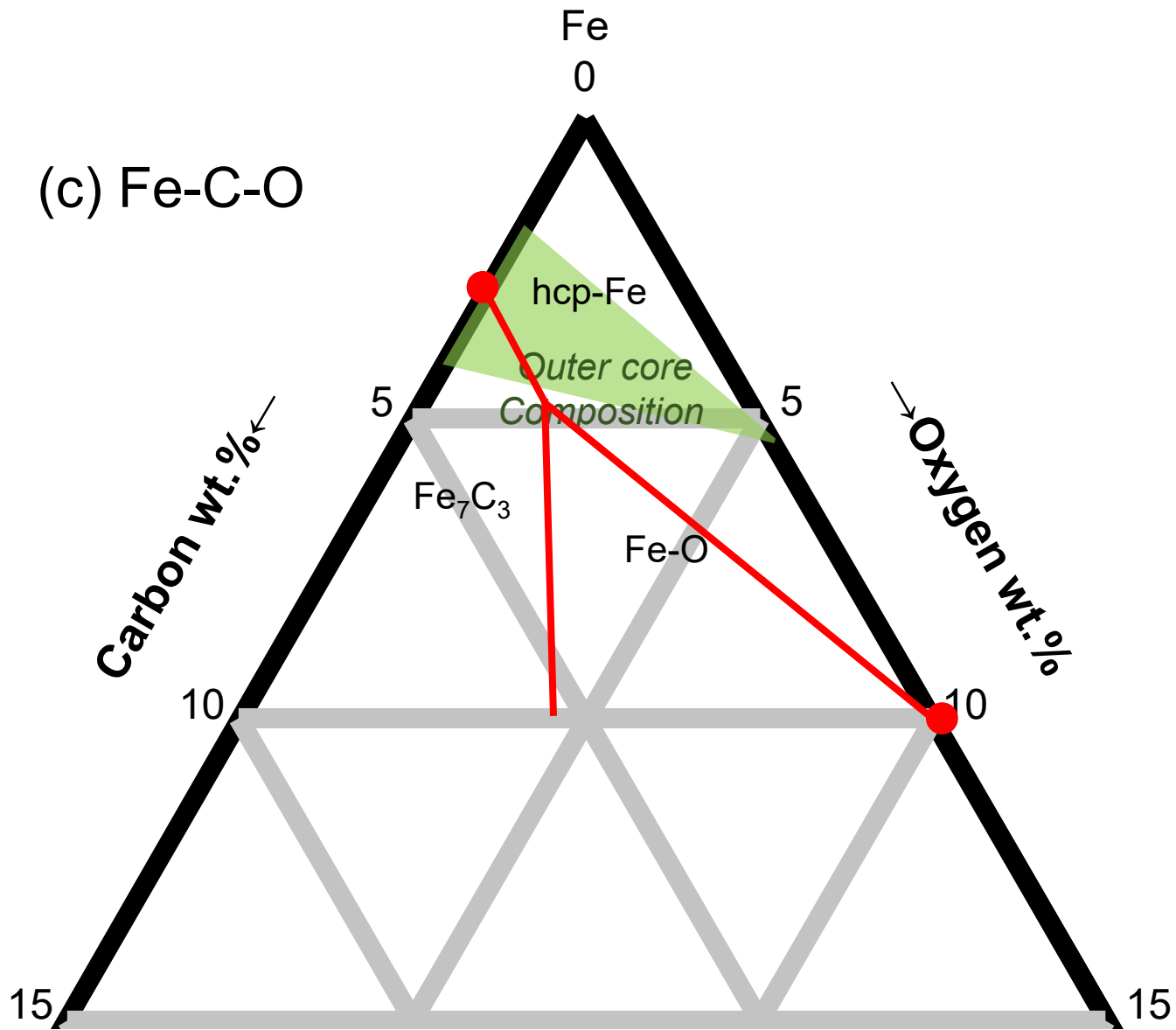


Fig. 9 (c)

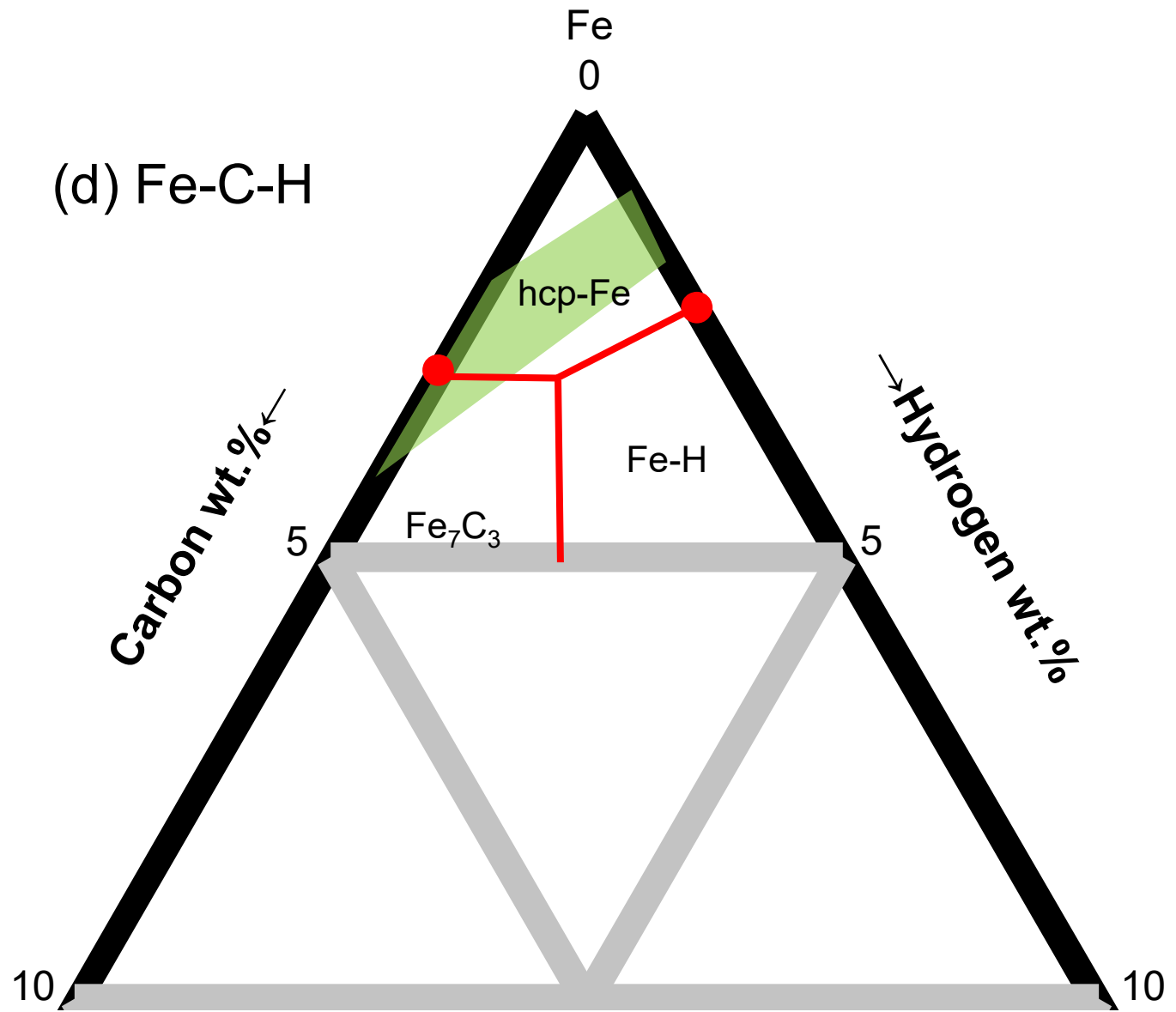


Fig. 9 (d)