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1   **Origin and consequences of non-stoichiometry in iron carbide Fe$_7$C$_3$**

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20 **ABSTRACT**

21   The Eckstrom-Adcock iron carbide, nominally Fe_7C_3, is a potential host of reduced

22 carbon in Earth's mantle and a candidate component of the inner core. Non-stoichiometry

23 in Fe_7C_3 has been observed previously but the crystal chemistry basis for its origin and

24 influences on the physical properties were not known. Here we report chemical and

25 structural analyses of synthetic Fe_7C_3 that was grown through diffusive reaction between

26 iron and graphite and contained 31 to 35 at.% carbon. We found that more carbon-rich

27 Fe_7C_3 has smaller unit-cell volume, suggesting that excess carbon atoms substituted for

28 iron atoms instead of entering the interstitial sites of closed-packed iron lattice as in FeC_x

29 steel. Carbon may be the lightest alloying element to substitute for iron. The substitution

30 leads to larger reduction in the unit-cell mass than the volume so that the carbon-rich end

31 member may be as much as 5% less dense than stoichiometric Fe_7C_3. If Fe_7C_3 solidifies

32 from Earth's iron-rich liquid core, it is expected to have a nearly stoichiometric

33 composition with a compositional expansion coefficient of ~1.0. However, laboratory

34 experiments using carbon-rich synthetic Fe_7C_3 to model the inner core may over-estimate

35 the amount of carbon that is needed to account for the core density deficit.

36 **Keywords:** Iron carbide, non-stoichiometry, substitution, interstice, light element,

37 density deficit, compositional expansion coefficient

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INTRODUCTION

40   Eckstrom-Adcock iron carbide (Fe_7C_3) was first discovered in a hydrocarbon synthesis

41   plant (Eckstrom and Adcock, 1950). Fe_7C_3 is considered a potential host of reduced

42   carbon in Earth's deep mantle, where metallic iron is expected to be stable (Rohrbach and

43   Schmidt, 2011). It is also a candidate component to explain the density deficit and

44   anomalously low shear wave velocity of the inner core (Chen et al., 2012; Chen et al.,

45   2014; Liu et al., 2016; Prescher et al., 2015). M_7C_3 (M_2C)-type intermediate transition-

46   metal carbides have been found as inclusions in superdeep diamonds together with

47   cementite M_3C, where M stands for Fe, Co, Ni, Cr, and Mn. These natural M_7C_3 (M_2C)

48   and M_3C samples can have ~6-8 at.% C content variation in the same structure.

49   (Kaminsky and Wirth, 2011; Smith et al., 2016). Synthetic iron carbides also show

50   considerable compositional variation, ranging from 29 to 36 at.% carbon in Fe_7C_3 and

51   from 17 to 31 at.% carbon in Fe_3C (Buono et al., 2013; Walker et al., 2013). Deviation

52   from stoichiometric composition led to a reduction of the Curie temperature of Fe_3C

53   (Walker et al., 2015). Moreover, a carbon-poor Fe_3C was found to have a smaller unit-

54   cell volume than a slightly carbon-rich phase, suggesting that the carbon deficiency

55   originates from carbon vacancy. The correlation between volume and composition is

56   similar to FeC_x or FeH_x alloys, where unit-cell volume increases with the increasing

57   amount of light element, and opposite to Fe-O, Fe-Si, and Fe-S alloys where the unit-cell

58   volume decreases with the increasing amount of light element (Table 1). On the other

59   hand, the origin and effects of non-stoichiometry on Fe_7C_3 are still not known. Here we

60   investigate the composition and structure of non-stoichiometry in Fe_7C_3 through

61   synchrotron X-ray diffraction (XRD) and electron probe microanalysis (EPMA) and

62   discuss the implications for the stability and properties of carbides in the deep Earth.

63

64   **METHODS**

65   Non-stoichiometric iron carbide Fe_7C_3 was synthesized using a multi-anvil

66   apparatus at the Lamont-Doherty Earth Observatory (LDEO serial #BB-1233) (Walker et

67   al., 2013). The starting material consists of a 250-µm-thick iron disc (Goodfellow hard

68   iron foil, >99.5%) sandwiched between two graphite cylinders (National Carbon

69   Spectroscopic grade graphite), surrounded by high-purity MgO sleeve. The sample was

70   contained in an 8 mm truncated edge length (TEL) octahedron of Ceramacast 584

71   castable ceramic (Aremco) and equilibrated at 7 GPa (350 US ton oil pressure) and 1300

72   ˚C for 19 hrs. The temperature difference across the sample is estimated to be <10 ˚C,

73   and the pressure uncertainty is estimated to be 0.5 GPa in the sample capsule. The

74   experimental product was ground to form a 1.8-mm-long, 0.4-mm-tall, and 300-µm-thick

75   pellet (parallel to the rotation axis of the original Fe disc and C cylinders) that presented

76   as a sectioned sandwich with carbide as the jelly between carbon bread slices for

77   synchrotron XRD measurements at 13-BM-C of the Advanced Photon Source (APS),

78   Argonne National Laboratory (ANL). The X-ray wavelength is 0.4340 ($\pm 2 \times 10^{-5}$) Å and

79   the beam size is 12×18 µm^2 at the full width at half maximum (FWHM)

80   (horizontal×vertical direction in Fig. 1). The sample to detector distance is 164.10 (±0.03)

81   mm. The slice was rotated around the original rotation axis of the Fe disc and C cylinders

82   (stacking direction of the sandwich) by ±30˚ to reduce the effect of preferred orientation

83   in the coarse-grained sample. The XRD data were processed using Dioptas (Prescher and

84   Prakapenka, 2015) and PDIndexer (Seto et al., 2010) software.

85   After the XRD measurements, the slice was coated with aluminum for electron

86   microprobe analysis, using the JOEL-7800FLV scanning electron microscope (SEM) and

87   Cameca SX100 EPMA at the Electron Microbeam Analysis Laboratory (EMAL) of

88   University of Michigan. No chemical contamination was detected in the SEM and EPMA

89   measurements. For the EPMA analysis, a 11 kV accelerating voltage and a 70 nA beam

90   focused to ~1 μm diameter was used to obtain compositional data (Dasgupta and Walker,

91   2008). The penetration depth of the beam was estimated to be <20 μm. Pure Fe and

92   synthetic stoichiometric Fe_3C were used as the standards (Liu et al., 2016). The

93   measurement time for the sample was 10 seconds on the peak positions and 5 seconds on

94   the background.

95

96   **RESULTS AND DISCUSSION**

97   **Anti-correlation between unit-cell volume and carbon content in non-stoichiometric**

98   **Fe_7C_3**

99   Back-scattered electron (BSE) image showed that the synthesis experiment

100   produced two layers of the Eckstrom-Adcock carbide, nominally Fe_7C_3, each sandwiched

101   between a layer of cementite, nominally Fe_3C, in the center of the sample and unreacted

102   carbon on both ends (Fig. 1). The layered structure indicates that the C and Fe_3C layers

103   were not fully equilibrated when the sample was quenched from high temperature. As a

104   result, ongoing C diffusion from the C layers to Fe_3C layer through the Fe_7C_3 layers in

105   between was preserved in the sample, creating the gradient of C content in the Fe_7C_3

106   layers, which points from the carbon-rich end near the Fe_7C_3/C boundary to carbon-poor

107   end near the Fe_7C_3/Fe_3C boundary.

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108   The layered distribution of the three phases was confirmed by XRD line scans

109   (Fig. 2). The phase assemblies evolve from $C+Fe_7C_3$ at the graphite ends to Fe_7C_3 and

110   then to Fe_3C. Some XRD patterns of the Fe_7C_3 contained variable amounts of Fe_3C.

111   Minor Fe_7C_3 phase was also found in the XRD collected from the Fe_3C band. The

112   occurrence of both carbides in the XRD patterns collected from the interior of different

113   bands appears inconsistent with the clear separation of the bands in the BSE and optical

114   images. We found that on the exiting side of the X-ray beam the center Fe_3C band is 40

115   μm thinner, suggesting that the boundaries between Fe_7C_3 and Fe_3C are not parallel and

116   therefore the beam that enters the sample near the interface would traverse both phases.

117   This effect is enhanced considering that 25% of X-ray intensity is outside the FWHM and

118   can produce diffraction signals from 40-micron areas. It is also possible that the stacking

119   direction of sample is slightly tilted towards or away from the X-ray beam direction and

120   therefore XRD patterns containing single carbide are only collected from measurements

121   near the center of each band, as we observed.

122   Despite these complications, a unit-cell volume composite map constructed from the

123   XRD line scans revealed a general trend that Fe_7C_3 closer to the carbon layer has smaller

124   unit-cell volume (Fig. 3). We used hexagonal structure ($P6_3mc$) (Herbstein and Snyman,

125   1964) to refine the structure of Fe_7C_3 since it better explained the observed patterns. Six

126   fixed peaks (112), (031), (022), (220), (033) and (232) which have no overlap with Fe_3C

127   strong peaks were used for the refinement of all present unit-cell volumes to avoid

128   complications, and the largest unit-cell of Fe_7C_3 was found in the Fe_3C center band,

129   where Fe_7C_3 occurred as a minor phase in the mixed XRD patterns. The trend of

130   decreasing volume towards the carbon layer is further confirmed by the stacked XRD

131   patterns showing a systematic shift of peak position towards larger 2θ as the X-ray beam

132   moved from the Fe_3C-Fe_7C_3 boundary towards the Fe_7C_3-C boundary (Fig. 4). Fe_3C

133   exhibits a similar correlation of higher carbon content with smaller unit-cell volume,

134   although there is considerable scatter and the trend is not as well resolved (Fig. 4a&d).

135   These peak shifts, although only ~0.02º, are much larger than the potential shifts caused

136   by uncertainties in X-ray wavelength (0.0006º at 2θ ~14º corresponding to 1 eV energy

137   fluctuation) and sample-to-detector distance (0.0024º at 2θ ~14º corresponding to 30 μm

138   sample distance variation). The sample-detector distance at the center band of Fe_3C

139   +Fe_7C_3 mixture can differ by up to ~100 μm from the Fe_7C_3 band at the edge.

140   Accordingly, the 2θ could shift up to 0.008º and may have visible influence on the unit-

141   cell volumes of the center-most Fe_7C_3, but not enough to account for the total observed

142   shift. Additionally, the peak shift was observed in Fe_7C_3 phase at the edge free of Fe_3C

143   (Fig. 4c), thus ruling out the possibility that the 2θ shift mainly comes from phase

144   mixture. In all seven line scans the largest volumes appear in the center, suggesting that

145   the 2θ shift does not come from random fluctuation. Therefore, the variation in cell

146   volume suggests non-stoichiometry in Fe_3C and Fe_7C_3. More importantly, the data

147   suggest an anti-correlation between cell volume and carbon content: As the carbon

148   concentration increases, the cell volume became smaller.

149   EPMA line scans showed two clusters of composition at ~24-27 at.% and ~31-35 at.%

150   carbon, corresponding to Fe_3C and Fe_7C_3, respectively (Fig. 5). The ranges of non-

151   stoichiometry agree with the previous studies (Buono et al., 2013; Walker et al., 2013).

152   The compositions of Fe_3C mostly fell on the carbon-rich side of the stoichiometric

153   compound, consistent with the fact that the iron in the starting material was fully

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154   consumed and the product still contains unreacted carbon. Overall the carbon content

155   decreases from the region next to unreacted carbon towards that next to the Fe_3C band,

156   consistent with the direction of C diffusion (Fig. 5). Compositional fluctuation exists in

157   individual line scan, especially Line A near the distal edge, due to the complexity in

158   carbon diffusion (Walker et al., 2013) and the large uncertainty in measuring C

159   concentration by EPMA.

160   Compared with EPMA measurements, less fluctuation of unit-cell volume was

161   observed in XRD (Fig. 3 and Fig. 5). This is mainly because the sample volume covered

162   by XRD is significantly larger than that by EPMA (12×18 μm beam size and 300 μm

163   depth in XRD compared with ~1 μm beam size and <20 μm penetration depth in EPMA).

164   With thousands of times volume coverage, together with the sample rotation, the XRD

165   measurements effectively reduced the scattering caused by complexity of local

166   composition and obtained the average lattice parameters for the covered volume.

167   From the most carbon-rich part with 35 at.% carbon to the least carbon-rich part

168   with 31 at% carbon in the Fe_7C_3 band, the unit-cell volume expands by ~0.3% from

169   ~186.2 $Å^3$ to 186.8 $Å^3$. Larger unit-cell volume up to ~187.4 $Å^3$ was obtained from the

170   Fe_7C_3-Fe_3C mixture in the center band, where carbon content may be lower than 31 at.%

171   and the XRD beam averaged less volume from carbon-rich Fe_7C_3 when it crossed the

172   Fe_7C_3-Fe_3C phase boundary. Because large uncertainty may exist in both the composition

173   and volume refinement in this phase mixture region, it is excluded from the latter density

174   calculation.

175

176   **Origin of non-stoichiometry in Fe_7C_3 and Fe_3C**

177   The composition-volume relation of iron carbides can be used to infer the

178   mechanism by which carbon is removed or added from the structures of stoichiometric

179   compounds. Cementite Fe_3C is usually considered an interstitial alloy, in which carbon

180   atoms adopt the six-fold interstitial sites of iron in *hcp* structure (Barrett, 1943; Scott et

181   al., 2001). First-principles calculations found that carbon enters the interstitial sites of

182   closed packed structure of iron and therefore adding a small amount of carbon (x < 0.1)

183   to *hcp* Fe expands the lattice (Caracas, 2017). The interstitial model, however, cannot

184   explain the smaller volumes of carbon-rich Fe_7C_3 and Fe_3C, suggesting that carbon-iron

185   substitution may be the cause of carbon-rich carbides.

186   By contrast, Walker et al. (2013) found that the unit-cell volume of a carbon-poor

187   Fe_3C with 22.3 at% carbon is smaller than that of a slightly carbon-rich Fe_3C with 25.6 at%

188   carbon. Petch (1944) also found that volume decreases with decreasing C content in Fe-

189   saturated cementites as they become less stoichiometric and C-poorer with rising

190   temperature. Results from the two literature studies on C-poor cementite, compared to the

191   present study of C-rich cementite therefore suggest that deviation from the stoichiometric

192   composition of Fe_3C in either direction reduces the cell volume and that the mechanisms

193   of non-stoichiometry may be different on different sides of stoichiometric Fe_3C. In light

194   of this new evidence, the supposition of Walker et al. (2015) that the non-stoichiometry

195   mechanism on the C-rich side of Fe_3C is interstitial, is less plausible than that it is

196   substitutional. Walker et al. (2015) found that the Curie temperature is lower on either

197   side of Fe_3C but the rate of T_c reduction on the C-rich side is twice that on the C-poor

198   side. They attributed the rate differences to larger configurational entropy production by

199   interstitial C on the C-rich side than by C vacancy on the C-poor side. We now regard

200 substitutional C as a more plausible mechanism on the C-rich side on the basis of the new

201 evidence presented here. The entropy argument, however remains unchanged because

202 there are still twice as many sites for substitution on the C-rich side as there are for C

203 vacancy on the C-poor side of Fe_3C. The entropy production rate in this particular case is

204 insensitive to compositional variation mechanism for introducing C richness.

205   A closer look at the structures of Fe_3C and Fe_7C_3 reveal that carbon takes a distinct

206 8-fold square antiprism site instead of the interstitial sites of close-packed iron lattice (Fig.

207 6). The presence of carbon distorts the 6-fold interstitial sites and enlarges the lattice. As

208 a result, 2/3 of the iron atoms in Fe_3C and 6/7 of that in Fe_7C_3 have only 11 nearest iron

209 neighbors and the sub-structures of iron atoms are no longer ideal *hcp* closest packing.

210 The 8-fold carbon sites and 11-fold iron sites in the carbide structures can be explained

211 by the nature of metallic bonding between carbon and iron, where carbon acts as an

212 electron donor and enhances the hybridization between the partially filled 3d orbital and

213 the 4s orbital of iron (Goldschmidt, 1967). As a result, C in iron carbides should be

214 treated as C^0, instead of C^{4-} as in covalent and stoichiometric compounds such as SiC,

215 Al_4C_3 and Mg_2C. For metallic bonding between Fe^0 and C^0 the radius ratio r_C/r_{Fe} is ~0.62

216 or slightly larger with corrections for electronegativity of Fe (1.83) and C (2.55) (Allred,

217 1961). According to Pauling's rules this ratio is slightly too high for carbon to take the 6-

218 fold interstitial site ($r_A/r_X = 0.414$) and too low for C-Fe substitution ($r_A/r_X = 1$).

219 Consequently, only a small amount of interstitial carbon is allowed in FeC_x alloys.

220 Carbon in Fe_3C and Fe_7C_3 adopts 8-fold square antiprism sites ($r_c/r_a = 0.645$ in Pauling's

221 rules) instead of entering the interstices of close-packed iron.

222   Because carbon adopts an 8-fold site that is not much smaller than 11-fold iron sites,

223   excess carbon atoms in Fe_3C and Fe_7C_3 may be incorporated into the structure through

224   substitution of carbon for iron (Fig. 6). This substitution explains the reduced volumes of

225   carbon-rich Fe_3C and Fe_7C_3. No carbon-poor Fe_7C_3 has been found in this study or

226   previous synthesis (Walker et al., 2013), suggesting that it is less stable than a two-phase

227   mixture of Fe_3C and stoichiometric Fe_7C_3.

228   The inferred origin of non-stoichiometry in carbon-poor and carbon-rich Fe_3C is

229   consistent with the relations between the lattice parameters and carbon content. An anti-

230   correlation in lattice parameters was reported in C-poor Fe_3C such that the b axis

231   elongates with decreased C content while the unit-cell volume (and a, c axes) shrinks

232   (Petch, 1944; Walker et al., 2013). This kind of anti-correlation was not observed in the

233   C-rich Fe_3C in this study. For example, in Line 1 the maximum unit-cell volume of Fe_3C

234   is 155.93(27) $Å^3$ with a = 5.098(2) Å, b = 6.760(4) Å and c = 4.525(2) Å, and the

235   minimum unit-cell volume is 155.47(38) $Å^3$ with a = 5.094(2) Å, b = 6.748(7) Å and c =

236   4.523(3) Å. Carbon in the antiprism site of Fe_3C introduces pleats to the close-packed Fe

237   in b direction, which changes the folding angle of the pleats from 180º (no folding) to

238   ~120º. The carbon vacancy unbends the pleats in the b direction and lets them stack

239   better in a and c direction, thus increasing the axial length in the b direction and

240   decreasing it in the a/c direction. On the C-rich side, all the antiprism sites are filled and

241   the excess carbon takes the Fe site instead. Because there is no further occupancy of the

242   antiprism sites, the anti-correlation between b and unit-cell volume disappears on the C-

243   rich side.

244   The inferred site occupancy is further corroborated by the diffusion rates of carbon

245   and iron in FeC_x alloy and iron carbides. Carbon diffusion in austenite and ferrite is

246 considered a typical example of rapid interstitial diffusion, whereas self-diffusion of iron

247 is a typical example of substitution (vacancy) diffusion. At 1 bar and 1000 K, the

248 diffusion coefficient of carbon in Fe_3C is $\sim 10^{-15}$ m^2/s, which falls between that of carbon

249 in *bcc* Fe ($\sim 10^{-10}$ m^2/s) or *fcc* Fe ($\sim 10^{-12}$ m^2/s) and that of iron in *bcc* Fe ($\sim 10^{-17}$ m^2/s) or

250 *fcc* Fe ($\sim 10^{-19}$ m^2/s) (Gale and Totemeier, 2003; Hillert et al., 2005; Ozturk et al., 1984).

251 The intermediate value of diffusion coefficient suggests that carbon in Fe_3C cannot be

252 treated as an interstitial constituent. Molecular dynamics simulations suggest that six-fold

253 interstitial sites may serve as transient "stepping stones" to facilitate diffusion of carbon

254 among anti-prismatic sites (Levchenko et al., 2009). This interstice-assisted diffusion

255 mechanism implies carbon diffusion in Fe_3C may include both interstitial and

256 substitutional mechanism, and the substitutional diffusion is likely the rate-limiting step

257 that caused the observed gradient non-stoichiometry in the diffusive reaction product in

258 this study.

259 The roughly planar boundaries between Fe_3C, Fe_7C_3, and C in the recovered samples

260 synthesized at 7 GPa from this and previous study suggested that the reactions were

261 controlled mainly by lattice diffusion, without significant transport along grain

262 boundaries (Walker et al., 2013). The widths of Fe_3C layer and Fe_7C_3 layer in either this

263 study or the previous study are comparable, thus indicating the lattice diffusion rates of

264 carbon in Fe_7C_3 and Fe_3C are similar, which in turn implies the same origin of non-

265 stoichiometry on the carbon-rich sides of these carbides.

266

267 **Density of non-stoichiometric iron-light element alloys**

268 The density of an iron carbide may be calculated from its unit-cell volume from

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269   XRD measurements and the composition as determined by microprobe analysis only if

270   we can infer the mechanism of non-stoichiometry. For a carbon-rich Fe_7C_3 with 35 at.%

271   carbon, the formula unit may be written as $Fe_{6.5}C_{3.5}$ for a substitution alloy or $Fe_7C_{3.77}$ for

272   an interstitial alloy. Depending on the mechanism of non-stoichiometry, the calculated

273   densities for the same unit-cell volume and chemical composition could differ by more

274   than 5% (Table 1). It is therefore important to understand the nature of non-stoichiometry.

275   The presence of a light element in an iron-alloy usually reduces its density. The

276   efficiency of density reduction can be described by the compositional expansion

277   coefficient α_c, the ratio between the relative density reduction and the concentration of

278   the light element in weight percent. With respect to *hcp* iron, the α_c of stoichiometric

279   Fe_3C and Fe_7C_3 is 1.4, corresponding to 1.4% density reduction for 1 wt.% of carbon in

280   the Fe-alloy (Fig. 7). Carbon excess in Fe_7C_3 leads to a local excursion of α_c to 2.6,

281   because replacing iron with carbon reduces the cell mass much more than the cell volume.

282   It is interesting to note that carbon vacancy in Fe_3C may give rise to local negative α_c

283   with respect to stoichiometric composition: Between carbon-poor Fe_3C with vacancy and

284   nearly stoichiometric Fe_3C, the local α_c is -0.9 (Fig. 7, Table 1).

285   Non-stoichiometry is common among iron-light-element alloys and may cause

286   variations in compositional expansion coefficient (Fig. 8). At ambient conditions,

287   however, the complexity in calculating density from measured cell volume and

288   composition may be applicable to carbon alone. This is because the atomic or covalent

289   radius of carbon makes a borderline case for it to act as an interstitial constituent as in

290   FeC_x, or as a substituent of iron as in carbon-rich Fe_3C and Fe_7C_3. With r_H/r_{Fe} ~0.29,

291   FeH_x is considered a typical interstitial alloy. Silicon is comparable to iron in size (r_{Si}/r_{Fe}

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292   ~0.94) and electronegativity and therefore all Fe-Si alloys are substitutional. Oxygen and

293   sulfur are highly electro-negative and their anions are much larger than an iron cation,

294   and therefore iron vacancy is the dominant mechanism for non-stoichiometry in $Fe_{1-x}O$

295   (Hazen and Jeanloz, 1984) and $Fe_{1-x}S$ (Palache et al., 1944). At high pressures, $Fe_{1-x}S_x$ (x

296   < 0 .1) solutions have been predicted and observed (Alfe et al., 2002; Kamada et al., 2012;

297   Kamada et al., 2010; Li et al., 2001). Pressure may influence the electronegativity and

298   radii of iron and sulfur differently, hence it may be necessary to examine the dissolution

299   mechanism of sulfur in iron in order to correctly calculate the density of Fe-S alloys at

300   high pressures.

301

302   **IMPLICATIONS**

303   As a candidate component of the Earth's inner core, Fe_7C_3 is likely nearly

304   stoichiometric because it solidifies from the outer core which contains at least 85 wt.%

305   iron. In recent mineral physics experiments, Fe_7C_3 samples are often synthesized in

306   graphite capsules and therefore carbon-saturated (Chen et al., 2014; Nakajima et al., 2011;

307   Prescher et al., 2015). In these studies, the density of Fe_7C_3 was calculated by assuming

308   stoichiometric composition because non-stoichiometry was not widely recognized at the

309   time, and the exact compositions of micrometer sized samples used for the diamond-anvil

310   cell measurements were not readily accessible. The calculated density of synthetic C-rich

311   Fe_7C_3 could be as much as 1.2% larger than nearly stoichiometric Fe_7C_3 in the core, and

312   therefore, the mass fraction of Fe_7C_3 that is needed to account for the density deficit of

313   the inner core was likely over-estimated by ~6%.

314   The above discussion assumes that the range of non-stoichiometry in Fe_7C_3

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315   determined here at 7 GPa and 1300 °C applies at deep mantle or inner core conditions.

316   The higher temperatures in the deep mantle likely make possible larger deviations from

317   stoichiometry (Buono et al., 2013; Walker et al., 2013). Pressure and/or temperature

318   induced exchanges in the compositions of non-stoichiometric iron carbides may lead to

319   consumption or production of diamonds during downwelling or upwelling processes and

320   influence chemical equilibrium in deep Earth.

321   Non-stoichiometry is common in iron-rich alloys and may influence the density,

322   sound velocity, and other physical properties. Further studies are needed to quantify the

323   effects of pressure and temperature on non-stoichiometry of iron-rich alloys at relevant

324   conditions and explore the implications for the light element composition of the core.

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447   **FIGURE CAPTIONS**

448   **Figure 1.** Back scattered electron (BSE) image of the diffusive reaction product

449   consisting of two layers of Fe_7C_3 (gray), each sandwiched between graphite (C, dark) and

450   Fe_3C (light gray). The white and black arrows mark the positions of the XRD and EPMA

451   line scans analyses, respectively. The sample was rotated around the stacking direction of

452   the sandwich, as indicated by the curved arrow.

453

454   **Figure 2.** Representative XRD patterns collected during line scan. The pattern of the

455   center Fe_3C band (lower) contains a minor amont of Fe_7C_3. The interior of the Fe_7C_3 band

456   (middle) is pure phase. Diamond, graphite and Fe_7C_3 are found in the upper pattern

457   collected from the C/Fe_7C_3 boundary.

458

459   **Figure 3.** Composite map constructed from seven line scans at 30-µm step. The largest

460   unit-cell volume of Fe_7C_3 was found in the center of the sample where Fe_7C_3 co-exists

461   with Fe_3C. The smallest volume is near the edge where Fe_7C_3 phase coexists with

462   unreacted carbon. The Fe_7C_3 in the center may have C concentration lower than 31 at.%.

463

464   **Figure 4.** Stacked XRD patterns from line scans. (a) Overall patterns showing that as the

465   X-ray beam moved towards carbon-rich areas, the Fe_7C_3 peaks grew at the expense of the

466   Fe_3C peaks, and both Fe_7C_3 and Fe_3C peaks shifted to higher 2θ (blue and red arrows). (b)

467   The Fe_7C_3 (022) peaks in a series of XRD patterns collected from C-Fe_7C_3 interface

468   (black, high carbon) to Fe_7C_3-Fe_3C interface (light gray, low carbon content). (c) The

469   Fe_7C_3 (121) peaks in several XRD patterns collected from the interior of the Fe_7C_3 layer

470   free of Fe_3C peaks shifted to higher 2θ as the carbon content increased. (d) Overall

471   patterns of Line 1 at the distant edge, where the variation of carbon content is less than

472   that in the central positions. Both Fe_7C_3 and Fe_3C peaks still shifted to higher 2θ as the X-

473   ray beam moved towards carbon-rich areas.

474

475   **Figure 5.** EPMA line scans showing compositional variations in Fe_3C and Fe_7C_3 and

476   carbon gradient in Fe_7C_3. Line A in the distal edge has less variation than Line C in the

477   central position, consistent with Walker et al. (2013).

478

479   **Figure 6.** (a) Structure model of Fe_7C_3 (*P6₃mc*) with locally close-packed iron atoms

480   (dashed circle); (b) CFe_8 polyhedron, which can be viewed as a distorted square antiprism

481   with a rhombus in front of a rectangle; (c) Interstitial carbon in Fe lattice (upper) and C-

482   Fe substitution (lower). The Pauling-Ahrens radii of Fe^0, Fe^{2+}, C^0 are from Ahrens (1952)

483   and Pauling (1960). The radius of C^{4-} is calculated from linear extrapolation of the radii

484   of O^{2-} and N^{3-}. The dashed circles represent the radii of Fe^0 and C^0 scaled to the

485   electronegativity of Fe and C at 2.55 and 1.83, respectively.

486

487   **Figure 7.** The (a) Volume and mass per iron atom, and (b) density of FeC_x, Fe_3C, and

488   Fe_7C_3 as a function of carbon content. In (b), the gray line is drawn through pure *hcp* Fe

489   and stoichiometric Fe_3C. The dotted lines represent densities calculated by assuming

490   stoichiometric composition. The dashed and solid lines correspond to the densities

491   calculated by applying the carbon vacancy or C-Fe substitution mechanism, respectively.

492

493   **Figure 8.** (a) Non-stoichiometry in iron-light element alloys. Open symbols represent

494   stoichiometric compounds. The radii of light elements and iron are represented by the

495   circles on the left. The radius of C^{4-} or S^{2-} (outer circles) is larger than that of C^{0} or S^{0}

496   (inner circles), respectively. (b) Density of iron-light-element alloys as a function of light

497   element concentration. The ranges of non-stoichiometric compositions are denoted by

498   horitizonal bars.

499

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500   **Table 1.** Density of iron-light-element alloys at 1 bar and 300 K.

	Z	Light element (wt.%)	Light element (at.%)	Cell Volume (Å³)	Cell Mass (g/mol)	mechanism	density (g/cm³)	α_c [a] (% per wt.%)	α_c^{*} [b] (% per wt.%)
α-Fe [c]	2	0	0	23.54	112	-	7.90		
γ-Fe [d]	4	0	0	44.83	224	-	8.30		
ε-Fe [e]	2	0	0	22.49	112	-	8.27		
γ-FeC$_x$ [d]	4	0.4	1.2	45.65	224.96	C interstice	8.183	2.5	
		1.8	8	47.24	228.18	C interstice	8.020	1.7	1.4
Fe$_3$C [f] (FeC$_{0.33\pm x}$)	4	5.8	22.3	154.39	713.33	C vacancy	7.672	1.3	
		6.7	25		720	assume stoichiometry [k]	7.744	1.1	
		6.9	25.6	154.73	714.14	substitution	7.664	1.1	-0.9
		6.7	25		720	assume stoichiometry [k]	7.727	0.96	
Fe$_7$C$_3$ [g] (FeC$_{0.43\pm x}$)	2	8.8	31	186.8(1)	847.32	substitution	7.532	1.0	
		8.4	30		856	assume stoichiometry [k]	7.610	0.93	
		10.3	35	186.2(1)	812.17	substitution	7.243	1.2	2.6
		8.4	30		856	assume stoichiometry [k]	7.634	0.74	
Fe$_{1-x}$O [h]	4	23.1	51.3	79.95	276.8	Fe vacancy	5.749	1.3	
		23.7	52.1	78.95	270.08	Fe vacancy	5.681	1.3	2.1
Fe$_{1-x}$Si$_x$ [i]	2	5.2	10	22.99	106.4	substitution	7.684	1.4	
		8.1	15	22.63	103.6	substitution	7.601	1.0	0.4
Fe$_{1-x}$S [j]	2	36.4	50	60.36	176	stoichiometric	4.840	1.1	
		38.6	52.4	59.27	166.7	Fe vacancy	4.670	1.1	1.6
		39.5	53.3	57.98	162	Fe vacancy	4.640	1.1	1.3

501   [a] Compositional expansion coefficient with respect to ε-Fe.
502   [b] Relative compositional expansion coefficient between two compositions with same
503   phase. The Fe$_{1-x}$S was calculated based on the stoichiometric FeS with 50 at.% S.
504   [c] Hull (1917).
505   [d] Okamoto (1992).The density of γ-Fe at 300 K was extrapolated from data at high
506   temperature, where it is stable.
507   [e] Fei et al. (2016). The density of ε-Fe was extrapolated from data at high pressure, where
508   it is stable.
509   [f] Walker et al. (2013).
510   [g] this study.
511   [h] Hazen and Jeanloz (1984).
512   [i] Machová and Kadečková (1977) and Routbort et al. (1971).
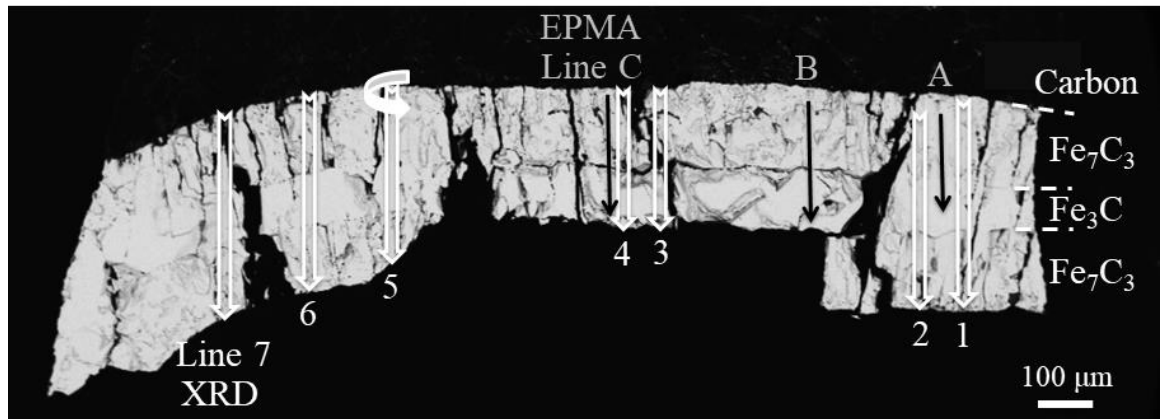513   [j] Koto et al. (1975) and Nakano et al. (1979).
514   [k] Incorrect density calculation using unit-cell mass from stoichiometric formula and unit-
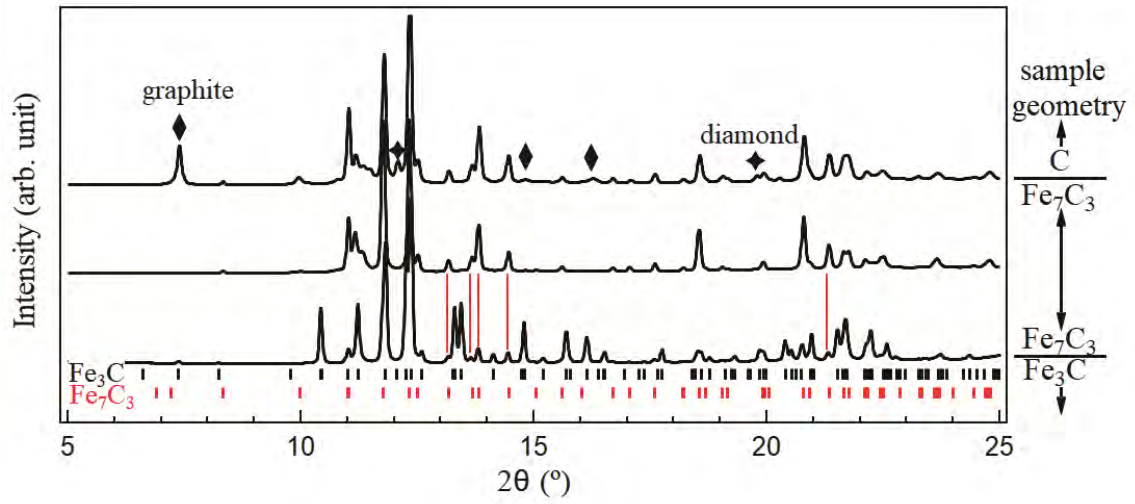515   cell volume from non-stoichiometric sample.

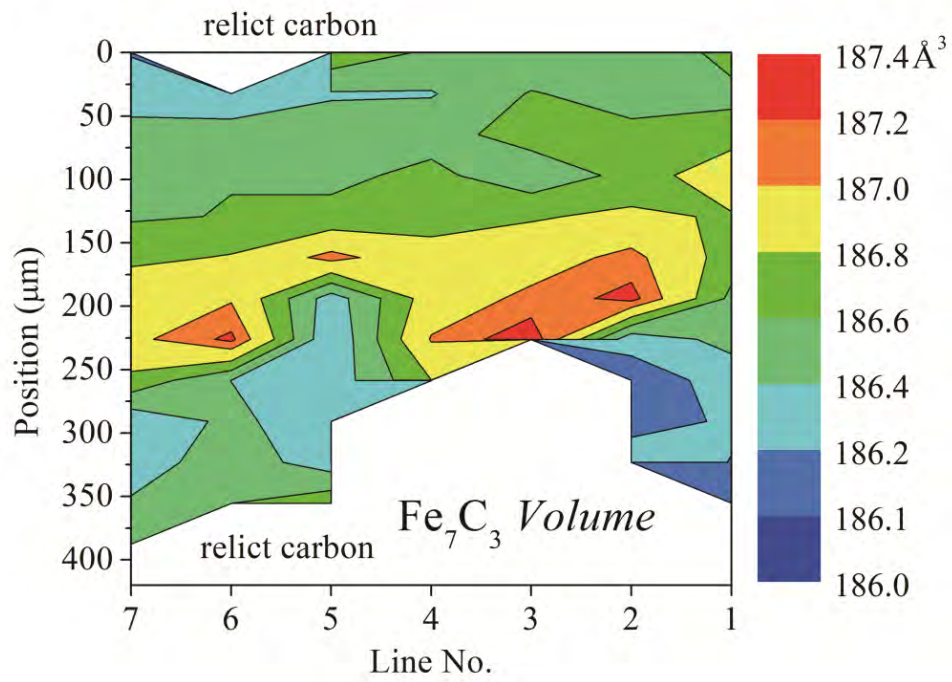**Revision 2**

Figure 1

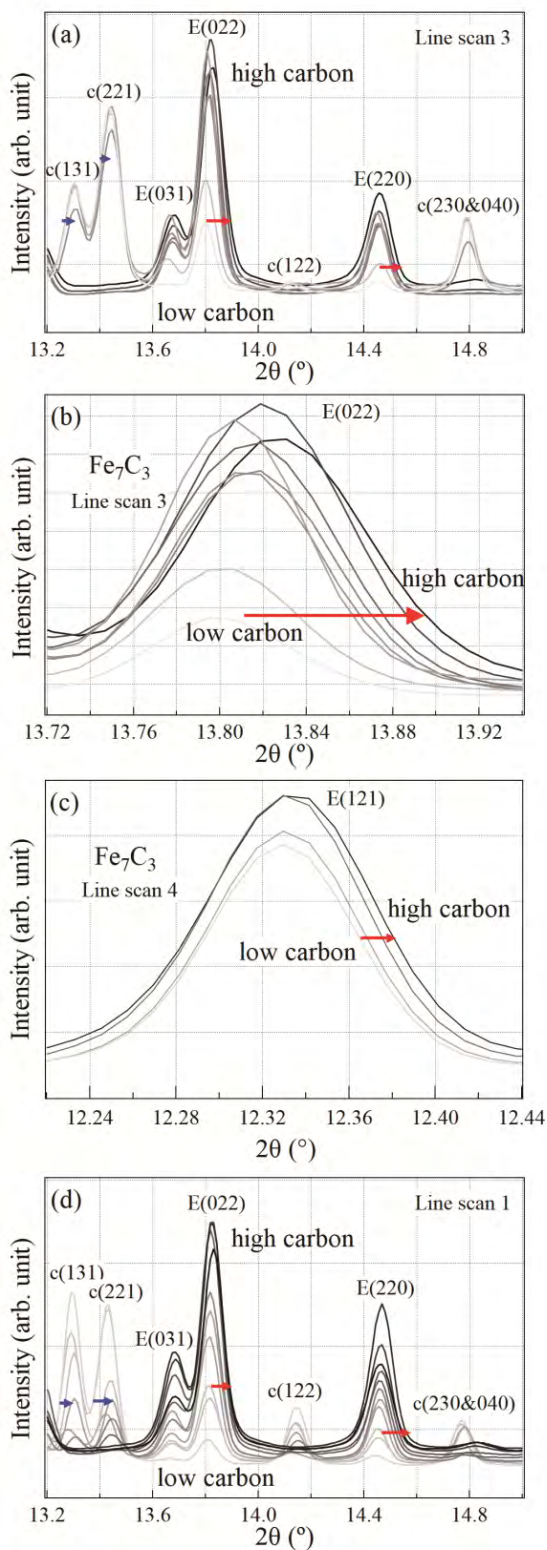516
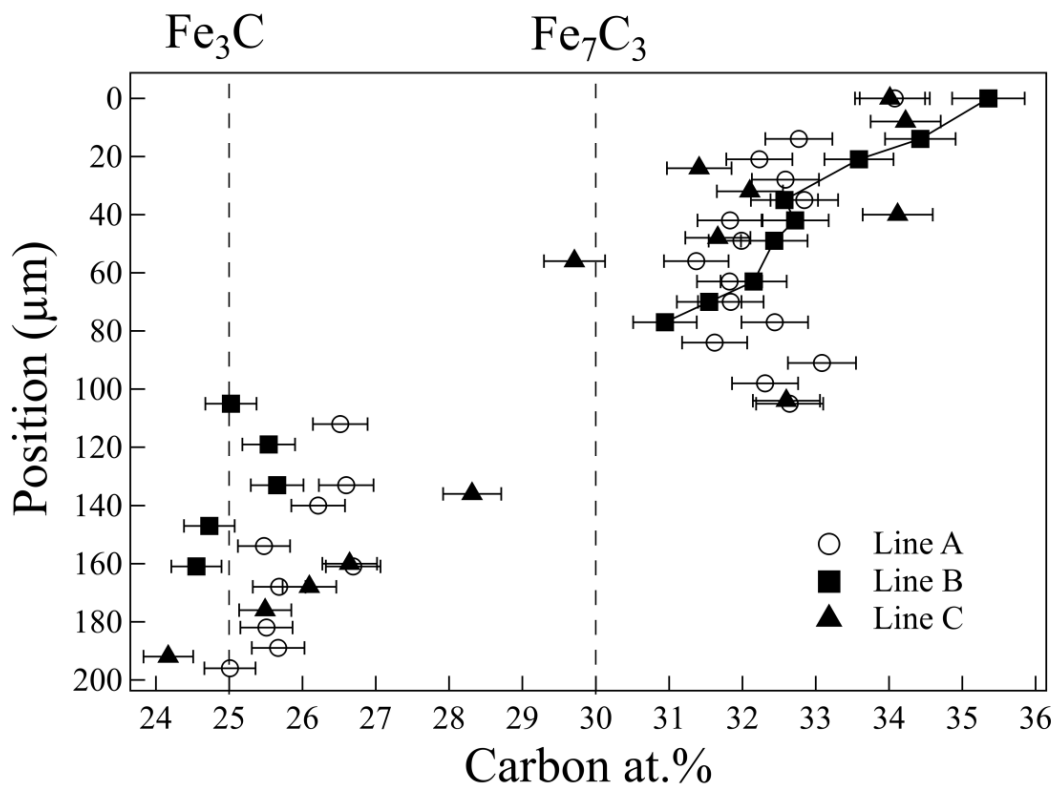517

Revision 2

Figure 2

518
519

Revision 2

Figure 3

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521

Revision 2

Figure 4

522
523

Figure 5

524
525

Figure 6

(a)

close packed Fe

Fe ● C

(b)

8 coordination CFe_8
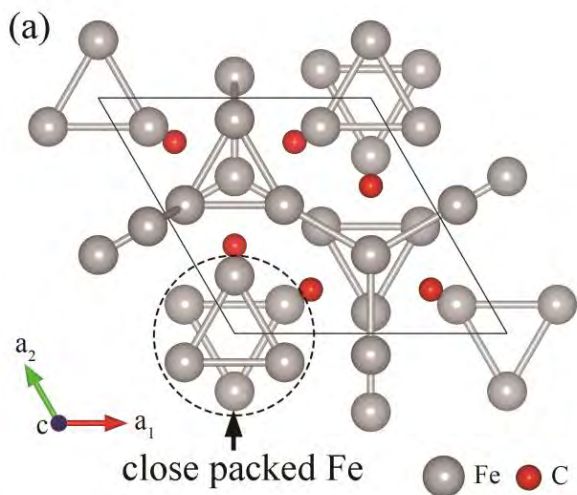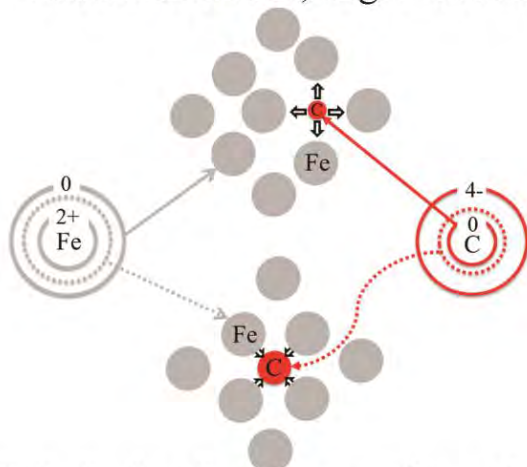distorted square antiprism

(c)
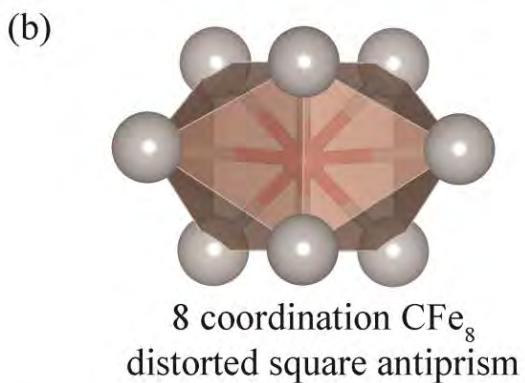
Interstitial carbon, larger volume

Fe

0
2+
Fe

4-
0
C

Fe

C

Substitutional carbon, smaller volume

526
527

Figure 7

528
529

Figure 8