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

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ABSTRACT

The Eckstrom-Adcock iron carbide, nominally Fe$_7$C$_3$, is a potential host of reduced carbon in Earth's mantle and a candidate component of the inner core. Non-stoichiometry in Fe$_7$C$_3$ has been observed previously but the crystal chemistry basis for its origin and influences on the physical properties were not known. Here we report chemical and structural analyses of synthetic Fe$_7$C$_3$ that was grown through diffusive reaction between iron and graphite and contained 31 to 35 at.% carbon. We found that more carbon-rich Fe$_7$C$_3$ has smaller unit-cell volume, suggesting that excess carbon atoms substituted for iron atoms instead of entering the interstitial sites of closed-packed iron lattice as in FeC$_x$ steel. Carbon may be the lightest alloying element to substitute for iron. The substitution leads to larger reduction in the unit-cell mass than the volume so that the carbon-rich end member may be as much as 5% less dense than stoichiometric Fe$_7$C$_3$. If Fe$_7$C$_3$ solidifies from Earth's iron-rich liquid core, it is expected to have a nearly stoichiometric composition with a compositional expansion coefficient of ~1.0. However, laboratory experiments using carbon-rich synthetic Fe$_7$C$_3$ to model the inner core may over-estimate the amount of carbon that is needed to account for the core density deficit.

**Keywords:** Iron carbide, non-stoichiometry, substitution, interstice, light element, density deficit, compositional expansion coefficient
INTRODUCTION

Eckstrom-Adcock iron carbide (Fe$_7$C$_3$) was first discovered in a hydrocarbon synthesis plant (Eckstrom and Adcock, 1950). Fe$_7$C$_3$ is considered a potential host of reduced carbon in Earth’s deep mantle, where metallic iron is expected to be stable (Rohrbach and Schmidt, 2011). It is also a candidate component to explain the density deficit and anomalously low shear wave velocity of the inner core (Chen et al., 2012; Chen et al., 2014; Liu et al., 2016; Prescher et al., 2015). M$_7$C$_3$ (M$_2$C)-type intermediate transition-metal carbides have been found as inclusions in superdeep diamonds together with cementite M$_3$C, where M stands for Fe, Co, Ni, Cr, and Mn. These natural M$_7$C$_3$ (M$_2$C) and M$_3$C samples can have ~6-8 at.% C content variation in the same structure (Kaminsky and Wirth, 2011; Smith et al., 2016). Synthetic iron carbides also show considerable compositional variation, ranging from 29 to 36 at.% carbon in Fe$_7$C$_3$ and from 17 to 31 at.% carbon in Fe$_3$C (Buono et al., 2013; Walker et al., 2013). Deviation from stoichiometric composition led to a reduction of the Curie temperature of Fe$_3$C (Walker et al., 2015). Moreover, a carbon-poor Fe$_3$C was found to have a smaller unit-cell volume than a slightly carbon-rich phase, suggesting that the carbon deficiency originates from carbon vacancy. The correlation between volume and composition is similar to FeC$_x$ or FeH$_x$ alloys, where unit-cell volume increases with the increasing amount of light element, and opposite to Fe-O, Fe-Si, and Fe-S alloys where the unit-cell volume decreases with the increasing amount of light element (Table 1). On the other hand, the origin and effects of non-stoichiometry on Fe$_7$C$_3$ are still not known. Here we investigate the composition and structure of non-stoichiometry in Fe$_7$C$_3$ through synchrotron X-ray diffraction (XRD) and electron probe microanalysis (EPMA) and
discuss the implications for the stability and properties of carbides in the deep Earth.

METHODS

Non-stoichiometric iron carbide Fe₇C₃ was synthesized using a multi-anvil apparatus at the Lamont-Doherty Earth Observatory (LDEO serial #BB-1233) (Walker et al., 2013). The starting material consists of a 250-μm-thick iron disc (Goodfellow hard iron foil, >99.5%) sandwiched between two graphite cylinders (National Carbon Spectroscopic grade graphite), surrounded by high-purity MgO sleeve. The sample was contained in an 8 mm truncated edge length (TEL) octahedron of Ceramacast 584 castable ceramic (Aremco) and equilibrated at 7 GPa (350 US ton oil pressure) and 1300 °C for 19 hrs. The temperature difference across the sample is estimated to be <10 °C, and the pressure uncertainty is estimated to be 0.5 GPa in the sample capsule. The experimental product was ground to form a 1.8-mm-long, 0.4-mm-tall, and 300-μm-thick pellet (parallel to the rotation axis of the original Fe disc and C cylinders) that presented as a sectioned sandwich with carbide as the jelly between carbon bread slices for synchrotron XRD measurements at 13-BM-C of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). The X-ray wavelength is 0.4340 (±2×10⁻⁵) Å and the beam size is 12×18 μm² at the full width at half maximum (FWHM) (horizontal×vertical direction in Fig. 1). The sample to detector distance is 164.10 (±0.03) mm. The slice was rotated around the original rotation axis of the Fe disc and C cylinders (stacking direction of the sandwich) by ±30° to reduce the effect of preferred orientation in the coarse-grained sample. The XRD data were processed using Dioptas (Prescher and Prakapenka, 2015) and PDIndexer (Seto et al., 2010) software.
After the XRD measurements, the slice was coated with aluminum for electron microprobe analysis, using the JOEL-7800FLV scanning electron microscope (SEM) and Cameca SX100 EPMA at the Electron Microbeam Analysis Laboratory (EMAL) of University of Michigan. No chemical contamination was detected in the SEM and EPMA measurements. For the EPMA analysis, a 11 kV accelerating voltage and a 70 nA beam focused to ~1 μm diameter was used to obtain compositional data (Dasgupta and Walker, 2008). The penetration depth of the beam was estimated to be <20 μm. Pure Fe and synthetic stoichiometric Fe$_3$C were used as the standards (Liu et al., 2016). The measurement time for the sample was 10 seconds on the peak positions and 5 seconds on the background.

RESULTS AND DISCUSSION

Anti-correlation between unit-cell volume and carbon content in non-stoichiometric Fe$_7$C$_3$

Back-scattered electron (BSE) image showed that the synthesis experiment produced two layers of the Eckstrom-Adcock carbide, nominally Fe$_7$C$_3$, each sandwiched between a layer of cementite, nominally Fe$_3$C, in the center of the sample and unreacted carbon on both ends (Fig. 1). The layered structure indicates that the C and Fe$_3$C layers were not fully equilibrated when the sample was quenched from high temperature. As a result, ongoing C diffusion from the C layers to Fe$_3$C layer through the Fe$_7$C$_3$ layers in between was preserved in the sample, creating the gradient of C content in the Fe$_7$C$_3$ layers, which points from the carbon-rich end near the Fe$_7$C$_3$/C boundary to carbon-poor end near the Fe$_7$C$_3$/Fe$_3$C boundary.
The layered distribution of the three phases was confirmed by XRD line scans (Fig. 2). The phase assemblies evolve from C+Fe$_7$C$_3$ at the graphite ends to Fe$_7$C$_3$ and then to Fe$_3$C. Some XRD patterns of the Fe$_7$C$_3$ contained variable amounts of Fe$_3$C. Minor Fe$_7$C$_3$ phase was also found in the XRD collected from the Fe$_3$C band. The occurrence of both carbides in the XRD patterns collected from the interior of different bands appears inconsistent with the clear separation of the bands in the BSE and optical images. We found that on the exiting side of the X-ray beam the center Fe$_3$C band is 40 μm thinner, suggesting that the boundaries between Fe$_7$C$_3$ and Fe$_3$C are not parallel and therefore the beam that enters the sample near the interface would traverse both phases. This effect is enhanced considering that 25% of X-ray intensity is outside the FWHM and can produce diffraction signals from 40-micron areas. It is also possible that the stacking direction of sample is slightly tilted towards or away from the X-ray beam direction and therefore XRD patterns containing single carbide are only collected from measurements near the center of each band, as we observed.

Despite these complications, a unit-cell volume composite map constructed from the XRD line scans revealed a general trend that Fe$_7$C$_3$ closer to the carbon layer has smaller unit-cell volume (Fig. 3). We used hexagonal structure ($P6_3mc$) (Herbstein and Snyman, 1964) to refine the structure of Fe$_7$C$_3$ since it better explained the observed patterns. Six fixed peaks (112), (031), (022), (220), (033) and (232) which have no overlap with Fe$_3$C strong peaks were used for the refinement of all present unit-cell volumes to avoid complications, and the largest unit-cell of Fe$_7$C$_3$ was found in the Fe$_3$C center band, where Fe$_7$C$_3$ occurred as a minor phase in the mixed XRD patterns. The trend of decreasing volume towards the carbon layer is further confirmed by the stacked XRD
patterns showing a systematic shift of peak position towards larger $2\theta$ as the X-ray beam moved from the Fe$_3$C-Fe$_7$C$_3$ boundary towards the Fe$_7$C$_3$-C boundary (Fig. 4). Fe$_3$C exhibits a similar correlation of higher carbon content with smaller unit-cell volume, although there is considerable scatter and the trend is not as well resolved (Fig. 4a&d). These peak shifts, although only $\sim$0.02°, are much larger than the potential shifts caused by uncertainties in X-ray wavelength (0.0006° at $2\theta \sim$14° corresponding to 1 eV energy fluctuation) and sample-to-detector distance (0.0024° at $2\theta \sim$14° corresponding to 30 μm sample distance variation). The sample-detector distance at the center band of Fe$_3$C +Fe$_7$C$_3$ mixture can differ by up to ~100 μm from the Fe$_7$C$_3$ band at the edge. Accordingly, the $2\theta$ could shift up to 0.008° and may have visible influence on the unit-cell volumes of the center-most Fe$_7$C$_3$, but not enough to account for the total observed shift. Additionally, the peak shift was observed in Fe$_7$C$_3$ phase at the edge free of Fe$_3$C (Fig. 4c), thus ruling out the possibility that the $2\theta$ shift mainly comes from phase mixture. In all seven line scans the largest volumes appear in the center, suggesting that the $2\theta$ shift does not come from random fluctuation. Therefore, the variation in cell volume suggests non-stoichiometry in Fe$_3$C and Fe$_7$C$_3$. More importantly, the data suggest an anti-correlation between cell volume and carbon content: As the carbon concentration increases, the cell volume became smaller.

EPMA line scans showed two clusters of composition at ~24-27 at.% and ~31-35 at.% carbon, corresponding to Fe$_3$C and Fe$_7$C$_3$, respectively (Fig. 5). The ranges of non-stoichiometry agree with the previous studies (Buono et al., 2013; Walker et al., 2013). The compositions of Fe$_3$C mostly fell on the carbon-rich side of the stoichiometric compound, consistent with the fact that the iron in the starting material was fully
consumed and the product still contains unreacted carbon. Overall the carbon content decreases from the region next to unreacted carbon towards that next to the Fe$_3$C band, consistent with the direction of C diffusion (Fig. 5). Compositional fluctuation exists in individual line scan, especially Line A near the distal edge, due to the complexity in carbon diffusion (Walker et al., 2013) and the large uncertainty in measuring C concentration by EPMA.

Compared with EPMA measurements, less fluctuation of unit-cell volume was observed in XRD (Fig. 3 and Fig. 5). This is mainly because the sample volume covered by XRD is significantly larger than that by EPMA (12×18 μm beam size and 300 μm depth in XRD compared with ~1 μm beam size and <20 μm penetration depth in EPMA). With thousands of times volume coverage, together with the sample rotation, the XRD measurements effectively reduced the scattering caused by complexity of local composition and obtained the average lattice parameters for the covered volume.

From the most carbon-rich part with 35 at.% carbon to the least carbon-rich part with 31 at% carbon in the Fe$_7$C$_3$ band, the unit-cell volume expands by ~0.3% from ~186.2 Å$^3$ to 186.8 Å$^3$. Larger unit-cell volume up to ~187.4 Å$^3$ was obtained from the Fe$_7$C$_3$-Fe$_3$C mixture in the center band, where carbon content may be lower than 31 at.% and the XRD beam averaged less volume from carbon-rich Fe$_7$C$_3$ when it crossed the Fe$_7$C$_3$-Fe$_3$C phase boundary. Because large uncertainty may exist in both the composition and volume refinement in this phase mixture region, it is excluded from the latter density calculation.

**Origin of non-stoichiometry in Fe$_7$C$_3$ and Fe$_3$C**
The composition-volume relation of iron carbides can be used to infer the mechanism by which carbon is removed or added from the structures of stoichiometric compounds. Cementite Fe₃C is usually considered an interstitial alloy, in which carbon atoms adopt the six-fold interstitial sites of iron in hcp structure (Barrett, 1943; Scott et al., 2001). First-principles calculations found that carbon enters the interstitial sites of closed packed structure of iron and therefore adding a small amount of carbon (x < 0.1) to hcp Fe expands the lattice (Caracas, 2017). The interstitial model, however, cannot explain the smaller volumes of carbon-rich Fe₇C₃ and Fe₃C, suggesting that carbon-iron substitution may be the cause of carbon-rich carbides.

By contrast, Walker et al. (2013) found that the unit-cell volume of a carbon-poor Fe₃C with 22.3 at% carbon is smaller than that of a slightly carbon-rich Fe₃C with 25.6 at% carbon. Petch (1944) also found that volume decreases with decreasing C content in Fe-saturated cementites as they become less stoichiometric and C-poorer with rising temperature. Results from the two literature studies on C-poor cementite, compared to the present study of C-rich cementite therefore suggest that deviation from the stoichiometric composition of Fe₃C in either direction reduces the cell volume and that the mechanisms of non-stoichiometry may be different on different sides of stoichiometric Fe₃C. In light of this new evidence, the supposition of Walker et al. (2015) that the non-stoichiometry mechanism on the C-rich side of Fe₃C is interstitial, is less plausible than that it is substitutional. Walker et al. (2015) found that the Curie temperature is lower on either side of Fe₃C but the rate of $T_c$ reduction on the C-rich side is twice that on the C-poor side. They attributed the rate differences to larger configurational entropy production by interstitial C on the C-rich side than by C vacancy on the C-poor side. We now regard
substitutional C as a more plausible mechanism on the C-rich side on the basis of the new evidence presented here. The entropy argument, however remains unchanged because there are still twice as many sites for substitution on the C-rich side as there are for C vacancy on the C-poor side of Fe₃C. The entropy production rate in this particular case is insensitive to compositional variation mechanism for introducing C richness.

A closer look at the structures of Fe₃C and Fe₇C₃ reveal that carbon takes a distinct 8-fold square antiprism site instead of the interstitial sites of close-packed iron lattice (Fig. 6). The presence of carbon distorts the 6-fold interstitial sites and enlarges the lattice. As a result, 2/3 of the iron atoms in Fe₃C and 6/7 of that in Fe₇C₃ have only 11 nearest iron neighbors and the sub-structures of iron atoms are no longer ideal hcp closest packing. The 8-fold carbon sites and 11-fold iron sites in the carbide structures can be explained by the nature of metallic bonding between carbon and iron, where carbon acts as an electron donor and enhances the hybridization between the partially filled 3d orbital and the 4s orbital of iron (Goldschmidt, 1967). As a result, C in iron carbides should be treated as C⁰, instead of C⁴⁻ as in covalent and stoichiometric compounds such as SiC, Al₄C₃ and Mg₂C. For metallic bonding between Fe⁰ and C⁰ the radius ratio r_C/r_Fe is ~0.62 or slightly larger with corrections for electronegativity of Fe (1.83) and C (2.55) (Allred, 1961). According to Pauling’s rules this ratio is slightly too high for carbon to take the 6-fold interstitial site (r_A/r_X = 0.414) and too low for C-Fe substitution (r_A/r_X = 1). Consequently, only a small amount of interstitial carbon is allowed in FeCₓ alloys. Carbon in Fe₃C and Fe₇C₃ adopts 8-fold square antiprism sites (r_C/r_a = 0.645 in Pauling’s rules) instead of entering the interstices of close-packed iron.

Because carbon adopts an 8-fold site that is not much smaller than 11-fold iron sites,
excess carbon atoms in Fe$_3$C and Fe$_7$C$_3$ may be incorporated into the structure through substitution of carbon for iron (Fig. 6). This substitution explains the reduced volumes of carbon-rich Fe$_3$C and Fe$_7$C$_3$. No carbon-poor Fe$_7$C$_3$ has been found in this study or previous synthesis (Walker et al., 2013), suggesting that it is less stable than a two-phase mixture of Fe$_3$C and stoichiometric Fe$_7$C$_3$.

The inferred origin of non-stoichiometry in carbon-poor and carbon-rich Fe$_3$C is consistent with the relations between the lattice parameters and carbon content. An anti-correlation in lattice parameters was reported in C-poor Fe$_3$C such that the $b$ axis elongates with decreased C content while the unit-cell volume (and $a$, $c$ axes) shrinks (Petch, 1944; Walker et al., 2013). This kind of anti-correlation was not observed in the C-rich Fe$_3$C in this study. For example, in Line 1 the maximum unit-cell volume of Fe$_3$C 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 minimum unit-cell volume is 155.47(38) Å$^3$ with $a = 5.094(2)$ Å, $b = 6.748(7)$ Å and $c = 4.523(3)$ Å. Carbon in the antiprism site of Fe$_3$C introduces pleats to the close-packed Fe in $b$ direction, which changes the folding angle of the pleats from 180º (no folding) to ~120º. The carbon vacancy unbends the pleats in the $b$ direction and lets them stack better in $a$ and $c$ direction, thus increasing the axial length in the $b$ direction and decreasing it in the $a/c$ direction. On the C-rich side, all the antiprism sites are filled and the excess carbon takes the Fe site instead. Because there is no further occupancy of the antiprism sites, the anti-correlation between $b$ and unit-cell volume disappears on the C-rich side.

The inferred site occupancy is further corroborated by the diffusion rates of carbon and iron in FeC$_x$ alloy and iron carbides. Carbon diffusion in austenite and ferrite is
considered a typical example of rapid interstitial diffusion, whereas self-diffusion of iron
is a typical example of substitution (vacancy) diffusion. At 1 bar and 1000 K, the
diffusion coefficient of carbon in Fe$_3$C is $\sim 10^{-15}$ m$^2$/s, which falls between that of carbon
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
$fcc$ Fe ($\sim 10^{-19}$ m$^2$/s) (Gale and Totemeier, 2003; Hillert et al., 2005; Ozturk et al., 1984).
The intermediate value of diffusion coefficient suggests that carbon in Fe$_3$C cannot be
treated as an interstitial constituent. Molecular dynamics simulations suggest that six-fold
interstitial sites may serve as transient “stepping stones” to facilitate diffusion of carbon
among anti-prismatic sites (Levchenko et al., 2009). This interstice-assisted diffusion
mechanism implies carbon diffusion in Fe$_3$C may include both interstitial and
substitutional mechanism, and the substitutional diffusion is likely the rate-limiting step
that caused the observed gradient non-stoichiometry in the diffusive reaction product in
this study.

The roughly planar boundaries between Fe$_3$C, Fe$_7$C$_3$, and C in the recovered samples
synthesized at 7 GPa from this and previous study suggested that the reactions were
controlled mainly by lattice diffusion, without significant transport along grain
boundaries (Walker et al., 2013). The widths of Fe$_3$C layer and Fe$_7$C$_3$ layer in either this
study or the previous study are comparable, thus indicating the lattice diffusion rates of
carbon in Fe$_7$C$_3$ and Fe$_3$C are similar, which in turn implies the same origin of non-
stoichiometry on the carbon-rich sides of these carbides.

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

The density of an iron carbide may be calculated from its unit-cell volume from
XRD measurements and the composition as determined by microprobe analysis only if
we can infer the mechanism of non-stoichiometry. For a carbon-rich Fe$_7$C$_3$ with 35 at.%
carbon, the formula unit may be written as Fe$_{6.5}$C$_{3.5}$ for a substitution alloy or Fe$_7$C$_{3.77}$ for
an interstitial alloy. Depending on the mechanism of non-stoichiometry, the calculated
densities for the same unit-cell volume and chemical composition could differ by more
than 5% (Table 1). It is therefore important to understand the nature of non-stoichiometry.

The presence of a light element in an iron-alloy usually reduces its density. The
efficiency of density reduction can be described by the compositional expansion
coefficient $\alpha_c$, the ratio between the relative density reduction and the concentration of
the light element in weight percent. With respect to hcp iron, the $\alpha_c$ of stoichiometric
Fe$_3$C and Fe$_7$C$_3$ is 1.4, corresponding to 1.4% density reduction for 1 wt.% of carbon in
the Fe-alloy (Fig. 7). Carbon excess in Fe$_7$C$_3$ leads to a local excursion of $\alpha_c$ to 2.6,
because replacing iron with carbon reduces the cell mass much more than the cell volume.
It is interesting to note that carbon vacancy in Fe$_3$C may give rise to local negative $\alpha_c$
with respect to stoichiometric composition: Between carbon-poor Fe$_3$C with vacancy and
nearly stoichiometric Fe$_3$C, the local $\alpha_c$ is -0.9 (Fig. 7, Table 1).

Non-stoichiometry is common among iron-light-element alloys and may cause
variations in compositional expansion coefficient (Fig. 8). At ambient conditions,
however, the complexity in calculating density from measured cell volume and
composition may be applicable to carbon alone. This is because the atomic or covalent
radius of carbon makes a borderline case for it to act as an interstitial constituent as in
FeC$_x$, or as a substituent of iron as in carbon-rich Fe$_3$C and Fe$_7$C$_3$. With $r_{\text{H}}/r_{\text{Fe}} \sim 0.29$,
FeH$_x$ is considered a typical interstitial alloy. Silicon is comparable to iron in size ($r_{\text{Si}}/r_{\text{Fe}}$
and electronegativity and therefore all Fe-Si alloys are substitutional. Oxygen and sulfur are highly electro-negative and their anions are much larger than an iron cation, and therefore iron vacancy is the dominant mechanism for non-stoichiometry in Fe$_{1-x}$O (Hazen and Jeanloz, 1984) and Fe$_{1-x}$S (Palache et al., 1944). At high pressures, Fe$_{1-x}$S$_x$ ($x < 0.1$) solutions have been predicted and observed (Alfe et al., 2002; Kamada et al., 2012; Kamada et al., 2010; Li et al., 2001). Pressure may influence the electronegativity and radii of iron and sulfur differently, hence it may be necessary to examine the dissolution mechanism of sulfur in iron in order to correctly calculate the density of Fe-S alloys at high pressures.

**IMPLICATIONS**

As a candidate component of the Earth’s inner core, Fe$_7$C$_3$ is likely nearly stoichiometric because it solidifies from the outer core which contains at least 85 wt.% iron. In recent mineral physics experiments, Fe$_7$C$_3$ samples are often synthesized in graphite capsules and therefore carbon-saturated (Chen et al., 2014; Nakajima et al., 2011; Prescher et al., 2015). In these studies, the density of Fe$_7$C$_3$ was calculated by assuming stoichiometric composition because non-stoichiometry was not widely recognized at the time, and the exact compositions of micrometer sized samples used for the diamond-anvil cell measurements were not readily accessible. The calculated density of synthetic C-rich Fe$_7$C$_3$ could be as much as 1.2% larger than nearly stoichiometric Fe$_7$C$_3$ in the core, and therefore, the mass fraction of Fe$_7$C$_3$ that is needed to account for the density deficit of the inner core was likely over-estimated by \(~6\%\).

The above discussion assumes that the range of non-stoichiometry in Fe$_7$C$_3$
determined here at 7 GPa and 1300 °C applies at deep mantle or inner core conditions.

The higher temperatures in the deep mantle likely make possible larger deviations from stoichiometry (Buono et al., 2013; Walker et al., 2013). Pressure and/or temperature induced exchanges in the compositions of non-stoichiometric iron carbides may lead to consumption or production of diamonds during downwelling or upwelling processes and influence chemical equilibrium in deep Earth.

Non-stoichiometry is common in iron-rich alloys and may influence the density, sound velocity, and other physical properties. Further studies are needed to quantify the effects of pressure and temperature on non-stoichiometry of iron-rich alloys at relevant conditions and explore the implications for the light element composition of the core.

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REFERENCES CITED


ocean environment and distribution of carbon between the Earth’s core and the mantle. Geochimica et Cosmochimica Acta, 72(18), 4627-4641.


from Juina, Brazil. The Canadian Mineralogist, 49(2), 555-572.

Koto, K., Morimoto, N., and Gyobu, A. (1975) The superstructure of the intermediate
pyrrhotite. I. Partially disordered distribution of metal vacancy in the 6C type, Fe11S12. Acta Crystallographica Section B: Structural Crystallography and
Crystal Chemistry, 31(12), 2759-2764.

simulation and theoretical analysis of carbon diffusion in cementite. Acta
Materialia, 57(3), 846-853.


Liu, J., Li, J., and Ikuta, D. (2016) Elastic softening in Fe7C3 with implications for
Earth's deep carbon reservoirs. Journal of Geophysical Research: Solid Earth,
121(3), 1514-1524.


Nakajima, Y., Takahashi, E., Sata, N., Nishihara, Y., Hirose, K., Funakoshi, K.-i., and
Ohishi, Y. (2011) Thermoelastic property and high-pressure stability of Fe7C3:
Implication for iron-carbide in the Earth's core. American Mineralogist, 96(7), 1158-1165.


35(3), 223-230.


FIGURE CAPTIONS

Figure 1. Back scattered electron (BSE) image of the diffusive reaction product consisting of two layers of Fe$_7$C$_3$ (gray), each sandwiched between graphite (C, dark) and Fe$_3$C (light gray). The white and black arrows mark the positions of the XRD and EPMA line scans analyses, respectively. The sample was rotated around the stacking direction of the sandwich, as indicated by the curved arrow.

Figure 2. Representative XRD patterns collected during line scan. The pattern of the center Fe$_3$C band (lower) contains a minor amount of Fe$_7$C$_3$. The interior of the Fe$_7$C$_3$ band (middle) is pure phase. Diamond, graphite and Fe$_7$C$_3$ are found in the upper pattern collected from the C/Fe$_7$C$_3$ boundary.

Figure 3. Composite map constructed from seven line scans at 30-µm step. The largest unit-cell volume of Fe$_7$C$_3$ was found in the center of the sample where Fe$_7$C$_3$ co-exists with Fe$_3$C. The smallest volume is near the edge where Fe$_7$C$_3$ phase coexists with unreacted carbon. The Fe$_7$C$_3$ in the center may have C concentration lower than 31 at. %.

Figure 4. Stacked XRD patterns from line scans. (a) Overall patterns showing that as the X-ray beam moved towards carbon-rich areas, the Fe$_7$C$_3$ peaks grew at the expense of the Fe$_3$C peaks, and both Fe$_7$C$_3$ and Fe$_5$C peaks shifted to higher 2θ (blue and red arrows). (b) The Fe$_7$C$_3$ (022) peaks in a series of XRD patterns collected from C-Fe$_7$C$_3$ interface (black, high carbon) to Fe$_5$C$_3$-Fe$_3$C interface (light gray, low carbon content). (c) The Fe$_7$C$_3$ (121) peaks in several XRD patterns collected from the interior of the Fe$_7$C$_3$ layer.
free of Fe$_3$C peaks shifted to higher 2$\theta$ as the carbon content increased. (d) Overall patterns of Line 1 at the distant edge, where the variation of carbon content is less than that in the central positions. Both Fe$_7$C$_3$ and Fe$_3$C peaks still shifted to higher 2$\theta$ as the X-ray beam moved towards carbon-rich areas.

**Figure 5.** EPMA line scans showing compositional variations in Fe$_3$C and Fe$_7$C$_3$ and carbon gradient in Fe$_7$C$_3$. Line A in the distal edge has less variation than Line C in the central position, consistent with Walker et al. (2013).

**Figure 6.** (a) Structure model of Fe$_7$C$_3$ ($P6_3mc$) with locally close-packed iron atoms (dashed circle); (b) CFe$_8$ polyhedron, which can be viewed as a distorted square antiprism with a rhombus in front of a rectangle; (c) Interstitial carbon in Fe lattice (upper) and C-Fe substitution (lower). The Pauling-Ahrens radii of Fe$^0$, Fe$^{2+}$, C$^0$ are from Ahrens (1952) and Pauling (1960). The radius of C$_4^-$ is calculated from linear extrapolation of the radii of O$_2^-$ and N$_3^-$. The dashed circles represent the radii of Fe$^0$ and C$^0$ scaled to the electronegativity of Fe and C at 2.55 and 1.83, respectively.

**Figure 7.** The (a) Volume and mass per iron atom, and (b) density of FeC$_x$, Fe$_3$C, and Fe$_7$C$_3$ as a function of carbon content. In (b), the gray line is drawn through pure hcp Fe and stoichiometric Fe$_3$C. The dotted lines represent densities calculated by assuming stoichiometric composition. The dashed and solid lines correspond to the densities calculated by applying the carbon vacancy or C-Fe substitution mechanism, respectively.
Figure 8. (a) Non-stoichiometry in iron-light element alloys. Open symbols represent stoichiometric compounds. The radii of light elements and iron are represented by the circles on the left. The radius of C⁺ or S⁻ (outer circles) is larger than that of C⁰ or S⁰ (inner circles), respectively. (b) Density of iron-light-element alloys as a function of light element concentration. The ranges of non-stoichiometric compositions are denoted by horizontal bars.
Table 1. Density of iron-light-element alloys at 1 bar and 300 K.

<table>
<thead>
<tr>
<th>Light element</th>
<th>Z</th>
<th>Cell Volume (Å³)</th>
<th>Cell Mass (g/mol)</th>
<th>mechanism</th>
<th>density (g/cm³)</th>
<th>αc (wt.%)</th>
<th>αc* (wt.%)</th>
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</thead>
<tbody>
<tr>
<td>α-Fe</td>
<td>2</td>
<td>0.0</td>
<td>23.54</td>
<td>-</td>
<td>7.90</td>
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<td></td>
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<tr>
<td>γ-Fe</td>
<td>4</td>
<td>0.0</td>
<td>44.83</td>
<td>-</td>
<td>8.30</td>
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<td></td>
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<tr>
<td>α-Fe*</td>
<td>2</td>
<td>0.0</td>
<td>22.49</td>
<td>-</td>
<td>8.27</td>
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<td></td>
</tr>
<tr>
<td>γ-FeCₓ</td>
<td>4</td>
<td>0.4, 1.2</td>
<td>45.65</td>
<td>C interstice</td>
<td>8.183</td>
<td>2.5</td>
<td>1.4</td>
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<tr>
<td>Fe₃Cₓ</td>
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<td>22.3</td>
<td>154.39</td>
<td>713.33</td>
<td>7.672</td>
<td>1.3</td>
<td>-0.9</td>
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<tr>
<td>Fe₇C₃</td>
<td>2</td>
<td>8.8, 31</td>
<td>186.8(1)</td>
<td>substitution</td>
<td>7.532</td>
<td>1.0</td>
<td></td>
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<tr>
<td>Fe₇C₃</td>
<td>2</td>
<td>8.4, 30</td>
<td>186.2(1)</td>
<td>substitution</td>
<td>7.243</td>
<td>1.2</td>
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<tr>
<td>Fe₁₋ₓO</td>
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<td>79.95</td>
<td>Fe vacancy</td>
<td>5.749</td>
<td>1.3</td>
<td>2.1</td>
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<tr>
<td>Fe₁₋ₓSi</td>
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<td>5.2, 10</td>
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<td>substitution</td>
<td>7.684</td>
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<tr>
<td>Fe₁₋ₓS</td>
<td>2</td>
<td>36.4, 50</td>
<td>60.36</td>
<td>stoichiometric</td>
<td>4.840</td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
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* Compositional expansion coefficient with respect to ε-Fe.
* Relative compositional expansion coefficient between two compositions with same phase. The Fe₁₋ₓS was calculated based on the stoichiometric FeS with 50 at.% S.
* Hull (1917).
* Ōkamoto (1992). The density of γ-Fe at 300 K was extrapolated from data at high temperature, where it is stable.
* Fei et al. (2016). The density of ε-Fe was extrapolated from data at high pressure, where it is stable.
* Walker et al. (2013).
* This study.
* Machová and Kadečková (1977) and Routbort et al. (1971).
* Koto et al. (1975) and Nakano et al. (1979).
* Incorrect density calculation using unit-cell mass from stoichiometric formula and unit-cell volume from non-stoichiometric sample.
Figure 1
Figure 2
Figure 5

![Graph showing Fe\(_3\)C and Fe\(_7\)C\(_3\) positions with different lines representing different data sets.](image-url)
Figure 6

(a) 

close packed Fe

(b) 

8 coordination CFe₈ 
distorted square antiprism

(c) 

Interstitial carbon, larger volume

Substitutional carbon, smaller volume
Figure 7

(a) Volume per Fe atom (Å$^3$) as a function of carbon at. % for hcp FeC$_x$, Fe$_3$C, and Fe$_7$C$_3$ phases.

(b) Density (g/cm$^3$) of hcp FeC$_x$, Fe$_3$C, and Fe$_7$C$_3$ phases as a function of carbon at. %.

Assume stoichiometry for FeC$_x$.

Vacancy and substitution are indicated for the Fe$_3$C phase.