Origin and consequences of nonstoichiometry in Fe_7C_3

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Abstract

The Eckstrom-Adcock iron carbide Fe_7C_3 is a candidate to explain the density deficit and anomalously low shear wave velocity in Earth's inner core with respect to iron or iron-nickel alloys (Lord et al. 2009; Nakajima et al. 2009; Chen et al. 2012; Chen et al. 2014). It is also a potential phase to host reduced carbon in Earth's deep mantle (Dasgupta 2013). A previous study on Fe_7C_3 found deviation from the stoichiometric composition with carbon content varying between 29 and 36 at.% (Walker et al. 2013). To investigate the origin and consequences of nonstoichiometry, we synthesized iron carbides by diffusion reaction between cylinders of iron and graphite at 7 GPa and 1300 ˚C for 19 hrs. The experimental product contained Fe_7C_3 carbide + diamond & graphite at the C-saturated end, and a mixture of Fe_7C_3 and Fe_3C at the iron-saturated end. Through synchrotron X-ray diffraction (XRD) mapping, we found that the length of *a* and *c*-axis and unit-cell volume of Fe_7C_3 decrease with increasing carbon content, just opposite to the previous result on Fe_3C (Walker et al. 2013). The unexpected volume and composition relation of Fe_7C_3 suggests that a small fraction of carbon substitutes for iron instead of entering the interstitial sites of the structures, leading to volume reduction, and that substitution is enhanced at higher carbon content. The nonstoichiometry in Fe_7C_3 has a higher influence on molecular weight than unit-cell volume. The iron-rich Fe_7C_3 is therefore expected to have a higher density. Solidification of an iron-rich liquid core is expected to produce iron-saturated Fe_7C_3 denser than the stoichiometric Fe_7C_3. Future research on carbon in Earth's deep mantle and inner core must consider the effects of

nonstoichiometry on the density and stability of Fe_7C_3.

References

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