Origin and consequences of non-stoichiometry in iron carbide Fe₇C₃

FENG ZHU¹*,‡, JIE LĪ², DAVID WALKER³, JIACHAO LIU⁴*, XIANGJING LAI⁵*, and DONGZHOU ZHANG⁷

¹Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48109, U.S.A. Orcid: 0000-0003-2409-151X
²Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48109, U.S.A. Orcid: 0000-0003-4761-722X
³Earth and Environmental Science, LDEO, Columbia University, Palisades, New York 10964, U.S.A.
⁴Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48109, U.S.A. Orcid: 0000-0001-9676-7473
⁵Hawaii Institute of Geophysics and Planetology, University of Hawaii at Manoa, Honolulu, Hawaii 96822, U.S.A. Orcid: 0000-0003-4451-9421
⁶Department of Geology and Geophysics, University of Hawaii at Manoa, Honolulu, Hawaii 96822, U.S.A.
⁷Hawaii Institute of Geophysics and Planetology, University of Hawaii at Manoa, Honolulu, Hawaii 96822, U.S.A. Orcid: 0000-0002-6679-892X

ABSTRACT

The Eckstrom-Adcock iron carbide, nominally Fe₇C₃, is a potential host of reduced carbon in Earth’s mantle and a candidate component of the inner core. Non-stoichiometry in Fe₇C₃ 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 Fe₇C₃ that was grown through a diffusive reaction between iron and graphite and contained 31 to 35 at% carbon. We found that more carbon-rich Fe₇C₃ 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 FeC₃ steel. Carbon may be the lightest alloying element to substitute for iron. The substitution leads to a 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 Fe₇C₃. If Fe₇C₃ 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 Fe₇C₃ to model the inner core may overestimate 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; Physics and Chemistry of Earth’s Deep Mantle and Core

INTRODUCTION

Eckstrom-Adcock iron carbide (Fe₇C₃) was first discovered in a hydrocarbon synthesis plant (Eckstrom and Adcock 1950). Fe₇C₃ 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, 2014; Prescher et al. 2015; Liu et al. 2016). M₇C₃ (M₇C) intermediate transition-metal carbides have been found as inclusions in superdeep diamonds together with cementite M₇C, where M stands for Fe, Co, Ni, Cr, and Mn. These natural M₇C₃ (M₇C) and M₇C 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 Fe₇C₃ and from 17 to 31 at% carbon in Fe₃C (Buono et al. 2013; Walker et al. 2013). Deviation from stoichiometric composition led to a reduction of the Curie temperature of Fe₇C₃ (Walker et al. 2015). Moreover, a carbon-poor Fe₇C₃ 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 FeC₃ or FeHₓ 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 Fe₇C₃ are still not known. Here we investigate the composition and structure of non-stoichiometry in Fe₇C₃ through synchrotron X-ray diffraction (XRD) and electron probe microanalysis (EPMA), and we 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 disk (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 Ceramaco 584 castable ceramic (Areco) and equilibrated at 7 GPa (350 U.S. tons from oil pressure) and 1300 °C for 19 h. 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 disk 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...