Melting in the Fe–C system to 70 GPa

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ABSTRACT

We determined high-pressure melting curves for Fe_3C, Fe_7C_3 and the $Fe–Fe_3C$ eutectic using laser-heated diamond anvil cell techniques. The principal criterion for melting is the observation of plateaus in the temperature vs. laser power function, which is an expected behavior at isobaric invariant points (e.g. congruent, eutectic, or peritectic melting) as increased power provides the latent heat of melting. We verified this technique by reproducing the melting curves of well-studied congruently melting compounds at high pressure (Fe, Pt, FeS, Pb), and by comparison with melting determinations made using thermocouple-based large-volume press techniques. The incongruent melting curve of Fe_3C measured to 70 GPa has an apparent change in slope at ~8 GPa, which we attribute to stabilization of Fe_7C_3 at the solidus and the creation of a $P–T$ invariant point. We observe that Fe_7C_3 melts at higher temperatures than Fe_3C between 14 and 52 GPa and has a steep $P–T$ slope, and on this basis predicts an expanding field of $Fe_7C_3 +$ liquid with pressure. The $Fe–Fe_3C$ eutectic melting curve measured to 70 GPa agrees closely with multi-anvil data and thermodynamic calculations. We also measured the eutectic composition as a function of pressure using an in situ X-radiographic imaging technique, and find a rapid drop in carbon in the eutectic composition above about 20 GPa, generally consistent with previous thermodynamic calculations, and predict that the eutectic lies close to pure iron by ~50 GPa. We use these observations to extrapolate phase relations to core-relevant pressures. Convergence of the Fe_3C and $Fe–Fe_3C$ eutectic melting curves indicate that Fe_3C is replaced at the solidus by Fe_7C_3 at ~120 GPa, forming another $P–T$ invariant point and a new eutectic between Fe and Fe_7C_3. Thus, Fe_3C is unlikely to be an important crystallizing phase at core conditions, whereas Fe_7C_3 could become an important crystallizing phase.

1. Introduction

The composition of Earth's core has long been subject to controversy. Measurements of the room temperature equation of state of pure iron and iron–nickel alloys to two megabars and beyond (Dewaele et al., 2006; Mao et al., 1990) have consistently yielded higher densities than predicted from geophysical models (Birch, 1952; 1964). Although thermal expansion at the temperatures likely to be relevant to the core partially mitigates the problem (Boehler, 1993; Shen et al., 1998; Alfè et al., 2004; Luo and Ahrens, 2004; Ma et al., 2004), recent determinations of the thermal equation of state of iron at high pressures (Dubrovinsky et al., 2000), extrapolated to core temperatures, still leaves the core insufficiently dense. Recent estimates of the core density deficit range from 3–10% for the outer core (Anderson and Isaak, 2002; Shanker et al., 2004) and 2.5–9% for

the inner core (Dubrovinsky et al., 2000; Dewaele et al., 2006), although the magnitude of the deficit depends strongly on the chosen thermal profile.

Several possible contenders have been proposed for the alloying elements, including hydrogen, carbon, oxygen, silicon and sulfur (Poirier, 1994), with the popularity of each waxing and waning, and some mixture seems most likely (e.g. Alfè et al., 2002; McDonough, 2003; Badro et al., 2007). Constraining the composition of the core is critical if we are to better understand it's thermal structure and crystallization history, dynamo action, energy balance, postulated interaction with the mantle, and the partitioning of siderophile elements (Jana and Walker, 1997; Lister and Buffett, 1998; Buffett et al., 2000; Walker, 2005; Chabot et al., 2006). Although a great deal has been achieved in this area (e.g. Li and Fei, 2003), much remains to be determined about the relevant iron-light element phase diagrams at pressures relevant to the core's formation and it's present state.

Carbon is the fourth most abundant element in the solar system, with the CI chondrites containing 3.5 wt.% C (Lodders, 2003). The potential importance of carbon in the cores of the terrestrial planets is suggested by the presence of both graphite and cohenite $(Fe,Ni)_3C$ in

iron meteorites (e.g. Goodrich, 1992). It is estimated that the bulk silicate Earth has about 120 ppm (McDonough and Sun, 1995) to 400 ppm (Javoy, 1997) carbon, which is a small amount when compared to the chondrites. Whether this mismatch reflects a low overall abundance in Earth due to volatile loss during accretion or to sequestration into the core during core formation is an open question. As a result of these difficulties, estimates of the Earth's carbon content are speculative and diverse, ranging from as low as 0.2 wt.% (McDonough, 2003; Dasgupta and Walker, 2008) to 4 wt.% (Hillgren et al., 2000). Carbon is thus a potential and interesting candidate for at least part of the light element budget of the core, which makes understanding the Fe–C phase diagram at high pressures a priority.

The iron-rich portion of the Fe–C binary system has been studied extensively at 1 atm and modest pressures due to its importance in metallurgy (e.g. Strong and Chrenko, 1971; Chipman, 1972), as shown in Fig. 1. At 1 atm (Fig. 1A) there is a eutectic, possibly metastable, between iron and graphite at 1420 K and 4.3 wt.% carbon. The compound, Fe_3C (cementite), melts incongruently to liquid + graphite at about the eutectic temperature. At higher pressure (e.g. 5.7 GPa; Fig. 1B), Fe_3C melts in a peritectic reaction to form liquid + diamond, and a eutectic exists between Fe and Fe_3C. At higher pressure still another important compound, Fe_7C_3, stabilizes and is known to melt incongruently to liquid + diamond at 9 GPa (Shterenberg et al., 1975; Tsuzuki et al., 1984).

Wood (1993) calculated phase relations up to 136 GPa in the Fe–C system on the basis of a thermodynamic model, and predicted that pressure would cause a decrease in the carbon content of the eutectic between Fe and Fe_3C, with the carbon content becoming negligible at core pressures. This was predicted to occur because of a rapid increase in the melting point of Fe_3C and a consequent expansion of the Fe_3C + liquid field. Wood (1993) also predicted that Fe_3C melts incongruently at low pressures to liquid + graphite, but that melting becomes congruent by 15 GPa. Thus, for a planetary core in which the entire light element budget consists of carbon, the inner core would consist of pure Fe_3C, with a residual outer core liquid that would have decreasing carbon content as crystallization progressed. However, neutron diffraction measurements (Wood et al., 2004) and ab initio calculations (Vocadlo et al., 2002) have established that the effect of the ferromagnetic to paramagnetic transition in Fe_3C (Häglund et al., 1991) changes its thermoelastic parameters relative to those used by Wood (1993). These changes are expected to substantially reduce the high-pressure stability field of Fe_3C, calling the predicted phase relations into question. Further, the presence of Fe_7C_3, which becomes stable above 6 GPa (Shterenberg, 1975; Tsuzuki et al., 1984; Nakajima et al., 2009), may also affect the phase diagram in ways not fully captured by the earlier modeling of Wood (1993).

Here we investigate melting phase relations at high pressures in the system Fe–C to further test the proposed phase relations of Wood (1993), corroborate more recent large-volume press studies, and extend our knowledge of the Fe–C system to pressures more relevant to the core. Specifically, we have measured the first melting curves of Fe_3C, Fe_7C_3 and the Fe–Fe_3C eutectic to ~70 GPa using the laser-heated diamond anvil cell (LHDAC), and determined the eutectic composition in situ to 44 GPa using a novel X-radiographic imaging technique (Walker et al., 2009). We also report piston-cylinder and multi-anvil quench determinations of Fe_3C melting at lower pressures. We use these data to construct phase diagrams for the Fe–C binary at high pressures, and to assess the role of carbon-rich phases during core crystallization in Earth.

2. Experimental methods

High-pressure melting experiments were made in symmetric diamond anvils cells (DAC) using diamonds with 200–300 μm diameter culets. Samples were loaded into 80–130 μm holes drilled in stainless steel or rhenium gaskets pre-indented to ~50 μm thickness. In conjunction with the DAC experiments, several synthesis and melting experiments were made in piston-cylinder and multi-anvil apparatus at Lamont-Doherty Earth Observatory (LDEO), for which the details of the experimental methods can be found elsewhere (Dasgupta and Walker, 2008).

2.1. Fe_3C and Fe_7C_3 melting experiments

The Fe_3C starting material was synthesized from pure iron wire placed in a graphite capsule and held for 2 days at 2 GPa and 1473 K in a piston-cylinder apparatus. The Fe_7C_3 starting material was synthesized at 7 GPa and 1623 K for 7 min in a multi-anvil press using the same method as for the Fe_3C. Both syntheses were carried out at LDEO, and phase purity was confirmed for each by XRD and EPMA (Dasgupta and Walker, 2008). Starting materials were ground under ethanol in an agate mortar to produce a fine powder with a grain size of ~3 μm, and then compressed into a dense foil with a thickness of ~10–15 μm. Fragments of these foils were used as samples instead of loose powder to minimize sample deformation and thickness variations during compression. Starting materials were placed in an oven at 125 °C for at least 1 h before loading. The carbide foils were loaded into a gasket hole between thermal insulating layers to allow efficient heating of the sample, to minimize temperature gradients, and to act as the pressure medium. We used several kinds of insulators including single-crystal sapphire discs (125 μm in diameter and 15–20 μm thick),
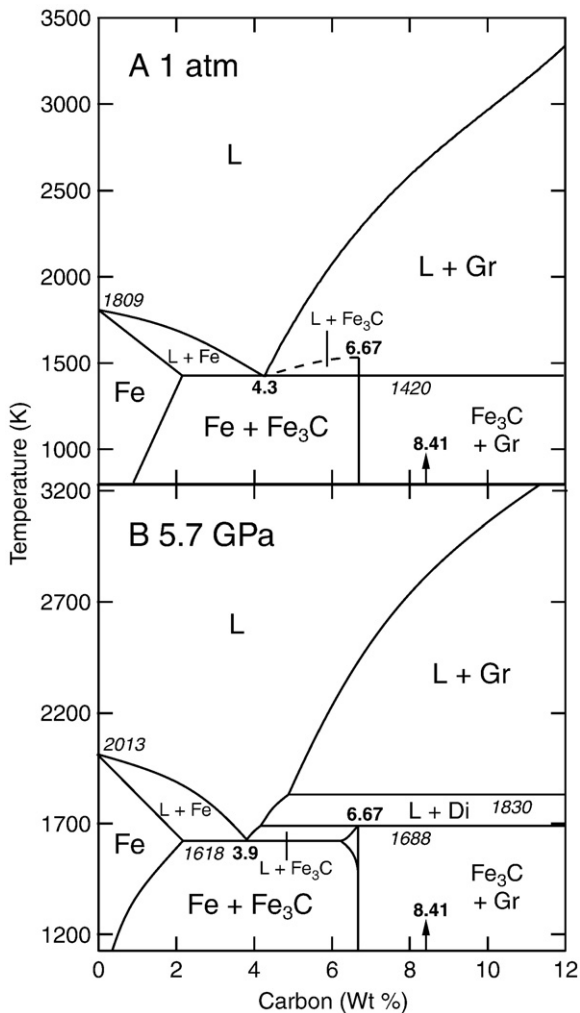

Fig. 1. The iron-rich portion of the Fe–C phase diagram at 1 atm after Chipman (1972) and at 5.7 GPa after Strong and Chrenko (1971). The dashed line in the 1 atm diagram indicates that the liquid + Fe_3C field is metastable. The arrow at 8.41 wt.% C indicates the location of Fe_7C_3, which does not become stable until higher pressure. L = liquid; Gr = graphite; Di = diamond.