Melting in the Fe-C system to 70 GPa

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Abstract

We determined high pressure melting curves for Fe$_3$C, Fe$_7$C$_3$ and the Fe–Fe$_3$C eutectic using laser-heated diamond anvil cell techniques. The principle 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$_3$C measured to 70 GPa has an apparent change in slope at ~8 GPa, which we attribute to stabilization of Fe$_7$C$_3$ at the solidus and the creation of a $P$-$T$ invariant point. We observe that Fe$_7$C$_3$ melts at higher temperatures than Fe$_3$C between 14 and 52 GPa and has a steep $P$-$T$ slope, and on this basis predict an expanding field of Fe$_7$C$_3$ + liquid with pressure. The Fe-Fe$_3$C 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$_3$C and Fe-Fe$_3$C eutectic melting curves indicate that Fe$_3$C is replaced at the solidus by Fe$_7$C$_3$ at ~120 GPa, forming another $P$-$T$ invariant point and a new eutectic between Fe and Fe$_7$C$_3$. Thus, Fe$_3$C is unlikely to be an important crystallizing phase at core conditions, whereas Fe$_7$C$_3$ could become an important crystallizing phase.

Keywords: Carbon; core; iron carbide; light element
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 (Alfè et al., 2004; Boehler, 1993; Luo and Ahrens, 2004; Ma et al., 2004; Shen et al., 1998), 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 (Dewaele et al., 2006; Dubrovinsky et al., 2000), 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; Badro et al., 2007; McDonough, 2003). 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 (Buffett et al., 2000; Chabot et al., 2006; Jana and Walker, 1997; Lister and Buffett, 1998; Walker, 2005). Although a great deal has been achieved in this area (e.g.: Li & 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)\textsubscript{3}C 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% (Dasgupta and Walker, 2008; McDonough, 2003) 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. Chipman, 1972; Strong and Chrenko, 1971), 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$_3$C (cementite), melts incongruently to liquid + graphite at about the eutectic temperature. At higher pressure (e.g. 5.7 GPa; Fig. 1b), Fe$_3$C melts in a peritectic reaction to form liquid + diamond, and a eutectic exists between Fe and Fe$_3$C. At higher pressures still another important compound, Fe$_7$C$_3$, 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$_3$C, 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$_3$C and a consequent expansion of the Fe$_3$C + liquid field. Wood (1993) also predicted that Fe$_3$C 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$_3$C, 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$_3$C (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$_3$C, calling the predicted phase relations into question. Further, the presence of Fe$_7$C$_3$, which becomes stable above 6 GPa (Shterenberg, 1975; Tsuzuki et al., 1984; Nakajima et al., in press), 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$_3$C, Fe$_7$C$_3$ and the Fe-Fe$_3$C 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$_3$C 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-indentend 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$_3$C and Fe$_7$C$_3$ Melting Experiments

The Fe$_3$C 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$_7$C$_3$ starting material was synthesized at 7 GPa and 1623 K for 7 minutes in a multi-anvil press using the same method as for the Fe$_3$C. 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 one hour before loading. The carbide foils were loaded into a gasket hole between thermal insulating layers to allow efficient heating of the sample, to minimise 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), dense foils of ruby powder (10-15 µm thick), sol gel deposited Al$_2$O$_3$, and NaCl. Dubrovinsky et al. (2001) observed the formation of Fe$_3$Al and an Fe-Al alloy when iron and Al$_2$O$_3$ were reacted in the LHDAC above 60 GPa, but we observe no such phases in our experiments in Al$_2$O$_3$ at similar conditions, based on synchrotron X-Ray Diffraction data. NaCl is preferred because it has a low shear strength, which promotes quasi-hydrostatic conditions in the sample chamber at high pressures and minimizes the pressure drop on heating caused by stress relaxation, but can only be used at higher pressures (e.g. > 40 GPa) where the NaCl melting curve rises above that of the samples (Boehler et al., 1997). A recent study by Rouquette et al. (2008) indicates that iron heated at 2700 K and 58 GPa in the LHDAC using NaCl insulators reacts to form Fe$_3$C, suggesting NaCl is not impervious to carbon diffusion. We see similar results in XRD analyses of quenched iron melting experiments using NaCl (but not Al$_2$O$_3$), though the amount of Fe$_3$C produced is very small. However, when different insulators are used over a similar pressure range, we find no resolvable dependence of melting temperatures on the pressure medium.
Melting experiments on Fe$_3$C were also carried out at 2 to 6 GPa using a piston cylinder (PC: 2±0.1 GPa: Dasgupta and Walker, 2008) and a Walker-style multi-anvil apparatus (MA: 5±0.5 and 6±0.5 GPa) at LDEO. All the experiments employed 1.5-2.0 mm long pure Fe wire of 1 mm diameter in graphite capsules as starting materials. The piston cylinder experiments used a standard ½” assembly with BaCO$_3$ pressure cell, graphite external heater, and crushable MgO spacers. The multi-anvil experiments were conducted using 8 mm truncation edge length WC cubes, castable MgO octahedral assemblies with LaCrO$_3$ heaters, and MgO spacers. Temperature during both the PC and the MA experiments was monitored using W$_{97}$Re$_3$/W$_{75}$Re$_{25}$ thermocouples placed against the capsule wall with uncertainties of ±10 K and ±15 K respectively. Polished sections of the quenched run products were studied by electron probe microanalysis.

2.2 Fe-Fe$_3$C Eutectic Melting Experiments

Eutectic melting experiments as well as in situ X-Radiographic imaging (XRI) experiments to determine the eutectic composition in the Fe-C system are made by melting at the boundary between spatially resolved ingredients of pure iron metal and Fe$_3$C (Walker, 2005; Walker et al., 2009). The following procedure is found to achieve a well defined and stable boundary even at high sample compression: (1) Pure hardened iron foil is indented in a DAC to ~15 GPa, which yields a metal thickness of ~20 µm. (2) The indented metal is then drilled with 50 µm holes, which are loaded with powdered Fe$_3$C and compressed until the material is sufficiently compacted to remain in place. (3) An ~100 µm diameter ‘donut’ consisting of the central plug of Fe$_3$C and a thin annulus of iron is then cut out using an UV laser. The donut with stuffing is then polished using 1 µm diamond-impregnated Mylar, cleaned under acetone and stored in an oven at 125°C until loading, typically between insulating muffins of sol gel bound Al$_2$O$_3$. The sample is then laser-heated at the boundary until first melting occurs as described in section 2.4.
2.3 Pressure measurement

Samples were compressed and pressure monitored using the ruby fluorescence scale as calibrated by Mao et al. (1986). Several ruby grains ~3–5 µm in diameter were placed within the sample chamber in early experiments, although we eventually opted for a thin layer of sub-micron ruby spread across the chamber in order to measure pressure exactly at the melted spot. Pressure was measured before and after melting. We assume that the post-melting pressure represents a minimum estimate of the pressure at melting, as no correction for thermal pressure has been made due to the uncertainty in its estimation. Samples were heated at subsolidus temperatures for several minutes before melting, which reduces considerably radial pressure gradients that can develop during initial compression. Measured pressure gradients across the sample chamber after melting, were generally less than ~1 GPa. Pressure losses of ~5 GPa due to annealing of stresses were observed in experiments using sol-gel Al₂O₃, compared to <2 GPa when using NaCl. The use of single-crystal sapphire resulted in a drastic pressure drop on annealing of ~10 GPa, and so it was abandoned as a pressure medium.

The biggest source of uncertainty in the reported pressures is the thermal pressure. Recent in situ melting experiments by Dewaele et al. (2007) using NaCl as a pressure medium indicate thermal pressures at melting of <3 GPa. However, because Al₂O₃ is much harder than NaCl, the thermal pressure in these experiments is likely to be greater and is a positive function of temperature, regardless of the medium employed. Therefore, while the pressures reported here have analytical uncertainties on the order of ±1-2 GPa it should be born in mind that these represent minima, underestimating the true pressure by perhaps 3-5 GPa.

2.4 Laser heating and temperature measurement

Samples were heated at pressure in a double-sided heating geometry using either a 50 W Nd:YLF CW infrared laser operating in TEM₀₁ mode, or a 100 W Nd:YAG CW multimode laser. This system produced stable heated spots with diameters of ~20–40 µm. The incandescent light
emitted from the sample was monitored using CCD cameras for visual observation on both sides. The temperature was raised in the sample by increasing the laser power in small increments (typically < 1 watt).

Temperatures were measured spectroradiometrically on one side using standard techniques employed at Bristol as described in detail elsewhere (Walter and Koga, 2004). In brief, a magnified image of the heated spot (20x) is focused onto the entrance slit (40 µm width) of an imaging spectrometer equipped with a 2-D CCD (e.g. 1024 x 256 pixels). We pre-align the system so that the image of the heated spot is centered on the slit. This allows sampling of a ‘one-dimensional’ temperature profile across the heated spot with a spatial resolution of ~2 µm² (see Supplemental Figure 1).

The precision of spectroradiometric temperature measurement is dependant upon the closeness of the fit of the measured spectrum to the Planck or Wien blackbody function (Heinz and Jeanloz, 1987; Kavner and Panero, 2004; Walter and Koga, 2004). Replicate analyses of the calibration lamp yield maximum instrumental precision in temperature measurement of ~0.1% relative (note that temperatures measured using the W lamp as an unknown are not subject to chromatic effects because the lamp is at constant temperature across the field of view).

Another potential source of uncertainty in both the precision and accuracy of measured temperatures is the chromatic dispersion introduced by the optical elements in the path to the spectrometer, which can have a large effect on calculated temperatures when a steep temperature gradient is present (Benedetti et al., 2007; Boehler, 2000; Walter and Koga, 2004). However, effective mitigation of chromatic effects can be achieved by placing an f-stop between the objective and focusing lens to sample only the near-paraxial rays that produce very little dispersion, and by choosing a wavelength range appropriate for the lens system (Benedetti et al., 2007; Walter and Koga, 2004). An example of fitted spectra and the resulting temperature profile across a laser-heated spot produced at optimum configuration is shown in Supplemental Figure 1. In our melting
experiments the precision in the fits to the Wien or Planck functions is typically in the range of 0.1-
0.4%, which indicates that chromatic effects are virtually eliminated.

To further assess the accuracy of our system we have measured the melting points of Pt, Nb, Mo, Ta, Re and W at 1 atm. A pure metal filament is resistively heated in an Ar gas chamber. Temperature is increased incrementally using a radiometric power supply, and is measured spectroradiometrically at the hot spot of the filament. When melting occurs, the filament breaks, and we estimate the melting temperature from the power-temperature path. Supplemental Figure 2 shows the results of replicate analyses of melting points for these metals. Relative to published melting data our results indicate a systematic overestimation of temperature by about 50 to 200 K for these metals. These differences may be a consequence of metal-specific deviations from wavelength independent emissivity (‘greybody’ behavior). We do not attempt to assign any formal uncertainty in accuracy to our measurements at this point, but caution that uncorrected deviations from greybody behavior will likely cause an overestimation in temperature of the order tens to a few hundred degrees K.

2.5 Melt detection

We rely on discontinuities in the temperature vs. laser power function to detect the onset of melting. During laser heating, when a sample reaches an invariant melting point, for example at a binary eutectic or peritectic, the temperature should plateau at the invariant temperature as the laser power provides the latent heat of melting. That is, increasing laser power serves only to increase the volume of melt rather than raise the temperature of the molten material, at least until a certain melt threshold is reached. We have observed that such melting discontinuities are easily and reproducibly detectible, and several typical examples are shown in Fig. 2. Figure 2a shows a common pathology in which peak temperature increases monotonically with laser current (i.e. power) until a threshold is reached, after which further power causes a temperature plateau with fluctuations often of the order ±50 K. In this particular case during heating of Fe₃C at 43 GPa, we
estimate the melting temperature by averaging over the points within the plateau, yielding 2650 K. The assigned uncertainty is derived to encompass the analytical precision in temperature measurement (usually 3-10 K), the position of the plateau (usually 10-50 K) and the temperature gradient within the heated spot (estimated at 40 K), in this case yielding a total of ± 98 K. Figure 2b shows another example in which a long plateau is reached after an initial temperature perturbation during heating at the junction of Fe-Fe₃C at 70 GPa. In this case we estimate melting at 2630 ± 40 K. A final and less common example is shown in Fig. 2c, in which a single, large temperature discontinuity occurs after a very systematic increase in temperature, and based on extrapolation we estimate melting at 2970 ± 55 K. We suggest that such large perturbations are related to the loss of the sample’s shear strength upon melting leading to a considerable change in sample absorption (as evidenced by holes in the sample foil after experiments in which this behaviour was observed), but consider this melting criterion less robust as such failure could be related to subsolidus softening. However, we have produced consistent melting points in replicate experiments in which both plateaus and extreme perturbations have been used as melting criteria.

As a means of validating our melting criteria we have measured the melting curves of Fe, Pt, FeS and Pb at pressures from 5 to 45 GPa (~1900 to 2600 K), and these data are compared to data from previous studies in Figure 3. Our melting curve for pure Fe closely matches the melting curve of Boehler (1993), which was determined in an LHDAC using visual identification of melt motion as a melting criterion. We also have acceptable correspondence with the data of Ringwood and Hibberson (1990) that is based on thermocouple temperature measurement in a large-volume apparatus. Overall our melting data show excellent consistency with previously measured melting curves in all cases (Boehler, 1992; Boehler, 1993; Dewaele et al., 2007; Kavner and Jeanloz, 1998). Further, we show below that where our new data overlaps most observations made in large volume apparatus we find good correspondence.
2.6 *Eutectic melt composition by X-radiography*

Determining the composition of a eutectic melt has thus far only been possible by ex situ analysis of quenched run products. However, due to the potential for exsolution of the light element from the melt during cooling, especially in slower quenching large-volume apparatus, re-integration of the melt composition is at best an uncertain task (O’Neill et al., 1998; Walker, 2005). Variation in quench rate among different-sized pressure cells may also contribute to error in measured melting curves (Walker, 2005). DAC experiments quench orders of magnitude more rapidly than large-volume experiments, but it is not clear whether exsolution can still cause problems in analysis. A compounding problem is the intrinsic difficulty in making accurate electron probe or TEM-EDX measurement of carbon in DAC samples. Clearly, an in situ method is preferable. For example, in the recent work of Seagle et al. (2008) the composition of liquids was bounded by in situ XRD determination of phase disappearance with temperature for particular bulk compositions. Another method for direct determination of liquid composition is to melt at the boundary between spatially resolved components (e.g. Fe and Fe$_3$C) and simultaneously measure the X-ray transmission through the sample. For a binary system, the transmissivity should be a simple function of density and, therefore, composition for samples of uniform thickness. By linear interpolation between the observed transmissivity of the pure solid end member compositions, the transmissivity of the molten regions can potentially yield the melt composition directly (Walker et al., 2009; Walker, 2005). Walker et al. (2009) tested this method in the system Fe-S where the change in eutectic melt compositions is well documented to ~30 GPa, and found excellent reproducibility of known results.

Fe-Fe$_3$C melting experiments were prepared as described above and were heated at beam-line 12.2.2 of the Advanced Light Source, which utilizes a double-sided heating similar to the Bristol system (Caldwell et al., 2007). Temperature measurement and melt detection was identical to the method described above. In all cases melting occurred within error of the melting curve constructed using the Bristol system. During the experiment the sample was bathed in a wide beam
of high energy X-rays (~18 KeV). Transmitted X-rays were then converted to visible light via a CdWO₄ phosphor, which was focused onto a high-resolution CCD camera. Images were taken before, during and after melting at each laser power increment with simultaneous temperature measurement. After acquisition, cross-sections through the images were taken normal to the boundary at the melting location, and the average transmissivity of solid Fe, solid Fe₃C and melt estimated. These values were then used to calculate the composition of the melt. For a detailed description of this technique, see Walker et al. (2009).

3. Results

3.1 The Fe₃C melting curve

Figure 4a shows our melting data for Fe₃C from both diamond anvil and large-volume press experiments (see Supplementary Table). In the piston-cylinder and multi-anvil experiments at 2, 5 and 6 GPa, melting was bracketed by textural analysis of quenched run products. Below the melting temperature, coarse crystalline Fe₃C was the sole phase present in graphite capsules, and above the melting point Fe₃C crystals coexisted with a quenched Fe-C melt, formed of dendritic iron and interstitial Fe₃C (see also Dasgupta and Walker, 2008). The carbon content of the quenched melt, near the Fe₃C out point was determined by EPMA and is 5.7 wt% at 2 GPa (Dasgupta and Walker, 2008), 5.7±0.1 wt% at 5 GPa, and 5.8±0.2 wt% at 6 GPa, which confirms a peritectic melting behavior of cementite to 6 GPa. Overall, our DAC melting determinations at similarly low pressures compare favorably with experiments in large volume apparatus (Fig 4b insert). The melting data have been fitted using the empirically derived Simon equation,

\[ T_m = \left( \frac{P_m}{A + 1} \right)^{1/C} \cdot T_0 \]

where \( T_m \) is the high-pressure melting point, \( T_0 \) is the ambient pressure melting point, \( P_m \) is the pressure at melting and the coefficients \( A \) and \( C \) are constants (Simon and Glatzel, 1929). This
equation is employed for convenience of extrapolation only, as it has no definite physical basis and is of doubtful applicability to an incongruently melting substance. A single, anomalously low melting point at 60 GPa has been omitted from the fit. The melting slope rises steeply up to ~10 GPa and then flattens off at higher pressures. The Simon fit smooths this transition, but the fit in the 10–30 GPa region is imperfect and suggests the possibility of a change in slope. We fitted the data using the Kraut-Kennedy equation (Kraut and Kennedy, 1966), which predicts a linear relationship between the melting temperature and the degree of isothermal compression,

\[ T_m = T_0 (1 + C \Delta V / V_0) \]

where \( \Delta V \) is the difference between the zero pressure volume, \( V_0 \), and the volume at the pressure of melting of the crystalline phase. The constant, \( C \), is equivalent to \( 2\gamma_{TH} - 2/3 \) where \( \gamma_{TH} \) is the thermal Grüneisen parameter (Hofmeister & Mao, 2003). As with the Simon equation, we employ this formulation for convenience. The absence of a definite physical basis for this form providing a meaningful proxy for pressure and its doubtful applicability to an incongruently melting compound, renders this convenience in making the point about the kink in slope in Fig. 4 at some sacrifice in theoretical purity. The high pressure volumes were calculated using a third order Birch-Murnaghan equation of state, with the parameters \( V_{0,483} \), \( K_{0,483} \) and \( K'_{0,483} \) taken from the ab initio calculations of Vocadlo et al. (2002) for the high temperature (>483 K) paramagnetic phase of Fe₃C relevant here. The results of this analysis are shown in Fig. 4c, and a break in slope in the region of 10 GPa is evident. This change in the melting slope likely corresponds to the required presence of two invariant points along the Fe₃C melting curve, one corresponding to the assemblage Fe₃C + graphite + diamond + liquid, and another corresponding to the assemblage Fe₃C + Fe₇C₃ + diamond + liquid. We describe these phase relations in more detail in the Discussion section below.

Above 10 GPa, our melting curve for Fe₃C is lower than that predicted by the thermodynamic calculations of Wood (1993), the discrepancy reaching ~900 K by 70 GPa. The
reason for the discrepancy between the calculated and measured melting curves may relate to the
magnetic transition in Fe$_3$C, which is a metallic ferromagnet at 1 atmosphere and 300 K (Tszuki et
al., 1984) but is paramagnetic above the Curie temperature of 483 K (Häglund et al., 1991). Several
studies have determined the pressure of this transition at 300 K: 25 GPa from X-ray Emission
Spectroscopy (Lin et al., 2004), 10 GPa from X-ray Circular Dichroism measurements (Duman et
al., 2005) and 4.3 – 6.5 GPa from Synchrotron Mössbauer Spectroscopy (Gao et al., 2008). Finally,
ab initio calculations predict this transition to occur above 60 GPa at 0 K (Vocadlo et al., 2002).
These studies also indicate considerable changes in thermoelastic properties across the transition.
For example, the 1 atm neutron diffraction data of Wood et al. (2004) show a distinct rise in the
coefficient of thermal expansion above the magnetic transition. At high temperatures and pressures,
the relevant phase is the non-magnetic form that has a higher bulk modulus and coefficient of
thermal expansion, which would tend to reduce the Fe$_3$C stability field. This seems the most likely
explanation for the substantial mismatch between the calculated melting temperatures of Wood
(1993) and the measured values presented here.

3.2 Fe-Fe$_3$C eutectic

Figure 5 shows the Fe-Fe$_3$C eutectic melting $P$-$T$ curve as determined using the ‘donut’
technique in the LH-DAC at Bristol and the ALS, fitted using the Simon equation (see
Supplemental Table). Data from both laser-heating systems agree closely, and our melting curve is
in excellent agreement with the multi-anvil quench data of Fei et al. (2007). At all pressures, the
data are slightly below the calculated values of Wood (1993) but within mutual error. Only the low-
pressure multi-anvil quench data of Hirayama et al. (1993) are anomalous relative to our melting
curve.

An example showing the temperature plateau behavior and demonstrating our ability to
produce a eutectic melt at the boundary between Fe and Fe$_3$C is shown in Fig. 6. Heating across the
boundary at subsolidus temperatures produces a bi-modal temperature profile with a high-
temperature peak on the Fe$_3$C side of the boundary, as this material heated preferentially to pure Fe.

Increased laser power resulted in an eventual plateau in the peak temperature on the Fe$_3$C side coincident with an increase in temperature on the Fe side. As power was increased further, the temperature on the Fe side rapidly caught up to that on the Fe$_3$C side, and a stable plateau formed across the boundary that was maintained upon further heating, which we interpret as the eutectic temperature. This example is also very informative because it was taken during X-radiographic imaging at beamline 12.2.2. The observed eutectic melting behaviour corresponds exactly with the emergence of the ledge shown on Fig. 7b as described below, giving us confidence in both the melting criterion and the interpretation of the ledge as a eutectic melt.

We have measured the composition of the eutectic liquid between 10 and 44 GPa using the X-radiographic imaging technique described briefly above and in detail in Walker et al. (2009). Figure 7 shows X-ray transmission cross-sections across the laser-heated spot for experiments at 10, 19 and 27 GPa. The first panel shows the precipitous drop in transmissivity across the boundary between the Fe$_3$C plug and iron annulus of the donut before heating. The second panel shows the formation of ledges of intermediate composition that formed at high temperature, representing the formation of a pool of eutectic liquid between the two components. Axial temperature gradients within the sample, probably on the order of 200 K (Campbell et al., 2007), may result in a non-cylindrical melt pool. This interleaving of melt and solid along the X-ray transmission direction may explain in part why the solid/liquid boundaries in the X-ray transmission cross-sections are not perfectly sharp. Linear interpolation of the transmissivity corresponding to the in situ ledges between the transmissivities of the end members yields compositions for the ledges, which are plotted for all experiments in Figure 8. The data show no statistically measurable change in the eutectic composition until ~20 GPa, at which point there is a rapid decrease in the eutectic composition to 37 GPa. An experiment carried out at 44 GPa failed to form a detectible ledge even though the melting point was reached and exceeded, which may indicate that the eutectic composition dropped below the detection limit of the technique (~0.6 wt%) as determined using the
method described in Walker et al. (2009). Our results are in good agreement with the multi-anvil quench data of Chabot et al. (2008) and Hirayama et al. (1993) to 12 GPa. Preliminary results of Fei et al. (2007) indicate little change or a slight reduction in eutectic C content to 20 GPa. The uncertainties in our results and those of Fei et al. (2007) (Fei, personal communication) are such that data from these two studies overlap.

The interpretation of the XRI data assumes that the intermediate ledge represents a eutectic liquid and not an Fe-C alloy produced by diffusion, and that the region of the transmission profile taken to represent pure Fe remains so. It is our contention that these assumptions are valid for three reasons: (1) Profiles across the heated region at sub-solidus temperatures show no change in shape compared to profiles taken at 300 K; (2) The observed ledges form immediately the temperature reaches the eutectic melting curve as determined from separate off-line experiments (described above; see figure 6) and do not evolve slowly with time as would be expected for diffusion; (3) The regions used to determine the end-member compositions to which the liquid is compared are well outside the heated region, and thus should not be subject to diffusion. On this basis, we believe the drop in the carbon content of the eutectic with pressure is real, and not the result of an increasing solubility of carbon in solid iron with pressure. Our confidence in the imaging technique is established by the successful determination of the pressure dependence of the composition of the eutectic in the Fe-S system, in which excellent agreement was found with the literature (Walker et al., 2009).

Wood (1993) predicted a rapid drop in eutectic carbon content with pressure, from 4.3 wt% C at 1 atm to 2.2 wt% C at 15 GPa. Extrapolation of that trend led Wood (1993) to predict a negligible carbon content at core relevant pressures. The decrease in eutectic composition we observe is similar to the prediction of Wood, although shifted to somewhat higher pressures. Chabot et al. (2008) and Hirayama et al. (1993) found no evidence for a change in the eutectic carbon content up to 5 GPa and 12 GPa respectively, consistent with our results. Fei et al. (2007) observed
no significant pressure dependence of the eutectic composition in multi-anvil experiments up to 20 GPa, within mutual error of our results.

3.2 Melting of Fe₇C₃

We measured the melting curve of Fe₇C₃ from 14 to 52 GPa (Fig. 5). The melting curve has a relatively steep slope compared to Fe₃C, such that by 50 GPa the melting point is about 500 K higher. In contrast, Wood (1993) predicted the two phases would have similar melting points at core conditions. Shterenberg et al. (1975) show that Fe₇C₃ melts incongruently to form diamond + liquid at 9 GPa and ~1950 K, eclipsing the Fe₃C melting temperature. The phase relations at 10 GPa shown by Nakajima et al. (in press) are consistent with this interpretation. Based on these observations we predict that in P-T space the Fe₇C₃ melting curve emerges from the Fe₃C melting curve at ~8 GPa from a P-T invariant point, as described below. We note, however, that while the temperature range of the Fe₇C₃ + liquid field determined here between 15 and 25 GPa is consistent with that measured using in situ XRD in the multi-anvil experiments of Nakajima et al. (in press), their absolute melting temperatures for both phases are considerably lower than those reported here (Fig. 4a). It is noteworthy that in the experiments of Nakajima et al. (2007) iron was loaded into graphite capsules, with no control on the system bulk composition during the experiment (i.e. the capsule becomes part of the system). This conceivably provides an explanation for why the melting temperatures for Fe₃C of Nakajima et al. (in press) coincide so closely with the eutectic temperatures determined in the this study using the LHDAC and in the multi-anvil study of Fei et al. (2007). As already mentioned, our own piston cylinder and multi-anvil experiments closely corroborate our Fe₃C melting temperatures determined in the LHDAC.
4. Discussion

4.1 The Fe-C system at high pressure

The data presented above are used to construct temperature-composition phase diagrams for
the iron-rich portion of the Fe-C system from 5 to 130 GPa, shown in Figure 9. Phase relations for
the composition Fe$_3$C are summarized in a pressure-temperature isopleth in Figure 10.

At 5 GPa, Fe$_3$C melts incongruently to liquid + graphite at a temperature about 270 K above
the Fe-Fe$_3$C eutectic (Fig. 9a). The shape of the liquidus is constrained by the eutectic composition,
which is unchanged from its one atmosphere composition at this modest pressure (Chabot et al.,
2008), and the measured composition of the peritectic liquid. It is possible that Fe$_7$C$_3$ is stable in the
subsolidus at this pressure, breaking down to Fe$_3$C + graphite, as shown schematically. At slightly
higher pressure graphite transforms to diamond, as shown in Fig. 1b (Strong and Chrenko, 1971),
forming another liquidus invariant point at higher temperature. The intersection of the Gr + liquid to
Di + liquid curve with the Fe$_3$C melting curve forms an invariant point in $P$-$T$ space where four
phases coexist (Fe$_3$C, Gr, Di, and liquid), and this is denoted as I1 in Fig. 10. Between 5 and 10
GPa Fe$_7$C$_3$ stabilizes and its melting temperature reaches that of Fe$_3$C, which corresponds to another
invariant point in $P$-$T$ space (point I2 in Fig. 10; See Supplemental Fig. 3a) where Fe$_3$C, Fe$_7$C$_3$, Di,
and liquid coexist. We estimate the position of invariant point I2 at ~8 GPa. At pressures higher
than 8 GPa the Fe$_7$C$_3$ melting point exceeds that of Fe$_3$C, creating a new peritectic reaction where
Fe$_3$C melts to form Fe$_7$C$_3$ + liquid (Fig. 9b). We show this peritectic at 10 GPa (Fig. 9b) and place
the peritectic composition between Fe$_3$C and Fe$_7$C$_3$, in accordance with the topology of Shterenberg
et al. (1975). We preserve this general topology for Fe$_7$C$_3$ melting at higher pressures in the absence
of further constraints. Overall, the topologies of phase relations in the pressure region of 5 to 10
GPa are drawn to be consistent in form with previous results (Nakajima et al., in press; Shterenberg
et al., 1975; Strong and Chrenko, 1971; Tsuzuki et al., 1984).

We note that the position of invariant point I2 in Fig. 10 (~8 GPa) corresponds well with the
inflection in the Fe$_3$C melting curve interpreted on the basis of the Kraut-Kennedy fits shown in
Fig. 4b. We speculate that this occurs because of the change in phase relations brought about by the emergence of Fe$_7$C$_3$ at the solidus, and a subsequent expansion of the Fe$_7$C$_3$ + liquid field with pressure as shown at 50 GPa in Fig. 9c. At 50 GPa the Fe$_7$C$_3$ melting point is about 500 K above that of Fe$_3$C, and we show an expansion of the Fe$_7$C$_3$ + liquid field and also infer a shift in Fe$_3$C peritectic melt composition to lower carbon contents. If true, this expansion of the Fe$_7$C$_3$ + liquid field necessitates that the change in partial molar volume of carbon in going from Fe$_7$C$_3$ to melt is positive. We also show that by 50 GPa the composition of the eutectic between Fe and Fe$_3$C is at less than 1 wt% carbon, as constrained by in situ measurements.

The Fe$_3$C and Fe–Fe$_3$C eutectic melting curves apparently converge at about 1.2 Mbar based on extrapolation of the Simon curves. The convergence of the Fe–Fe$_3$C eutectic with the Fe$_3$C → Fe$_7$C$_3$ + liquid peritectic may occur because the melting point of pure Fe increases at a faster rate than does Fe$_3$C, eventually resulting in the breakdown of Fe$_3$C to Fe + Fe$_7$C$_3$ in the subsolidus. In $P$-$T$ space this reflects another invariant point where the subsolidus reaction intersects the Fe$_3$C melting curve at which four phases coexist (Fe, Fe$_3$C, Fe$_7$C$_3$ and liquid), shown as I3 in Fig. 10 (See supplemental Fig. 3b). At pressures above the invariant point a new eutectic would form between Fe and Fe$_7$C$_3$, as shown in Fig. 9d. The composition of the eutectic is impossible to predict reliably but could be richer in carbon than the carbon-poor Fe–Fe$_3$C eutectic it replaces, with important implications for crystallization of Earth’s inner core.

4.2 Constraints on Earth’s Core

Although the Earth’s metallic core is unlikely to be a binary Fe-C alloy, binary phase relations can be instructive as to the nature of phases that might have crystallized in the solid inner core, as well as to the relative concentration of carbon in the liquid outer core. For example, Wood (1993) predicted that Fe$_3$C would melt congruently at 136 GPa, and that the Fe–Fe$_3$C eutectic composition would be nearly pure Fe. On this basis Wood suggested that the inner core might have crystallized an Fe$_3$C phase, resulting in an outer core that would become carbon depleted as the
inner core crystallized, and predicted an inner core density that matches closely constraints from seismology. Vocadlo et al. (2002), however, have convincingly showed on the basis of new elastic parameters that nonmagnetic Fe$_3$C would have too low a density to match the inner core. Further, Fiquet et al. (2009) have measured $V_p$ in Fe$_3$C to 83 GPa and found it to be too high to match the inner core. Indeed the authors estimate that the inner core can contain only $\sim$1wt % carbon to satisfy both the density and compressional wave velocity predicted by PREM. Using a similar technique, Gao et al. (2008) determined both $V_s$ and $V_p$ up to 50 GPa, and found both to be larger than PREM after extrapolation to core conditions, ruling out Fe$_3$C as a sole inner core phase, though the authors suggest some lesser amount of carbon as an excellent candidate for reconciling the sound velocity and density of Fe-Ni alloys with the measured values in the inner core.

Similar to the model of Wood (1993), we also find that the Fe-Fe$_3$C eutectic moves to nearly pure Fe at high pressures. However, Wood has a steep $P$-$T$ slope for the Fe$_3$C melting curve, which results in congruent melting of Fe$_3$C at core pressures, effectively eliminating a role for Fe$_7$C$_3$. In contrast, our phase relations, as well as those of Shterenberg et al. (1975) and Nakajima et al. (in press), suggest an important role for Fe$_7$C$_3$ in the Fe-rich region of the phase diagram at high pressures. Our results indicate that the melting point of Fe$_7$C$_3$ rapidly diverges from Fe$_3$C at high pressure, and that the Fe$_3$C and eutectic melting curves converge (Fig. 10). These features conspire to eliminate Fe$_3$C at the solidus, with replacement by Fe$_7$C$_3$ (Fig. 9d). Thus, the important point for understanding the carbon partitioning between Earth’s inner and outer core is the carbon content of the eutectic formed between Fe and Fe$_7$C$_3$, as this together with the bulk core carbon content will control the nature of the crystallizing phase in Earth’s core.

The carbon content of Earth during core formation is poorly constrained, but likely is in the range of 0.2 to 4 wt.%. If the predicted eutectic between Fe and Fe$_7$C$_3$ were close to pure iron, then we would expect that for much of the predicted range of core carbon contents the inner core would crystallize an Fe$_7$C$_3$ phase (Nakajima et al., in press). Little is known about the thermoelasticity of this phase at core conditions, but we can predict that given its higher carbon content Fe$_7$C$_3$ might
provide a poor match for Earth’s inner core, at least as a sole crystallizing phase. Conversely, if the
Fe–Fe$_7$C$_3$ eutectic is at moderate carbon contents as drawn in Fig. 9d, then the core could crystallize
a carbon-poor Fe phase, with the carbon content in the outer core increasing as crystallization
proceeds. In this case effectively all the core’s carbon budget would reside in the liquid outer core.

5. Conclusions

We have measured the melting curves of Fe$_3$C, Fe$_7$C$_3$, and the Fe-Fe$_3$C eutectic up to ~70
GPa. We find a change in slope of the Fe$_3$C melting curve at ~8 GPa that corresponds with the
emergence of Fe$_7$C$_3$ at the solidus and the creation of a $P$-$T$ invariant point. At pressures below the
invariant point our Fe$_3$C melting curve is consistent with that predicted from thermodynamic
calculations (Wood, 1993), but at pressures higher than the invariant point our melting curve
flattens and by 70 GPa is ~1000 K below that of Wood (1993). In contrast to Fe$_3$C, we find a steep
$P$-$T$ slope for the Fe$_7$C$_3$ melting curve, and on this basis predict an expanding field of Fe$_7$C$_3$ + liquid
with pressure. Our measurements of the Fe-Fe$_3$C eutectic temperature are in close agreement with
the multi-anvil data of Fei et al. (2007) and to the thermodynamic calculations of Wood (1993). The
eutectic composition, measured in situ using a novel X-radiographic imaging technique, drops
rapidly with pressure, generally consistent with the prediction of Wood (1993), and has a
composition with less than 1% carbon by ~50 GPa. The resulting phase relations, though requiring
significant extrapolation to core pressures, suggest that Fe$_3$C will be replaced at the solidus by
Fe$_7$C$_3$ at ~120 GPa, thereby forming a new eutectic between Fe and Fe$_7$C$_3$. Until phase relations are
determined at megabar pressures and beyond we can only speculate regarding the nature of a
carbon-bearing phase that might be crystallizing in the inner core. For Fe$_7$C$_3$ to crystallize in the
inner core the proposed eutectic between Fe and Fe$_7$C$_3$ would have to be at a composition poorer in
carbon than the bulk core carbon content. We speculate that the opposite case is also possible, and
that the core carbon content is on the carbon-poor side of the eutectic such that carbon is expelled
nearly wholesale to the liquid outer core.
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Figure Captions

Fig. 1. The iron rich portion of the Fe-C phase diagram at 1 atmosphere after Chipman (1972) and at 5.7 GPa after Strong and Chrenko (1971). The dashed line in the 1 atmosphere diagram indicates that the liquid + Fe$_3$C field is metastable. The arrow at 8.41 wt% C indicates the location of Fe$_7$C$_3$, which does not become stable until higher pressure. L = liquid; Gr = graphite; Di = diamond.

Fig. 2. Typical power vs. temperature functions from Fe$_3$C melting experiments. (a-b) In these two cases the temperature plateaus with increasing power, and the melting point is taken as the average of the points within the plateau, while the error bars represent their standard deviation. (c) In this less common example, the temperature drops suddenly on melting. Here, a linear fit to the power vs. temperature function is extrapolated to the next acquisition. The melting temperature is taken as the center point between this and the previous measured temperature, with the uncertainty encompassing the two points. Within each experiment, care was taken to ensure the time between acquisitions remained constant, and is on the order 5-20 seconds in most experiments. Uncertainty due to the precision of temperature measurement is smaller than the symbol size in all cases. Each acquisition number (x-axis) represents an increase in laser current; the increments are equal, and so the axis is simply a proxy for power, which was not directly measured.

Fig. 3. Melting data for FeS (open diamonds), Fe (open squares), Pt (open circles) and Pb (open triangles) using our laser DAC, temperature measurement techniques and melting criteria. Our data is compared to literature melting data as a test of consistency. Solid line, DAC melting data for FeS from Boehler (1992); filled squares, multi anvil melting point of iron from Ringwood and Hibberson (1990); short dashed line, DAC melting data for Fe from Boehler (1993); dotted line, DAC melting data for Pt from Kavner and Jeanloz, (1998) and long dashed line, DAC melting data for Pb from Dewaele et al. (2007).
Fig. 4. The Fe₃C melting curve. (a) Melting temperatures from DAC laser heating experiments (open circles, Bristol; closed circles, ALS) and melting brackets from piston cylinder and multi-anvil quench experiments (closed triangles) are shown. The solid line is a fit to the data, excluding the anomalously low point at 60 GPa, using the empirically derived Simon equation, and the dotted line indicates the Fe₃C melting curve from the thermodynamic calculations of Wood (1993). The long dashed line represents the multi-anvil melting data of Nakajima et al. (in press). The inset (b) shows the low-pressure region of the melting curve from (a) expanded for clarity, illustrating the close agreement between DAC and large volume press melting data. The 2 GPa piston cylinder data were previously reported in Dasgupta and Walker (2008), and along with the multi-anvil data at 5 and 6 GPa have uncertainties in temperature and pressure much smaller than the symbol size. (c) Melting data plotted against isothermal compression of the paramagnetic phase of Fe₃C. The compression has been calculated using a 3rd order Birch-Murnaghan Equation of State and the calculated parameters V₀,483, K₀,483 and K′₀,483 taken from Vocadlo et al. (2002). The solid lines are fits to the data using the Kraut-Kennedy equation (Kraut and Kennedy, 1966). The low pressure curve was fitted to the black circles, the high pressure curve to the white ones, while the grey symbols were included in both fits. Note the inflexion around a compression value of 0.03. We interpret this as possibly representing a change in the peritectic melting reaction from Fe₃C $\rightarrow$ liquid + diamond to Fe₃C $\rightarrow$ liquid + Fe₇C₃, which also produces an invariant point in P-T space (~8 GPa). The grey region represents an estimate of uncertainty on the position of this invariant point.

Fig. 5. Melting curves of Fe₇C₃ and the Fe-Fe₃C eutectic. The eutectic melting curve is determined from LH-DAC experiments using the ‘donut’ technique for melting at a boundary between spatially resolved ingredients (open circles, Bristol; closed circles, ALS). The data are fitted to a Simon equation (solid line). The dotted line is the calculated eutectic curve of Wood (1993), the dashed line is a linear fit to the multi anvil quench data of Fei et al. (2007), and the dash-dot line a linear fit
to the data of Hirayama et al. (1993). The solid squares show melting determinations for Fe$_7$C$_3$, which have been fitted with a Simon equation.

Fig. 6. Sequence of temperature profiles acquired during heating at the boundary between Fe and Fe$_3$C, with an approximate boundary denoted by the dashed line. At first the temperature in the Fe$_3$C is higher than the iron, as it more readily absorbs the laser radiation (lightest grey line). As laser power is increased the temperature rises and then plateaus around 1900 K, indicating melting has occurred. Simultaneously, the temperature of the Fe rises, until it equalizes with the Fe$_3$C temperature, suggesting the formation of a homogenous melt pool at the boundary. These data were acquired simultaneously with X-radiographic images of the boundary region, which show the formation of the melt (see figure 7b).

Fig. 7. Examples of cross sections from X-radiographic images of Fe-Fe$_3$C ‘donuts’ used to determine eutectic composition. The left hand panel in each case shows the initial boundary at 300 K before laser heating. The X-ray transmissivity is higher on the left (the Fe$_3$C) than the right (the Fe) (a) 10 GPa: In the right hand panel, during in situ laser heating, a small but well-defined ledge has formed, representing the presence of a eutectic melt. (b) 19 GPa: The ledge in the example formed at 1875 K, simultaneously with a plateau in the measured temperature (see figure 6). The contrast between the iron and Fe$_3$C is larger in this example than the others, because the exposure time was longer. (c) 27 GPa: In this case, the ledge formed at 2160 K. For the sake of clarity, in each panel the y-axis scaling has been altered so that the positions of the lines representing the transmissivity of Fe and Fe$_3$C line up across the diagram.

Fig. 8. The pressure dependence of the Fe-Fe$_3$C eutectic as determined by in situ LH-DAC X-radiographic imaging. Error bars represent the estimated uncertainty in finding the plateau position, except where this is smaller than the uncertainty due to the detection limit. The filled diamond
represents an experiment at 44 GPa which yielded no ledge during heating, suggesting the solubility
may have dropped to less than the detection limit; the error bar encompasses the noise within the Fe
baseline where a plateau might be hidden. The open circles and open square represent the multi-
anvil quench data of Hirayama et al. (1993) and Chabot et al. (2008), respectively. The filled square
indicates the 1 atmosphere eutectic from Chipman (1972).

Fig. 9. The Fe-rich portion of the Fe-C phase diagram at 5, 10, 50 and 130 GPa, inferred from
measurements of the melting curves of Fe$_7$C, Fe$_7$C$_3$ and the Fe-Fe$_7$C eutectic, as well as eutectic
compositions determined from X-radiographic imaging experiments. The melting curve of iron is
from Shen et al. (1998; 2004). L, liquid; Gr, graphite; Di, diamond; Values in italics represent
melting temperatures and those in bold represent compositions. Dashed lines are used where the
phase relations are inferred.

Fig. 10. Pressure-temperature phase diagram for Fe$_7$C (the Fe-Fe$_7$C melting curve is also shown as
grey line). Construction and symbols as in Figure 9. Filled circles represent $P$-$T$ invariant points.
Point I1 represents the intersection of the graphite + liquid to diamond + liquid curve with the Fe$_7$C
melting curve. Point I2 represents a change in the Fe$_7$C peritectic reaction products from diamond +
liquid below ~8 GPa to Fe$_7$C$_3$ + liquid at higher pressures. Point I3 represents the predicted
intersection between the Fe$_7$C and Fe-Fe$_7$C melting curves, at which point a new $P$-$T$ invariant
forms that also corresponds to the elimination of Fe$_7$C at the solidus (also shown as a dashed line is
a subsolidus univariant reaction where Fe$_7$C breaks down to Fe + Fe$_7$C$_3$). At pressures higher than
point I3, Fe$_7$C composition melts at a new eutectic between Fe and Fe$_7$C$_3$. The graphite to diamond
transition is after Bundy et al. (1994).

Supplemental Fig. 1. A typical spectroradiometric temperature measurement for Fe$_7$C$_3$ at 52 GPa in
the laser heated diamond cell. (a) Normalised intensity ($J$) vs. normalized wavelength ($\omega$), where
$c_1 = 2hc^2$ and $c_2 = hc/k$ (c, speed of light; $h$, Planck’s constant; $k$, Boltzman’s constant). Each curve represents the system response to the incandescent light emitted from a region along a transect across the laser heated spot, fitted using the Wien approximation. (b) A fit to each wavelength-intensity spectrum yields a temperature, which is used to produce a cross-section. The fitting error averaged over all points in the profile is 5.6 K. For a melting determination, the peak temperature is used, which in this case is 3280 K. Fitting the data using the Wien approximation (solid line) and Planck function (dashed line) yield temperatures which deviate by only ~20 K at ~3300 K.

Supplemental Fig. 2. Determination of metal melting points at 1 atm using resistance heating and spectroradiometry. The filled circles represent replicate analyses except for Nb and Ta, which represent a single analysis. The solid line indicates the expected 1:1 correspondence between known and measured melting points. In all cases the symbol size is larger than the error bars. The markers on the right hand y-axis indicate the melting points as derived from the literature (Weast et al., 1985).

Supplemental Fig. 3. The phase reaction topology around invariant points I2 and I3 in Figure 10. Di, diamond; L, liquid. Solid lines are univariant equilibria and dashed lines are their metastable extensions. The phase in parentheses labeling each univariant curve is the ‘phase out’ in the given reaction.
Figure 1
Figure 2

![Graph showing temperature changes with acquisition number and laser power](image)

- **A**: Fe$_3$C (43 GPa)
- **B**: Fe-Fe$_3$C (70 GPa)
- **C**: Fe$_3$C (70 GPa)

Temperature (K) vs Acquisition No. with Increasing Laser Power
Figure 3
Figure 4

![Graph showing temperature vs. pressure and isothermal compression](image)

- Panel A: Temperature (K) vs. Pressure (GPa) with data points and trend lines.
- Panel B: Inset showing the pressure range 0 to 8 GPa.
- Panel C: Temperature (K) vs. Isothermal Compression ($\Delta V/V_0$) with a shaded area indicating the pressure range of 7 to 12 GPa.
Figure 5

[Graph showing temperature vs. pressure with different phases identified: Fe₃C, FeC, and Fe-Fe₃C Eutectic]
Figure 6
Figure 7

[A graph showing three sets of data labeled A, B, and C, indicating before and during heating at 10 GPa, 19 GPa, and 27 GPa, respectively. Each set is divided into 'Before heating' and 'During heating' sections. The graphs display changes in X-ray counts (x10^5) against pixels. The data points indicate the percentage change in carbon content: 4.4±0.4 wt% C, 3.7±0.3 wt% C, and 2.3±0.5 wt% C at 10 GPa, 19 GPa, and 27 GPa, respectively.]
Figure 8

![Graph showing the relationship between Composition (Wt% C) and Pressure (GPa). The graph includes data points with error bars.]
Figure 10

![Diagram showing temperature vs. pressure phase transitions for iron-carbon system.](image-url)
Supplemental Figure 1

A

\[ J = \ln(\lambda e^{-1}) \]

\[ \omega = c_2 \lambda^{-1} (x10^3) \]

B

Temperature (K)

Distance (\(\mu m\))
Supplemental Figure 2
A: Invariant I2

(Fe\textsubscript{3}C) \quad Fe\textsubscript{7}C\textsubscript{3} = L + Di

(Di) \quad Fe\textsubscript{3}C = Fe\textsubscript{7}C\textsubscript{3} + L

(L) \quad Fe\textsubscript{3}C + Di = Fe\textsubscript{7}C\textsubscript{3}

(Fe\textsubscript{7}C\textsubscript{3}) \quad Fe\textsubscript{3}C = L + Di

B: Invariant I3

(Fe\textsubscript{3}C) \quad Fe + Fe\textsubscript{7}C\textsubscript{3} = L

(Fe) \quad Fe\textsubscript{3}C = Fe\textsubscript{7}C\textsubscript{3} + L

(L) \quad Fe\textsubscript{3}C = Fe + Fe\textsubscript{7}C\textsubscript{3}

(Fe\textsubscript{7}C\textsubscript{3}) \quad Fe + Fe\textsubscript{3}C = L
Table 1: Experimental run conditions

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*Data points RD3 (piston cylinder), MA1 and MA2 (multi-anvil) each represent the center point of a bracket, and are not single experiments. See section 3.1 of the main text for details.