Equation of State and Phase Diagram of Fe-16Si Alloy as a Candidate Component of Earth’s Core

Rebecca A. Fischer¹,*, Andrew J. Campbell¹, Razvan Caracas², Daniel M. Reaman¹, Przmyslaw Dera³, and Vitali B. Prakapenka³

¹Department of the Geophysical Sciences, University of Chicago, 5734 S Ellis Ave, Chicago, IL 60637, USA
²Centre National de la Recherche Scientifique, Laboratoire de Sciences de la Terre, Ecole Normale Supérieure de Lyon, 46, allee d’Italie, 69364 Lyon cedex 07, France
³GeoSoilEnviroCARS, University of Chicago, 5640 S Ellis Ave, Chicago, IL 60637, USA

*Corresponding author. Phone: 773.834.1085. Email: rfischer@uchicago.edu

Abstract

The outer core of the Earth contains several weight percent of one or more unknown light elements, which may include silicon. Therefore it is critical to understand the high pressure-temperature properties and behavior of an iron-silicon alloy with a geophysically relevant composition (16 wt% silicon). We experimentally determined the melting curve, subsolidus phase diagram, and equations of state of all phases of Fe-16wt%Si to 140 GPa, finding a conversion from the D0₃ crystal structure to a B2+hcp mixture at high pressures. The melting curve implies that 3520 K is a minimum temperature for the Earth’s outer core, if it consists solely of Fe-Si alloy, and that the eutectic composition in the Fe-Si system is less than 16 wt%
silicon at core-mantle boundary conditions. Comparing our new equation of state to that of iron and the density of the core, we find that for an Fe-Ni-Si outer core, 11.3 ± 1.5 wt% silicon would be required to match the core’s observed density at the core-mantle boundary. We have also performed first-principles calculations of the equations of state of Fe$_3$Si with the D0$_3$ structure, hcp iron, and FeSi with the B2 structure using density-functional theory.

Keywords: Earth’s core, equation of state, phase diagram, iron alloys

1. Introduction

The Earth’s core is comprised mostly of iron, with some nickel, and several weight percent of one or more light elements (Birch, 1952). Candidates for this light element component include silicon, oxygen, sulfur, carbon, and hydrogen (e.g. McDonough, 2003). There is evidence that silicon is present in the core to at least some degree, and it may be the dominant light element. For example, silicon is known to partition into iron under reducing conditions, it is found in the metal of some enstatite chondrites, and silicon in the core is permitted by comparisons of Mg/Si and Fe/Si ratios between the Earth and chondrites (Allègre et al., 1995; McDonough, 2003). Silicon partitioning into the core may explain the difference between $^{30}$Si/$^{28}$Si ratios in terrestrial rocks versus meteorites (Fitoussi et al., 2009; Georg et al., 2007; Shahar et al., 2009). Experimental studies have demonstrated the ability of silicon to partition into liquid iron metal at high pressures (e.g. Knittle and Jeanloz, 1991; Ozawa et al., 2009; Takafuji et al., 2005), though this may require very reducing conditions (Malavergne et al.,
Estimates of the maximum silicon content of the core vary widely, from ~6-7 wt% (Allègre et al., 1995; Javoy et al., 2010; McDonough, 2003; Shahar et al., 2009) to 8-11 wt% (Lin et al., 2003; Ricolleau et al., 2011) to up to 20 wt% (Balchan and Cowan, 1966; Ringwood, 1959), if silicon is the dominant light element.

If silicon is a primary light element component in the core, its impact on the density of iron-rich melts is vital to interpretation of the composition, dynamics, and evolution of the core. Knowledge of its melting curve and phase relations can be used to constrain the thermal structure of the core and crystal structure of the inner core. Therefore, it is critical to understand the high pressure, high temperature phase relations, melting curve, and thermodynamics of the Fe-Si system. In this study, we focus on the equations of state and phase diagram of Fe-16wt%Si (hereafter Fe-16Si). This information can be compared to the Preliminary Reference Earth Model (PREM), a seismologically determined model of the Earth’s density structure (Dziewonski and Anderson, 1981), to evaluate its importance as a core component. The composition we investigated is within the range expected for the Earth’s core, but its high P-T phase diagram has not been established. Additionally, thermal equations of state of iron-silicon alloys to high pressures have not been the subject of any recent studies. By determining the equation of state of Fe-16Si, the results from this study will allow us to constrain the amount of silicon needed to match the core density deficit.

Fe-16Si is close to stoichiometric Fe$_3$Si, or suessite (Keil et al., 1982). Alloys with similar compositions have been the subjects of several previous studies using varying methods. Yu and Secco (2008) investigated the equation of state of liquid alloy containing 17 wt% Si to 12 GPa using the sink/float technique, while Lin et al. (2003) and Hirao et al. (2004) performed static compression on solid Fe-17Si and Fe-18Si, respectively, at room temperature. Zhang and Guyot
(1999) studied Fe-17Si in a large volume press. Asanuma et al. (2010) measured the melting curve of Fe-18Si to 119 GPa, and Morard et al. (2011) determined the melting curve of Fe-5Ni-15Si to 80 GPa. Moroni et al. (1999) calculated an equation of state of Fe$_3$Si using density-functional calculations based on ultrasoft pseudopotentials and all-electron methods. Fe$_3$Si was predicted to have the D0$_3$ (Strukturbericht designation), or BiF$_3$-type, crystal structure at ambient conditions using LSDA methods (Christensen et al., 2008; Rhee, 2004). The one bar lattice parameter of Fe$_3$Si has been predicted by Christensen et al. (2008) and Rhee (2004), and measured by Mishra et al. (1985). The one bar phase diagram in the Fe-FeSi system at high temperatures was reported by Massalski (1986). Kuwayama and Hirose (2004) studied phase relations in the Fe-FeSi system at 21 GPa, finding a eutectic point at 26 wt% Si and ~2100 K. Detailed theoretical analyses of the same system were performed by Zhang and Oganov (2010) and Côté et al. (2008), suggesting that silicon may stabilize the bcc structure in iron.

In this study, we determine the subsolidus phase diagram of Fe-16Si at high pressures and temperatures using synchrotron X-ray diffraction in a laser-heated diamond anvil cell. We measure its melting curve by looking for diffuse scattering in the diffraction patterns, and determine which phase is stable on the liquidus. We also determine the equations of state of all phases up to pressures of the Earth’s outer core, by measuring the volumes of our samples under pressure by X-ray diffraction or calculating sample volumes using density functional theory. This allows for calculation of the amount of silicon required to match the observed core density deficit.

2. Methods
The starting material was Fe-Si alloy containing 15.9 wt% silicon (Fe_{0.73}Si_{0.27} by mole), based on electron microprobe measurements performed at the University of Maryland, and was found to be chemically homogeneous (Miller, 2009). The material was obtained from Keokuk Electro-Metals Company. The powder, with initial grain size ~5-20 µm, was pressed in a diamond anvil cell to form a foil approximately 3-5 µm thick. Gaskets, initially 250 µm thick, were made of rhenium or stainless steel and were preindented to ~27 GPa or ~18 GPa, respectively. A hole 50-120 µm in diameter was drilled in the center of the indentation to form the sample chamber. Diamond anvils used had 300 or 400 µm culets, or they were beveled, with 120, 150, or 250 µm flats and an 8° bevel out to 300 µm. For high temperature experiments, the sample was loaded between two layers of KBr ~10 µm thick, which served as the pressure medium, pressure standard, and thermal insulator (Campbell et al., in prep). The sample assembly was oven-dried at 85°C for approximately one hour prior to compression. For 300 K experiments, the sample was loaded as a loose powder with a few grains of KBr and ruby to serve as pressure standards (Campbell et al., in prep; Mao et al., 1986), then neon was loaded into the sample chamber as a pressurized gas to serve as the hydrostatic pressure medium using the COMPRES/GSECARS gas-loading system at the Advanced Photon Source (APS), Argonne National Laboratory (Rivers et al., 2008).

Laser-heating experiments were performed with angle-dispersive X-ray diffraction at beamline 13-ID-D (GeoSoilEnviroCARS) of the APS (Prakapenka et al., 2008; Shen et al., 2005). Room temperature experiments were performed with angle-dispersive X-ray diffraction at beamline 12.2.2 of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (Kunz et al., 2005), and beamline X17C of the National Synchrotron Light Source (NSLS),
Brookhaven National Laboratory (Hu et al., 2006). Incident X-ray beams were monochromatic, and sample-to-detector distances were calibrated by 1 bar diffraction of CeO$_2$ (APS and NSLS) or LaB$_6$ (ALS). At the APS, $\lambda=0.3344$ Å, and the incident X-ray beam measured ~3 µm x 4 µm (FWHM). Diffraeted X-rays were recorded using a MAR165 detector, with typical exposure times of 5 seconds. At the ALS, $\lambda=0.41323$ Å, and a MAR345 image plate or Bruker CCD detector was used. The incident beam measured 30 µm x 30 µm, and exposures were typically 20 seconds. At the NSLS, $\lambda=0.37677$ Å, and the incident beam was 26 µm x 25 µm. A Fuji image plate was used, with typical exposure times of 5 minutes.

The X-ray diffraction patterns were integrated to produce 20 plots using Fit2D (Hammersley et al., 1996). Peak fitting of the integrated patterns was performed using PeakFit (Systat Software). Overlapping peaks were resolved in nearly all cases, and were not used in lattice parameter calculations if they could not be separated. Pressures were determined from the volume of B$_2$-KBr, using the thermal equation of state of Campbell et al. (in prep). The equation of state parameters for KBr used in this study are listed in Table 1. This equation of state calibrates KBr against platinum, gold, hcp-iron, and MgO at room temperature and during laser heating, up to pressures of >100 GPa. When calibrating the equation of state at high temperatures, KBr served as the thermal insulator, as in the present study. To measure the pressure in this study, the lattice parameter of KBr, and its uncertainty, was determined as the average and standard error from four to thirteen $d$-spacings. Uncertainties in pressure were propagated through the KBr equation of state from the uncertainty in temperature and the uncertainty in the lattice parameter. In the room temperature experiments, ruby fluorescence and the lattice parameter of neon served as secondary pressure standards (Dewaele et al., 2008; Mao et al., 1986).
The temperature of the KBr insulator/calibrant in our experiments was not the same as the sample temperature, because of axial gradients through the insulating layer. The KBr temperature was corrected downward from the measured temperature to $T_{KBr} = (3T_{meas} + 300)/4 \pm (T_{meas} - 300)/4$ (Campbell et al., 2009). The resulting error in pressure due to this large uncertainty in the temperature of the KBr is typically only a few percent, because the compressibility of KBr is high relative to its thermal expansion (Campbell et al., 2009, in prep).

In using KBr as the pressure standard, we are assuming mechanical equilibrium between the sample and the pressure medium. Deviatoric stresses on the sample are expected to be negligible at high temperatures, compared to our experimental uncertainties.

The sample was compressed to a target pressure and laser-heated from each side by 1.064 μm Yb fiber lasers with ‘flat top’ profiles created by pi-shaping optics, with the laser power on each side being independently adjustable (Prakapenka et al., 2008). The diamond cells were water-cooled during heating. The temperature was slowly stepped up by increasing the laser power on both sides until a target temperature was reached, and then the laser power was gradually decreased to zero, with diffraction patterns being obtained on both heating and cooling cycles. Temperatures were determined spectroradiometrically (Heinz and Jeanloz, 1987) using the graybody approximation, and were measured during the collection of each diffraction pattern.

The laser-heated spots were 20-25 μm in diameter, much larger than the X-ray beam to minimize radial temperature gradients, and were coaligned with the beam using X-ray induced fluorescence from the KBr pressure medium. Temperatures were measured both upstream and downstream of the sample from a region 5 μm in diameter in the center of the laser-heated spot, comparable to the size of the area probed by the X-rays.

Temperatures measured on the upstream and downstream sides of the sample were
averaged to obtain the sample temperature. For subsolidus phase diagram and equation of state measurements, the temperatures were then corrected downward by 3% to account for an axial temperature gradient through the thickness of the sample (Campbell et al., 2007, 2009). Reported uncertainties in the temperature incorporate an analytical uncertainty of 100 K from the temperature measurement system (Shen et al., 2001), the difference between the upstream and downstream temperatures (typically less than 100 K), and the uncertainty from the correction for the axial temperature gradient (Campbell et al., 2007, 2009), if applicable.

To benchmark the temperature measurements, a sample of pure iron loaded in an MgO pressure medium was analyzed using the methods outlined above to check the location of the hcp-fcc phase transition in iron, after Fischer et al. (2011). The sample was pressurized and laser-heated, and the phase transition in iron was bracketed between volumes and temperatures (Supplemental Table S1) that agree with the published phase diagram of Komabayashi and Fei (2010) upon heating.

Molar volumes of the Fe-16Si samples were determined from their measured d-spacings, and phase transitions were identified from the appearance and disappearance of peaks in the diffraction pattern. Melting was determined by the appearance of diffuse scattering in the pattern, sometimes accompanied by the disappearance of the peaks of one of the sample phases.

In the room temperature experiments, we used the unit cell volume of KBr at 300 K to calculate the pressure (Campbell et al., in prep). Again, we assume mechanical equilibrium between the Fe-Si alloy and the KBr, based on the hydrostaticity of the neon pressure medium (Klotz et al., 2009). Deviatoric stresses on the sample are small but not negligible in neon for a material as compressible as KBr, so we performed a small correction to the measured KBr lattice parameters (after Singh, 1993). Details of this correction may be found in the Supplemental
In parallel to experiments, we performed first-principles calculations based on the projected augmented wavefunction method (Blochl, 1994) of the density-functional theory (DFT), as implemented in the ABINIT package (Gonze et al., 2002, 2009; Torrent et al., 2008). We worked on three ideally stoichiometric phases: Fe$_3$Si with the D0$_3$ structure, hcp iron, and FeSi with the B2 structure. We employ the Generalized Gradient Approximation (GGA) of DFT, in the Perdew-Burke-Erzhof formulation (Perdew et al., 1996). We performed calculations on the D0$_3$ structure of Fe$_3$Si with a ferromagnetic configuration, and did non-spin-polarized calculations for the other two phases, as they are non-magnetic. For Fe$_3$Si we repeated the calculations using the Local Density Approximation (LDA). We used 15 Hartrees for the kinetic energy cutoff and 8x8x8 grids of special k points (Monkhorst and Pack, 1976) for all three phases. These parameters ensure a precision better than 1 mHa/formula unit in energy and better than 1 GPa in pressure.

3. Results

At pressures below ~50-65 GPa, our Fe-alloy containing 16 wt% Si was stable in the D0$_3$ (BiF$_3$- or AlFe$_3$-type) structure, while above these pressures it was stable as a mixture of B2 (CsCl-type) and hcp phases (Figure 1). The D0$_3$ structure, which belongs to space group $Fm\overline{3}m$, has been recognized in iron-silicon alloys with slightly lower silicon contents at 1 bar (Christensen et al., 2008; Massalski, 1986; Rhee, 2004), but has not previously been reported in Fe-Si alloys at high pressures and temperatures. The D0$_3$ structure can be thought of as a
doubling of the B2 unit cell in each dimension, with a higher degree of ordering. It produces all of the B2 diffraction peaks (the D0₃ peaks with even Miller indices, which are doubled relative to the B2 Miller indices) plus several additional peaks (those D0₃ peaks with odd Miller indices). Supplemental Figure S1 illustrates the D0₃ structure.

Figure 2a and b illustrates an example of an X-ray diffraction pattern of our sample collected at 44 GPa and 1840 K, with peaks corresponding to B2-KBr and D0₃ Fe-Si alloy. KBr tends to produce smooth diffraction rings, while the thinner, hotter alloy produces discrete spots (Figure 2a). Figure 2c shows a pattern collected at 137 GPa and 2130 K, with peaks from B2-KBr, B2 Fe-Si alloy, and hcp Fe-Si alloy. The KBr peaks at these high temperatures are broader than those of the sample, due to the wider range of temperatures experienced by the thicker layer of the KBr pressure medium. The lower intensity odd peaks of the D0₃ structure sometimes appeared in the integrated diffraction pattern, as can be seen in Figure 2b, but frequently required examination of the 2D image to locate diffraction spots. In all of our diffraction patterns, all peaks were identified as corresponding to KBr, some structure of Fe-Si alloy, or neon (300 K data only).

The pressure-volume-temperature (P-V-T) data from the synchrotron X-ray diffraction experiments are listed in Supplemental Table S2. The lattice parameter of D0₃ Fe-Si alloy was calculated from two to ten of the following hkl peaks: 111, 200, 220, 311, 222, 400, 331, 420, 511+333, 440, and 422. The lattice parameter of B2 Fe-Si alloy was calculated from two to six of the following peaks: 100, 110, 111, 200, 210, 211, 220, and 221+300. Those of hcp Fe-Si alloy, and its c/a ratio, were calculated from up to five of the following peaks: 100, 002, 101, 102, and 110. KBr was stable in the B2 structure over the pressure range of interest. Its lattice parameter was determined from the observed d-spacings of four to thirteen of the following hkl peaks: 100,
110, 111, 200, 210, 211, 220, 221+300, 310, 311, 222, 320, and 321. Uncertainties on the lattice parameters are standard errors from the variations in lattice parameters from these $d$-spacings.

Figure 3 shows our $P$-$V$-$T$ data for the D0$_3$ structure and for the B2+hcp mixture of Fe-16Si.

It is not straightforward to determine the bulk molar volume of the B2+hcp mixture, because we cannot quantify the amount of each phase present. When both phases are visible in the diffraction pattern, we use the mean of the volumes of the two endmembers, with these averages plotted in Figure 3. The bulk volume of the two-phase assemblage must lie between that of the end members, so we incorporate the difference in their volumes into the uncertainty in mixture volume. This approach constrains the volume of the assemblage with acceptable uncertainty because of the similarity of the B2 and hcp volumes, which typically differ by <0.5%.

Also shown in Figure 3 are calculated volumes of Fe$_3$Si in the D0$_3$ structure at 0 K, determined using LDA and GGA. These results are listed in Supplemental Table S3. Supplemental Table S3 also lists data on the magnetization of Fe$_3$Si as a function of pressure, which is illustrated in Supplemental Figure S2.

Figure 4 shows an example of the appearance of diffuse scattering in X-ray diffraction patterns during laser heating at 110 GPa. These diffraction patterns were all obtained with a fixed exposure time, and were offset (by <1%) to match intensities at $2\theta = 5.0^\circ$. At temperatures of 3605 K and greater, a broad elevated bump in the background appears at approximately $2\theta = 9$-$12^\circ$, representing the X-ray scattering by the liquid alloy. The diffuse scattering continues to increase with increasing temperature, indicating a higher fraction of partial melt. Pressures and temperatures of upper and lower bounds on melting from X-ray diffuse scattering are listed in Supplemental Table S4.
4. Discussion

4.1. Subsolidus phase relations

The phase diagram of Fe-16Si had not previously been determined at the pressures and temperatures of the deep Earth. We determined this phase diagram to 140 GPa, as shown in Figure 1. We find the D0$_3$ structure stable at lower pressures and high temperatures, where studies on similar alloys observed the bcc or B2 structures (Asanuma et al., 2010; Lin et al., 2003; Zhang and Guyot, 1999). It is possible that that the D0$_3$ phase was present but not detected in these earlier studies, because it is a more ordered version of these other structures, and the X-ray diffraction peaks that indicate this higher degree of ordering are typically small and difficult to detect. In our data, they are present only as spots, not as diffraction rings (Figure 2a), and in many instances we were only able to identify these spots in the 2D diffraction image, not in the integrated patterns. At higher pressures, we find a B2+hcp mixture. This was likely undetected during compression at room temperature by Lin et al. (2003) and Hirao et al. (2004) due to a kinetic barrier of this transition; we also fail to observe the transition to a B2+hcp mixture at room temperature.

We find that the intensity of the hcp peaks relative to that of the B2 peaks generally increases with pressure, suggesting that the mixture contains more hcp alloy at higher pressures. This implies that at even higher pressures, beyond those of the present study, the alloy will convert completely to an hcp structure, analogous to the phase diagram of Fe-7.9Si reported by

In one region of $P$-$T$ space, between ~50-90 GPa and ~2100-2800 K, we observe the B2 structure only (Figure 1). This transition from the D0$_3$ phase to the B2 structure represents disordering upon heating. It may be a gradual or sudden transition; this is difficult to determine due to the many diffraction peaks that are produced by both structures and the relatively low intensities of the D0$_3$-only (odd) peaks. Asanuma et al. (2010) reported seeing the bcc structure in this region of $P$-$T$ space, at ~57 GPa and temperatures near the melting curve. This may represent a misidentification of the B2 structure, since the B2 and bcc structures share half of their diffraction peaks and the B2-only peaks are relatively low intensity compared to those of the bcc structure. Alternatively, this discrepancy may be due to differences in composition (Asanuma et al. (2010) studied Fe-18Si). Our $P$-$V$-$T$ data on the B2 structure in this region were not used in any of our equation of state fits.

The appearance and disappearance of the hcp phase at high pressures and temperatures is abrupt, and we have used our data to constrain the slope of this phase boundary (Figure 1). We find a positive Clapeyron slope of this transition of approximately 46 K/GPa, with the phase boundary intersecting the melting curve at ~99 GPa and ~3375 K. Our results on the phase diagram of this alloy demonstrate that it is stable as a B2+hcp mixture at the pressures of the core-mantle boundary (136 GPa; Figure 1).

### 4.2. Melting curve

The melting curve of Fe-16Si was measured to 140 GPa using synchrotron X-ray scattering measurements (Figure 5). Each data point in Figure 5 representing a lower bound from
the present study was the highest temperature at which diffuse scattering was not observed, and
the upper bounds are the lowest temperatures at which it was observed. Our data agree well with
the data of Asanuma et al. (2010) and Morard et al. (2011) up to ~60 GPa. At higher pressures,
our data are broadly compatible with, though slightly higher than, those earlier studies.

Asanuma et al. (2010) studied the melting of Fe-18Si up to 120 GPa. They placed lower
bounds on the melting point by identifying discontinuities in the laser power-temperature
relationship, and placed upper bounds based on the presence of quenched texture in recovered
samples. Above ~60 GPa, their melting data systematically fall a couple hundred degrees lower
than ours (Figure 5). Morard et al. (2011) studied Fe-5Ni-15Si to 80 GPa using diffuse
scattering. The presence of nickel in their alloy might explain divergence of our melting curves.
The variation in silicon content between these three studies should not be relevant at higher
pressures, where two phase eutectic melting is likely.

At lower pressures, below ~95 GPa (Figure 1), single phase melting occurs, from either
the B2 or D0₃ crystal structure. Presumably Fe-16Si passes through a small solid+melt loop
during melting at these pressures, but the width of this loop is not easily quantifiable using our
experimental methods. Above ~95 GPa, two phase melting occurs from the mixture of the B2
and hcp structures, implying the presence of a eutectic. At 137 GPa, we bracket the melting point
between 3520 and 3720 K. Since there is a eutectic for this composition and pressure, 3520 K is
the minimum temperature for the Earth’s outer core if it were to consist exclusively of Fe-Si
alloy.

We observed that at pressures above ~95 GPa, when our alloy was stable as a B2+hcp
mixture, it was the hcp phase that disappears at the eutectic temperature, while the B2 phase
remains and coexists with the melt (Figure 4). This implies that the eutectic composition in the
Fe-Si system over this \( P-T \) region has a lower silicon content than our starting composition of 16 wt%. At 21 GPa, Kuwayama and Hirose (2004) found a eutectic composition in the Fe-FeSi system of 26 wt% Si, suggesting that the eutectic is shifting to more iron-rich compositions with increasing pressure. Alternatively, the eutectic we report here might be a different one than that identified by Kuwayama and Hirose (2004). Further work is necessary to better resolve the evolution of the eutectic in the Fe-Si system at high pressures.

The melting curve is thermodynamically required to have a kink in it where it intersects the subsolidus phase boundary, but this is not resolvable in our melting data. In Figures 1 and 5, we illustrate an approximate melting curve that includes a small kink at 95 GPa, where our bounds on melting reach the extrapolated boundary between the \( D0_3 \) and \( B2+\text{hcp} \) phase fields.

Even very thin samples will sustain an axial temperature gradient of a few percent (Campbell et al., 2007, 2009). When determining melting, we use the measured sample temperatures without correcting for an axial temperature gradient. The measured temperature should reflect the temperature at the surface of the sample, where it is the hottest, which is where melting begins. However, since it is uncertain how much partial melt must be present in the volume probed by the X-ray for liquid scattering to be efficient enough to be detected, our measurements may slightly overestimate the true melting point.

### 4.3. Equations of state

We fit our \( P-V-T \) dataset for \( D0_3 \) Fe-16Si to a Mie-Grüneisen equation of state,

\[
P(V,T) = P_{300}(V) + \left(\frac{\gamma}{V}\right)[E(\theta_D,T)-E_{300}(\theta_D,300)]
\]

with the 300 K isothermal pressure \( P_{300} \) described by the third-order Birch-Murnaghan
equation of state (Birch, 1952), and the thermal pressure term based on a Debye model of vibrational energy \( (E) \), with Grüneisen parameter \( \gamma = \gamma_0 (V/V_0)^{\theta} \) and Debye temperature \( \theta_0 = \theta_0 \exp[\gamma_0 (1 - (V/V_0)^{\theta}/q] \). We did not explicitly include any anharmonic or electronic contributions to the thermal pressure, instead allowing all thermal pressure variation to be described by \( \gamma \) and \( q \) (e.g. Fei et al., 2007). This reduced the number of fitted parameters, which was necessary given the resolution of our data.

Table 2 shows the equation of state parameters we found for D\(_0\)\(_3\) Fe-16Si alloy. We fit the one bar isothermal bulk modulus (\( K_0 \)) and its pressure derivative (\( K_0' \)) using only the room temperature compression data, fixing the zero-pressure volume to the value we measured experimentally. We then fit the one bar Grüneisen parameter (\( \gamma_0 \)) from the high temperature data, fixing the one bar Debye temperature (\( \theta_0 \)) to that of hcp-iron (417 K, from Dewaele et al., 2006) and fixing \( q \) to one. Our value for \( K_0 \) for D\(_0\)\(_3\) Fe-16Si alloy is similar to that reported in the static compression study of Lin et al. (2003) for Fe-17Si (193.4 ± 4.8 GPa vs. 199.0 ± 5.3 GPa), but we found a slightly lower value of \( K_0' \) than Lin et al. (2003) (4.91 ± 0.59 vs. 5.66 ± 0.61). Our zero pressure volume, 6.799 ± 0.004 cm\(^3\)/mol, is also smaller than that found by Lin et al. (2003) (6.887 ± 0.007 cm\(^3\)/mol), but larger than the values predicted by Christensen et al. (2008) (6.631 cm\(^3\)/mol) and Rhee (2004) (6.642 cm\(^3\)/mol), and slightly larger than that measured by Mishra et al. (1985) (6.789 ± 0.09 cm\(^3\)/mol).

As expected, theoretical volumes calculated using LDA (Figure 3) are lower than those predicted from our equation of state at 0 K by ~9%, but they show similar compressibility to the experimental data. GGA yields a higher one bar volume than we measured experimentally (6.907 cm\(^3\)/mol), but also predicts a higher compressibility. With this tradeoff, there is excellent agreement (<1% volume difference) between the experimentally determined volumes and those
calculated using GGA at 20 and 40 GPa. The EOS fit to the static (0 K) GGA results yield $V_0 = 6.851 \text{ cm}^3/\text{mol}$, $K_0 = 200 \text{ GPa}$, and $K_0' = 4.44$. Similar relationships between data obtained experimentally versus by LDA and GGA have already been recorded in previous studies on the Fe-Si system (Vočadlo et al., 1999; Moroni et al., 1999; Caracas and Wentzcovitch, 2005). The magnetization of Fe$_3$Si decreases smoothly with decreasing volume and increasing pressure (Supplemental Figure S2), and remains positive even at core pressures.

We have also determined an equation of state for the B2+hcp mixture of our alloy by fitting our data to a Mie-Grüneisen equation of state as described above. The resulting equation of state parameters are listed in Table 2. It is not typical to construct an equation of state for a two-phase mixture, but in this case there was no better alternative, since we have no knowledge of how silicon partitioning between the two phases varies with pressure and temperature or of the relative abundances of the two phases. In addition, constructing an equation of state for the mixture seems justified in this case, because the volume difference between the B2 and hcp phases is small (mean of 0.4% ± 0.6%). The modal abundances of B2 and hcp are varying with pressure and partitioning silicon in such a way as to keep the bulk composition fixed. Finally, this approximation is validated by the fact that the goal is to make a comparison to the Earth’s core at core-mantle boundary conditions (Section 4.4), not to establish the mixture’s physical parameters.

For the B2+hcp mixture, we fit $K_0$ and $\gamma_0$ (Table 2). We fixed $V_0$ to that of the D0$_3$ structure, $\theta_0$ to that of hcp-iron (Dewaele et al., 2006), and $q = 1$. We also fixed $K_0'$, finding the best fit to our data with $K_0' = 4$. We find a lower value of $K_0'$ and a higher value of $K_0$ for the B2+hcp mixture than for the D0$_3$ structure. We find very similar values of $\gamma_0$ for the D0$_3$ phase and the B2+hcp mixture. Isotherms calculated from our equations of state are shown in Figure 3.
for a variety of temperatures.

The hcp Fe-Si phase has a slightly larger volume than the B2 Fe-Si phase under almost all experimental conditions investigated. This may be due to silicon partitioning between the two phases producing a more iron-rich hcp phase. Since we expect the hcp structure to be the high pressure phase (Section 4.1), it should have a greater molar density than the B2 phase for a fixed composition, but the slightly larger volume can be explained by its higher Fe content. We find no obvious pressure or temperature dependence on the volume difference between the two phases. This further justifies our use of a single equation of state to describe the two-phase mixture.

These considerations are supported by the first-principles results. The static equation of state of hcp-Fe has $V_0 = 6.466 \text{ cm}^3/\text{mol}$, $K_0 = 244 \text{ GPa}$, and $K_0' = 4.55$, while B2-FeSi has a static equation of state with $V_0 = 6.523 \text{ cm}^3/\text{mol}$, $K_0 = 220 \text{ GPa}$, and $K_0' = 4.39$. Calculated $P-V$ data for these phases are shown in Supplemental Tables 5 and 6, respectively. Regardless of the relative volumes at one bar, differences in compressibility within the stability field of the hcp and B2 phases produce the same relative relation as seen experimentally: hcp-Fe has a larger volume than B2-FeSi. The volume difference is slightly enhanced by increasing pressure, but it remains less than 1.8% even at 200 GPa. The corresponding stoichiometric mechanical mixture, an average of the B2 and hcp phases, yields an EOS with $V_0 = 6.4925 \text{ cm}^3/\text{mol}$, $K_0 = 234 \text{ GPa}$, and $K_0' = 4.43$.

Supplemental Table S2 lists the $c/a$ ratio for the hcp Fe-Si phase. It is fairly constant over the entire $P-T$ range explored, though it decreases slightly with pressure, from $\sim 1.620$ near 70 GPa to $\sim 1.615$ at 135 GPa. It does not have any resolvable temperature dependence.

4.4. Comparison to the core density deficit
Earth's core is known to be an iron rich alloy, yet the density of the core is lower than that of pure iron under the appropriate pressure-temperature conditions; this difference is known as the core density deficit. Assuming that the Earth's core may be predominantly an Fe-Si alloy, we can place constraints on the silicon content of the core by comparing the equation of state of Fe-Si alloys to the seismologically determined density profile in the outer core. Since our alloy is stable as a B2+hcp mixture at core-mantle boundary pressures, it is the equation of state of this mixture that we apply to calculations of the core density deficit. We use a core-mantle boundary (CMB) pressure of 135.8 GPa and a density of 9.9 g/cm³ in the outer core at the CMB from PREM (Dziewonski and Anderson, 1981). The outer core temperature at the CMB is taken to be 4000 ± 500 K, based on the analysis of Anderson (2003). We assume that the outer core temperature profile is adiabatic (Birch, 1952), and that iron and iron-rich alloys experience a 1-2% volume increase upon melting at core pressures (Anderson, 2003). Although it is likely that the outer core contains more than one light element, such as Si, S, O, and/or C (McDonough, 2003), for this analysis we consider an outer core whose light element component is comprised solely of silicon.

Figure 6 illustrates the density difference between pure solid hcp-iron, calculated along an adiabat from the equation of state of Dewaele et al. (2006), and PREM, the seismically determined density of the Earth’s outer core (Dziewonski and Anderson, 1981). Based on the assumptions outlined above, we find that PREM at the CMB is 10.4 ± 0.9% less dense than solid hcp-Fe at the same conditions. Approximately 1-2% of this density deficit can be explained by the volume change that iron experiences upon melting at high pressures (Anderson, 2003), but the remainder of this deficit must be due to the presence of light elements in the outer core, such
Our equation of state for the B2+hcp mixture of Fe-16Si can be used to constrain the amount of silicon required to match the density deficit in the Earth’s outer core. This analysis requires no extrapolation in pressure and only a small extrapolation in temperature to apply our equation of state at CMB conditions. We corrected the outer core density to account for a Ni/Fe atomic ratio of 0.058 in the core (McDonough, 2003). A silicon content of 11.3 ± 1.5 wt% is required to match PREM in the outer core at the CMB for a purely Fe-Ni-Si outer core. The uncertainty in this calculation is based upon the stated uncertainties in the CMB temperature, the volume change of melting, and the equation of state, with the uncertainty in CMB temperature dominating. Varying the amount of nickel in the core has very little effect on the amount of silicon needed to match PREM (less than ± 0.1 wt%).

The core’s light element component is likely to be comprised of multiple light elements, which may or may not include silicon. If the core contains other light elements, then 11.3 wt% is effectively the maximum amount of silicon that may exist in the Earth’s outer core, with the remainder of the core density deficit being comprised of other light elements. This composition is consistent with a eutectic in the Fe-Si system of less than 16 wt% Si, as established above, because the coexisting solid phase (inner core) must be more Fe-rich. Assuming that this eutectic composition doesn’t decrease dramatically at higher pressures, it is plausible on this basis that silicon could be the dominant light element in the Earth’s core.

Figure 6 shows that the density profile of the B2+hcp mixture of our alloy approximately matches the slope of PREM when its equation of state is extrapolated through the $P-T$ range of the Earth’s outer core. This is not the case for density profiles of FeO (Fischer et al., 2011) and Fe$_3$S (Seagle et al., 2006) calculated from their published equations of state. This lends support
to the idea that silicon is the dominant light element in the Earth’s core. However, this comparison to PREM does require large extrapolations in the equations of state of these alloys, and alternative explanations for variations in density profile slopes have been proposed (Fischer et al., 2011).

A similar calculation may be performed to assess the amount of silicon needed to match the density deficit of the Earth’s inner core. We assume an inner core boundary (ICB) temperature of 5000 ± 1000 K (Boehler, 2000), pressure of 328.85 GPa, and density of the inner core of 12.76 g/cm$^3$ at the ICB (Dziewonski and Anderson, 1981). The density was again corrected for a Ni/Fe atomic ratio of 0.058 in the core (McDonough, 2003). Under these assumptions, for an Fe-Si-Ni inner core, the density deficit at the ICB can be explained by the presence of 7.7 ± 1.3 wt% silicon in the inner core. However, it should be emphasized that this calculation requires large extrapolations in temperature, pressure, and silicon content. This calculation is also performed with the equation of state of the B2+hcp mixture. While we predict an eventual transition to the hcp structure at higher pressures, this transition is unlikely to have a very large effect on the density of our alloy, since the relative proportions of B2 and hcp structures are changing gradually across the phase loop. Nevertheless, this extrapolation should be used with caution.

5. Conclusions

The phase diagram of an iron-silicon alloy containing 16 wt% silicon has been determined to high temperatures and pressures reaching those of the Earth’s outer core. This
phase diagram includes the D0$_3$ structure, which has not previously been reported in an Fe-Si alloy at high pressures and temperatures, and the location and slope of the phase boundary between the D0$_3$ structure and a B2+hcp mixture at higher pressures and temperatures has been measured. Equations of state of this alloy’s D0$_3$ structure and its B2+hcp assemblage were also determined. The eutectic composition in the Fe-Si system at CMB conditions is less than 16 wt% silicon. The melting curve indicates that 3520 K is a minimum temperature for the Earth’s outer core, if it consists exclusively of Fe-Si alloy. LDA calculations accurately predict the compressibility of D0$_3$ Fe$_3$Si, whereas GGA calculations match its volume at high pressures.

The equation of state for the B2+hcp mixture of Fe-16Si can be compared to that of hcp-Fe (Dewaele et al., 2006) and PREM, the seismologically determined density of the Earth’s outer core (Dziewonski and Anderson, 1981) to perform an analysis of the core density deficit. For an outer core containing only iron, nickel, and silicon, 11.3 ± 1.5 wt% silicon would be required to match PREM at the core-mantle boundary, making this the maximum amount of silicon that may exist in the Earth’s outer core.

References


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Figure Captions

Figure 1: High $P$-$T$ phase diagram of Fe-16Si alloy. Red triangles: D0$_3$ structure. Purple diamonds: B2 structure only. Blue circles: B2+hcp mixture. Black line represents the appearance of the hcp phase at high pressures. Grey dashed curve: approximate melting curve, based on Figure 5.

Figure 2: A: Diffraction image before integration, collected at 44 GPa and 1840 K. White tick marks represent KBr peaks, and red tick marks represent Fe-16Si alloy peaks. B: Diffraction pattern from part A, integrated azimuthally. Peaks correspond to B2-KBr and D0$_3$ Fe-Si alloy. C: Diffraction pattern collected at 137 GPa and 2130 K, with peaks from B2-KBr, B2 Fe-Si alloy, and hcp Fe-Si alloy. These patterns were collected using an X-ray wavelength of $\lambda$=0.3344 Å.

Figure 3: Equations of state and $P$-$V$-$T$ data of D0$_3$, Fe-Si alloy, and of the mixture of B2+hcp structures of Fe-Si alloy. All data and isotherms are color-coded by temperature range according to the legend. Triangles indicate volumes of the D0$_3$ structure, and diamonds indicate averages of the volumes of the B2 and hcp phases. $\times$ symbols and crosses indicate volumes of D0$_3$ Fe$_3$Si, calculated at 0 K using LDA and GGA methods, respectively. Isotherms are calculated using the parameters in Table 2 for the midpoint of the temperature range indicated, and they do not extend above the melting curve. Solid curves are isotherms for the D0$_3$ structure, while dashed curves are isotherms for the B2+hcp mixture.

Figure 4: Diffuse scattering in X-ray diffraction patterns at 110 GPa, color-coded according to
temperature. The bump in the background at approximately \( \theta = 9-12^\circ \) at the highest

temperatures represents scattering by the liquid alloy, bracketing the melting point between 3430 K and 3605 K.

**Figure 5:** Melting data on iron-silicon alloy. Data shown are for Fe-16Si alloy (this study, red circles), Fe-5Ni-15Si (Morard et al., 2011, green triangles), and Fe-18Si (Asanuma et al., 2010, orange diamonds). Open symbols represent lower bounds, while solid symbols represent upper bounds. This study and Morard et al. (2011) determined bounds on melting using X-ray diffuse scattering. Asanuma et al. (2010) placed lower bounds using laser power-temperature discontinuities, and upper bounds based on quench texture of recovered samples. Phase identification and appearance of hcp phase (black line) are based on data shown in Figure 1. Melting curve is the same as in Figure 1.

**Figure 6:** Comparison to the core density deficit. Black curve: PREM (Dziewonski and Anderson, 1981). Blue curve: density profile for solid B2+hcp Fe-16Si, calculated from the equation of state parameters listed in Table 2. Orange curve: density profile for solid hcp-Fe, calculated from the equation of state of Dewaele et al. (2006). Solid curves follow an adiabatic temperature profile for a CMB temperature of 4000 K. Dashed curves indicate the effect of a 500 K uncertainty in the CMB temperature, which is the dominant uncertainty when evaluating the core density deficit. As discussed in the text, these equations of state impose an upper bound on the silicon content of the outer core of \( 11.3 \pm 1.5 \) wt%.

**Table 1:** Equation of state parameters for B2-KBr used for pressure calibration, from Campbell
et al. (in prep). Entries with no stated uncertainties were held fixed in the fit.

<table>
<thead>
<tr>
<th></th>
<th>B2 KBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_0 ) (cm(^3)/mol)</td>
<td>37.901</td>
</tr>
<tr>
<td>( K_0 ) (GPa)</td>
<td>21.04 ± 0.08</td>
</tr>
<tr>
<td>( K'_0 )</td>
<td>4.55 ± 0.01</td>
</tr>
<tr>
<td>( \theta_0 ) (K)</td>
<td>290</td>
</tr>
<tr>
<td>( \gamma_0 )</td>
<td>1.37 ± 0.10</td>
</tr>
<tr>
<td>( q )</td>
<td>1</td>
</tr>
</tbody>
</table>

**Table 2:** Equation of state parameters for D0\(_3\) Fe-Si alloy, and for the B2+hcp mixture of Fe-Si alloy. Zero pressure volume of the B2+hcp mixture was set equal to that of the D0\(_3\) structure.

Zero pressure Debye temperatures (\( \theta_0 \)) were set to the value for iron (Dewaele et al., 2006).

Entries with no stated uncertainties (and the zero pressure volume of the D0\(_3\) structure, which was measured experimentally) were held fixed in the fits.

<table>
<thead>
<tr>
<th></th>
<th>D0(_3) Fe-Si alloy</th>
<th>B2+hcp Fe-Si alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_0 ) (cm(^3)/mol)</td>
<td>6.799 ± 0.004</td>
<td>6.799</td>
</tr>
<tr>
<td>( K_0 ) (GPa)</td>
<td>193.4 ± 4.8</td>
<td>206.5 ± 2.0</td>
</tr>
<tr>
<td>( K'_0 )</td>
<td>4.91 ± 0.59</td>
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</tr>
<tr>
<td>( \theta_0 ) (K)</td>
<td>417</td>
<td>417</td>
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<tr>
<td>( \gamma_0 )</td>
<td>1.89 ± 0.06</td>
<td>1.80 ± 0.10</td>
</tr>
<tr>
<td>( q )</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 1

A graph showing the relationship between pressure (GPa) and temperature (K) with various data points. The graph is divided into different regions labeled as 'melt', 'B2', 'B2+hcp', and 'DO$_3$'. The x-axis represents pressure, and the y-axis represents temperature.
Figure 2

A

B

2θ (degrees)

Intensity

44 GPa and 1840 K

KBr 110

D03 Fe-Si 220

KBr 111

D03 Fe-Si 311

KBr 210

D03 Fe-Si 420

KBr 220

D03 Fe-Si 200

D03 Fe-Si 331

D03 Fe-Si 222
137 GPa and 2130 K
Figure 5

A graph showing the phase transition of a material under varying temperature and pressure. The graph indicates different phases such as melt, B2, and B2+hcp. Data points from different studies are represented by various symbols. The x-axis represents pressure (GPa), and the y-axis represents temperature (K).

- This study
- Morard et al. (2011)
- Asanuma et al. (2010)
Figure 6
Supplemental Methods:

**Correction to KBr lattice parameters:**

We performed a small correction to the measured lattice parameters of KBr at 300 K to account for deviatoric stresses (after Singh, 1993). We plotted the measured lattice parameter of KBr computed from each $d$-spacing versus the 2θ angle of that peak (Supplemental Figure S3), finding a linear trend, which indicates that the θ dependence of the strain dominates over the $hkl$ dependence, contrary to the results of Shim et al. (2000). Therefore, we then performed an unweighted linear fit to the data, taking the intercept (the extrapolation to 2θ=0) as the lattice parameter, and the uncertainty in the intercept as the uncertainty in the lattice parameter. The average correction was a 0.08% decrease in KBr lattice parameter, which translated to 1.4% increase in pressure. The corrected and uncorrected KBr lattice parameters are shown as a function of the corrected pressure in Supplemental Figure S4. Performing the same analysis with the sample lattice parameters revealed no systematic relationship between strain and 2θ angle, so the measured sample lattice parameters were not corrected.

**Supplemental Figure S1:** A unit cell of the D0₃ structure, generated using XtalDraw.

For Fe-16Si, green atoms represent sites mostly occupied by iron, and blue atoms represent sites mostly occupied by silicon.

**Supplemental Figure S2:** Magnetism of Fe₃Si in the D0₃ crystal structure, calculated using LDA and GGA methods at 0 K.
**Supplemental Figure S3:** Uncorrected KBr lattice parameters determined from multiple \(d\)-spacings in a pattern collected at 11 GPa and 300 K, as a function of 2\(\theta\) angle. The linear trend of the data reflects the dominance of the \(\theta\) dependence of the strain over any \(hkl\) effects, which may cause the scatter in the data. Since the \(\theta\) dependence dominates, we performed an unweighted linear fit (black line) and extrapolated to 2\(\theta\)=0 to find a corrected KBr lattice parameter of 3.617 Å.

**Supplemental Figure S4:** Corrected and uncorrected KBr lattice parameters as a function of pressure (calculated from the corrected lattice parameter) at room temperature.

**Supplemental Table S1:** Pressure-volume-temperature brackets on the hcp-fcc transition in pure iron, used to benchmark temperature measurements (Fischer et al., 2011). Measured volumes and temperatures are compared to those of Komabayashi and Fei (2010).

**Supplemental Table S2:** Pressure-volume-temperature data from synchrotron X-ray diffraction experiments.

**Supplemental Table S3:** Magnetism and volumes of Fe\(_3\)Si in the D0\(_3\) structure at 0 K calculated using LDA and GGA methods.
**Supplemental Table S4:** Pressures and temperatures of upper and lower bounds on melting from X-ray diffuse scattering.

**Supplemental Table S5:** Volumes of hcp iron at high pressures, calculated using GGA.

**Supplemental Table S6:** Volumes of B2-FeSi at high pressures, calculated using GGA.

**References:**


