Fe- and C-self-diffusion in liquid Fe$_3$C to 15 GPa

David P. Dobson[1]

Bayerisches Geoinstitut, Universität Bayreuth, Germany

Michael Wiedenbeck

Geo Forschungs Zentrum, Potsdam, Germany

[1] Iron- and C-self diffusion have been measured in Fe$_3$C composition liquids at 8 and 15 GPa. Diffusivities fall within the range of values for molten metals and scale inversely to the atomic radius of each species. This supports models such as the Stokes-Einstein relation and the free volume model which relate transport properties to the atomic radius. Along the melting curve, diffusivity is predicted to be constant and we tentatively predict outer core diffusivities at the inner core boundary of 5×10^{-9} m^2 s^{-1} and 7×10^{-9} m^2 s^{-1} for iron and carbon, respectively. This would correspond to a viscosity of around 15 mPas.   INDEX TERMS: 1507 Geomagnetism and Paleomagnetism: Core processes (8115); 5139 Physical Properties of Rocks: Transport properties; 5754 Planetology: Fluid Planets: Physical properties of materials. **Citation:** Dobson, D. P., and M. Wiedenbeck, Fe- and C-self-diffusion in liquid Fe$_3$C to 15 GPa, *Geophys. Res. Lett.*, *29*(21), 2006, doi:10.1029/2002GL015536, 2002.

1. Introduction

[2] The transport properties of the outer core are among the least well known physical properties of the Earth, but are fundamental for understanding the origin, evolution and current dynamics of the core. Geophysical measurements do not provide strong constraints on outer core viscosity and experimental studies and *ab initio* simulations currently provide the best estimates of outer core viscosity and diffusivity. In order for any estimate of the transport properties of the outer core to be meaningful we require (1) appropriate high *P-T* measurements and/or extrapolations to outer core conditions on candidate outer core alloys and (2) a knowledge of the likely outer core composition.

[3] In order to address requirement 1 we have developed a method to measure diffusivity in liquid iron alloys at high pressure [*Dobson*, 2000, 2002]. The results for Fe and Fe-S liquids are consistent with, and cover a wider pressure range than, recent high-pressure viscosity measurements [*Dobson et al.*, 2000, 2001; *Urakawa et al.*, 2001; *Terasaki et al.*, 2001, 2002] and demonstrate the validity of using diffusivity as a proxy for other transport properties under extreme conditions.

[4] In terms of the second requirement, seismological observations suggest that the Earth's outer core consists of Fe-Ni alloy with several wt% of alloying light elements. Recently *Wood* [1993] presented a persuasive argument that carbon might contribute significantly to the outer core's light element inventory. Here we present results of Fe- and C- self-diffusion measurements in liquid Fe$_3$C.

2. Experimental

[5] Experiments were performed in split-cylinder type multi-anvil-presses at the Bayerisches Geoinstitut using an experimental design described elsewhere [*Dobson*, 2000]. Fe$_3$C samples were synthesized, following the technique of *Tsuzuki et al.* [1984], from powder mixtures of Fe and C with a small excess of carbon. X-ray diffraction confirmed the resulting powder to be essentially pure Fe$_3$C. Fe$_3$C powders of natural isotopic composition were packed into 200 μm wall thickness corundum capsules. A thin foil of Fe$_3$C which had been synthesized with ^{57}Fe enriched to 50% and ^{13}C enriched to 95% was added to the end of the sample as the isotopic tracer. The packed corundum capsule was then loaded into a second Zr-foil capsule which acted as an oxygen getter during the experiment. This was then loaded into the horizontal furnace arrangement such that the thermal gradient developed a stable non-convecting density profile when the sample melted. Experiments were performed in 14 mm edge length MgO octahedra, compressed by 8 mm WC anvils. Pressure was increased at room temperature to the desired value and the sample was then heated at 400 or 500°C/min to the set point temperature when furnace power was immediately cut. This resulted in quench rates in excess of 500°C/s. Temperature was monitored using W95Re5/W75Re25 thermocouples located within 200 μm of the capsule; no EMF correction was applied for pressure.

2.1. Analytical Techniques

[6] Point profiles of Fe and C isotopic composition were measured along the diffusion profile using the Cameca ims 6f ion microprobe in Potsdam at a spacing of 20 or 25 μm per point. Analyses were performed using a nominal 12.5 kV, ^{16}O$^-$ primary beam in conjunction to a nominal 10 kV secondary extraction potential. The mass spectrometer was operated at low mass resolution M/δM = 360, in conjunction with a 125 V offset and a 25 eV energy band pass. All analyses used a 60 μm field-of-view and were preceded by a 90 s automatic pre-sputter. All data were collected in pulse counting mode.

[7] Iron analyses were performed over 10 cycles of the mass spectrum: 53.5 background (0.1 s), ^{54}Fe (2 s), ^{56}Fe (2 s) and ^{57}Fe (2 s). A single analysis, using a 2 nA primary beam

[1]Now at Department of Geological Sciences, University College London, London, United Kingdom.
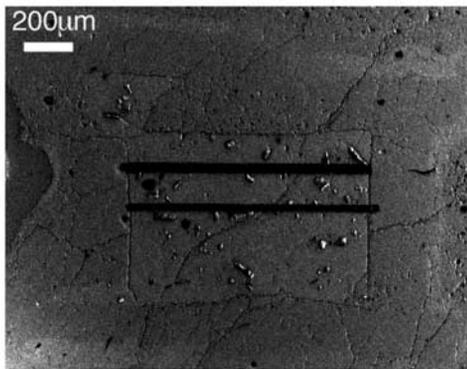
Figure 1. Secondary electron image of sample recovered from 15 GPa and 2130°C. The traces of analyses are clear within the rectangular sample region. The large pits are from a C-analysis profile and the small pits are from an Fe-profile. The outer edge of the corundum capsule, which maintains the sample geometry during melting is delineated by the slightly brighter Zr-foil.

providing a ~10 μm diameter spot, lasted 3 minutes including the pre-sputtering time. The count rate for ^{56}Fe was typically around 5×10^5 s^{-1}, yielding an observed internal precision of approximately 2% 1σ. Carbon analyses were performed using 10 cycles of the mass spectrum: 11.5 background (0.1 s), ^{12}C (10 s) and ^{13}C (30 s). A single analysis, using a 20 nA primary beam providing a ~20 μm diameter spot, lasted 9 minutes including the pre-sputtering time. The count rate for ^{12}C was typically around 2×10^3 s^{-1}, yielding an internal precision of around 5% 1σ.

2.2. Errors

[8] Repeat diffusion measurements often show a reproducibility significantly poorer than the formal analytical and fitting errors. These result from uncertainties in the T-t path and in the sample geometry. Figure 1 shows a secondary electron image of a cell recovered from 15 GPa. The traces of analysis profiles are clear; small pits are from Fe-analyses and large pits are from C-analyses. Repeat profiles, measured on some samples, were reproducible within the analytical error. This, combined with the observation that the sample geometry was maintained during the experiments, confirms that diffusion occurred in essentially a 1-D geometry. We did not correct the measured profiles for compression and thermal expansion, since these parameters are poorly known for solid Fe$_3$C and unknown for the liquid. However, assuming equations of state similar to that of Fe suggests that errors arising from this omission are <4% at 15 GPa.

[9] Errors arising from uncertainties in the T-t path are as follows: (1) t-errors are negligible since the experiments were quenched immediately at the end of the PID-controlled ramp. (2) Temperature errors arise from the thermal gradient between the sample and thermocouple, and from the lag in thermocouple response. Temperature gradients are approximately 20°C at 1500°C between the thermocouple and sample in the stepped furnace arrangement used. T-lags due to thermal mass of the thermocouple will not affect the ramp-rate since the lag produces a constant t-offset, but will result in an under-estimation of peak wiedemperature by <8°C. Thus a generous estimate of the T-errors is that we under-

estimate temperature by some 40°C. The errors discussed here will affect all the samples in the same way, resulting in an internal precision in the series of experiments significantly better than the estimated accuracy. The excellent fit of the diffusivity model to the measured Fe-diffusion suggests that our analysis of internal precision is sound.

[10] The derived pressure and temperature dependencies depend on the precision, but the preexponential term is affected by the accuracy which will result in an additional error of around 15%.

3. Results

[11] The tracer concentration was estimated by taking the ratio of the count rates of masses 57/56 for Fe and 13/12 for C. The initial concentration of the tracer isotope in the foil is denoted by X_F^{Tr} and in the bulk sample by X_S^{Tr}, and the initial concentration of reference isotope is X_F^{Ref} and X_S^{Ref} in the foil and bulk, respectively. In the recovered sample, the composition at a distance, x, from the initial position of the foil consists of a contribution from the tracer foil, C, and from the sample, B; $C + B = 1$. The measured ratio of the tracer isotope to the reference isotope, m, at x is given by:

$$m = \frac{C X_F^{Tr} + B X_S^{Tr}}{C X_F^{Ref} + B X_S^{Ref}}. \quad (1)$$

The contribution from the tracer foil at x is, thus:

$$C = \frac{X_S^{Tr} - m X_S^{Ref}}{m X_F^{Ref} + X_S^{Tr} - m X_S^{Ref} - X_F^{Tr}}. \quad (2)$$

[12] Figure 2 shows a plot of ^{57}Fe and ^{13}C tracer concentrations normalized to the concentration at x_0, C/C_0, for
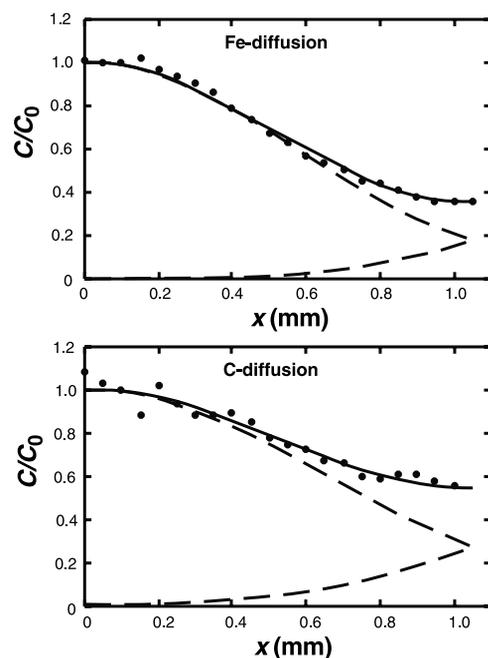
Figure 2. Observed diffusion profiles for Fe and C in liquid Fe$_3$C at 8 GPa and 2040°C. The solid lines show the fit to the data, comprising the sum of the reflected diffusion profile (dashed lines).

an experiment. Because of the high diffusivity of liquid Fe$_3$C, the diffusion profiles reach the impermeable boundary at the end of the capsule and reflect in the normal way [*Crank*, 1975]. These profiles are fitted according to the tracer equation:

$$C/C_0 = \exp - \left(x^2/4Z\right) \qquad (3)$$

where Z is the diffusivity, D, integrated over time, t;

$$Z = \int_0^t D(t)\mathrm{d}t \qquad (4)$$

[13] Traditional diffusion experiments on slow diffusing materials are performed with sufficiently long dwell times at the target temperature for the effects of diffusion during the heating and cooling stages to be negligible; in this case $Z = Dt$ and (4) is the standard tracer equation. In the current experiments, the high diffusivity of the sample forced extremely short dwell times at temperature (0 s dwells) and the heating phase provides the major contribution to the diffusion profile (quench rates are sufficiently fast for diffusion during quenching to be ignored). In this case D varies with t according to the temperature ramp rate and the integral Z must be numerically evaluated. All of the data are simultaneously fitted using a least-squares procedure and the parameters of the diffusion model are adjusted in the fit. Measured values of Z for Fe and C diffusion at 8 and 15 GPa are presented in Table 1.
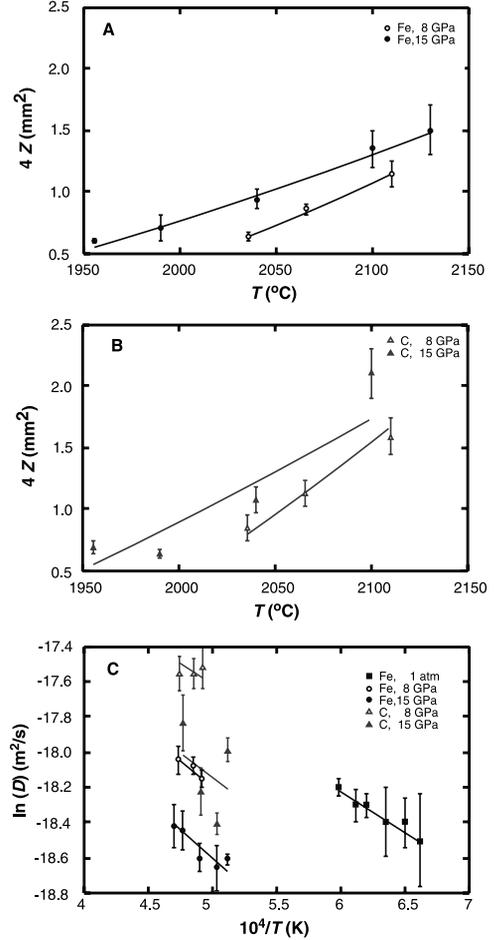
[14] We have fitted the present results to an Arrhenian P-T dependence:

$$D = D_0 \exp - \left(\frac{\Delta H + P\Delta V}{RT}\right), \qquad (5)$$

where ΔH and ΔV are the apparent activation enthalpy and apparent activation volume, respectively, and R, P and T have the usual meanings. Because experiments were performed at only two pressures, the error in ΔV is rather large. We could not perform experiments at lower pressures because of the large field of incongruent melting at low pressure [e.g.; *Wood*, 1993]. We have, however, extrapolated the one atmosphere Fe-diffusion data of *Yang et al.* [1956] on Fe-C alloys to Fe$_3$C composition, and the averages of their extrapolated diffusivities are included in our fitted dataset. Figures 3a and 3b shows the fitted Z data for Fe and C and Figure 3c shows the same data converted

Figure 3. Fitted diffusion data for liquid Fe$_3$C. A and B; measured 4Z and numerical fits to the data, assuming an Arrhenius P-T dependence, for Fe and C, respectively. C; the same data converted to diffusivities.

to self-diffusivities between 0 and 15 GPa. The experimentally determined parameters are:

$$D_0^{\mathrm{Fe}} = 3.0 \pm 0.9 \times 10^{-7} \ \mathrm{m^2 s^{-1}}; \Delta H^{\mathrm{Fe}} = 52 \pm 3 \ \mathrm{kJmol^{-1}};$$
$$\Delta V^{\mathrm{Fe}} = 1.1 \pm 0.1 \times 10^{-6} \ \mathrm{m^3 mol^{-1}}$$

and

$$D_0^{\mathrm{C}} = 2.9 \pm 2.1 \times 10^{-7} \ \mathrm{m^2 s^{-1}}; \Delta H^{\mathrm{C}} = 37 \pm 70 \ \mathrm{kJmol^{-1}};$$
$$\Delta V^{\mathrm{C}} = 1.3 \pm 0.5 \times 10^{-6} \ \mathrm{m^3 mol^{-1}}$$

[15] The fit for Fe diffusivity is rather good, and reproduces all data to within experimental error. We believe that the poor precision of the diffusion parameters for carbon is due in part to the lower measurement precision for carbon and to the higher carbon diffusivities, which resulted in flatter profiles. Furthermore, the lack of 1 atmosphere data for carbon diffusivity along with the small accessible temperature range results in quite strongly correlated parameters in the fit.

4. Discussion

[16] Iron diffusion in liquid Fe$_3$C has substantially smaller apparent activation parameters than in pure liquid

Table 1. Measured Z (= $\int_0^t D(t)\ \mathrm{d}t$) for Liquid Fe3C

P (GPa)	T (°C)	Ramp (°Cs^{-1})	4Z Fe (mm^2)	4Z C (mm^2)
8	2035	400	0.64 ± 0.03	0.85 ± 0.1
8	2062	400	0.86 ± 0.04	1.13 ± 0.1
8	2100	400	1.3 ± 0.1	1.6 ± 0.15
8	2140	400	2.15 ± 0.2	2.8 ± 0.5
15	1955	500	0.61 ± 0.02	0.69 ± 0.05
15	1990	500	0.71 ± 0.1	0.64 ± 0.04
15	2040	500	0.94 ± 0.08	1.06 ± 0.1
15	2101	500	1.35 ± 0.16	1.28 ± 0.13
15	2130	500	1.5 ± 0.14	

iron, where $\Delta H \sim 100$ kJmol^{-1} and $\Delta V \sim 2.8 \times 10^{-6}$ m^3 mol^{-1} [*Dobson*, 2002]. According to the free volume model of *Cohen and Turnbull* [1959] the pressure and temperature dependencies of diffusivity are related to the compressibility and thermal expansivity of the liquid. The low apparent activation parameters in liquid Fe$_3$C may, therefore, be related to a low compressibility, which would mirror the behaviour of solid Fe$_3$C. Alternatively, the low apparent activation parameters of Fe$_3$C may be related to the higher configurational entropy in the liquid. It is interesting to note in this context that Fe and S diffusion, and viscosity in Fe$_{0.61}$S$_{0.39}$ show lower apparent activation parameters than in liquid Fe, which might also be attributable to higher configurational freedom in the melt.

[17] It is always risky to extrapolate low-pressure experimental results to outer core conditions. *Poirier* [1988] observed, however, that along the melting curve many liquid metals display nearly constant transport properties. Although this has recently been questioned for liquid iron, which has a particularly large apparent activation volume [*Brazhkin*, 1999; *Dobson*, 2002], it appears to hold for Fe-S alloys [*Rutter et al.*, 2002]. Using the calculated melting curve of *Wood* [1993] we observe that the predicted melting-temperature Fe-diffusivity is constant to within error across the fitted pressure range (0–15 GPa). We conclude, therefore, that if the outer core can be approximated by liquid Fe$_3$C, its diffusivity at the inner core boundary is likely to be close to 5×10^{-9} m^2 s^{-1} for Fe and, from the Stokes-Einstein relation, $\sim 7 \times 10^{-9}$ m^2 s^{-1} for C.

[18] According to the Stokes-Einstein relation, melt viscosity can be related to the diffusivity of a species, i, in the melt via the relationship:

$$\eta = \frac{k_B T}{D_i \lambda_i} \qquad (6)$$

where η is the viscosity, D and λ are the diffusivity and jump distance (taken to be the interatomic distance) T is absolute temperature and k_B is the Boltzmann constant. If this relation holds for liquid alloys [as we have recently demonstrated in Fe-S; *Dobson et al.*, 2002] then the ratio of diffusivities of the different species should be the inverse of the ratio of the atomic sizes. We note that although the fit parameters for carbon diffusivity are rather poor in the present study, the ratio of measured D^C/D^{Fe} is 1.7 ± 0.1 and 1.6 ± 0.2 at 8 and 15 GPa, respectively. This compares favourably with the ratio of ionic radii: $r_{Fe}/r_C = 1.66$, suggesting that the Stokes-Einstein relation holds in this system to at least 15 GPa. Using the 1 atmosphere atomic radii of Fe and C, we would thus predict a viscosity of approximately 15 mPas along the melting curve. This is in excellent agreement with the 1 atmosphere melting temperature viscosity of Fe$_{83}$C$_{17}$, which is 13 mPas [*Nishi et al.*, 1980]. Using Fe atomic radius from the liquid Fe EOS of *Anderson and Ahrens* [1994] yields $\eta \sim 19$ mPas at the inner core boundary.

5. Summary

[19] We have measured Fe- and C-self-diffusivity in liquid Fe$_3$C at 8 and 15 GPa. Diffusivities are in the typical range of liquid metals, with Arrhenius parameters of $D_0^{FE} = 3.0 \pm 0.9 \times 10^{-7}$ m^2 s^{-1}, $\Delta H^{Fe} = 52 \pm 3$ kJmol^{-1} and $\Delta V^{Fe} = 1.1 \pm 0.1 \times 10^{-6}$ m^3 mol^{-1} for FE, and C diffusivity approximately 1.6 times faster. These values suggest that the Stokes-Einstein relation holds for liquid Fe$_3$C, and allow us to predict a viscosity of 15 mPas at the melting temperature. We tentatively suggest that, at the inner core boundary, an outer core with a composition close to Fe$_3$C would have a viscosity of ~ 19 mPas and diffusivity of D^{Fe} 5×10^{-9} m^2 s^{-1} and D^C 7×10^{-9} m^2 s^{-1}.

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D. P. Dobson, Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany. (d.dobson@ucl.ac.uk)
M. Wiedenbeck, Geo Forschungs Zentrum, Potsdam, D-14473, Germany.