Diamond Formation under Lower Mantle Redox Conditions: Experimental Constraints on the Mineralogical Host of Carbon in Earth’s Mantle

A Thesis

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By

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Abstract

The oxidation state of the Earth is an area of great interest in petrology and mineral physics, as it plays a key role in governing mantle mineralogy and determining mineralogical host of elements with multiple valence states, such as iron and carbon. The amount of oxygen available to drive reactions in a system, as measured by oxygen fugacity, dictates a system’s mineralogy, as controlled by reactions with oxygen, including the oxidation of iron to form wüstite: \( \text{Fe} + \frac{1}{2}\text{O}_2 = \text{FeO} \) (iron wüstite buffer, \( IW \)), or the simultaneous oxidation of iron and diamond to form siderite: \( \text{Fe} + \text{C} + \frac{3}{2}\text{O}_2 = \text{FeCO}_3 \) (siderite diamond iron buffer, \( SDI \)). The degree of oxidation of the lower mantle has been the subject of recent interest, particularly in light of the recently reported crystal-chemically controlled, pressure-induced auto-oxidation-reduction reaction in iron (Frost et al., 2004) and debates on the oxidation state of carbon in the mantle (Brenker et al., 2007; McCammon et al., 2004). In that pressure-induced iron self-reduction is independent of oxygen fugacity, it is likely that the coexistence of metallic iron and wüstite buffers mantle redox state at or near \( IW \), as well as determines whether the host of carbon is either diamond or a carbonate. Therefore, knowledge of the relationship between the buffer assemblage containing both reduced and oxidized carbon (SDI buffer) and that containing both reduced and oxidized iron (IW buffer) is critical to knowing the mineralogical host of carbon throughout the mantle as a function of redox state.
Thermodynamic modeling of iron, carbon, wüstite, and siderite suggests the IW buffer lies between 1.5 and 2.5 log units above the SDI buffer across the pressure and temperature range of Earth’s mantle, suggesting that FeCO$_3$ (siderite) will reduce to diamond. This model is supported by high-pressure, high-temperature experiments carried out in the laser-heated diamond anvil cell from 21-62 GPa and 2100-2300K, with starting material: Fe metal, FeCO$_3$, and FeO. Diamond was detected by x-ray diffraction and Raman spectroscopy, as well as STEM-EDX on a thin foil prepared by focused ion beam milling (FIB). These findings suggest that in the more reducing regions of a laterally and axially heterogeneous mantle, carbonates will be reduced to diamond and/or iron carbide(s), with the greatest reduction potential occurring just before the siderite spin transition. In the more oxidizing regions, such as those near subduction zones and below D”, carbonate will be the stable host of carbon. If carbon is a major light element of the core, it is likely that it would have to have been sequestered prior to the formation of the post-perovskite phase and the D” region.
This thesis is dedicated to Jenny McNamara Rue, who sparked an interest so long ago
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1. Introduction

The cycling of terrestrial carbon at the Earth’s surface has long been recognized as an essential factor making this planet’s climate habitable. Exchange of carbon between surface reservoirs allows for the utilization of atmospheric carbon by photoautotrophic biota and eventual respiration throughout the biosphere. For this process to remain active over geologic time, it requires a constant flux of carbon to the surface. The Earth’s interior is thought to be the largest reservoir of carbon (Javoy et al., 1982; Javoy 1997; Sleep and Zahnle, 2001). Evolution of the surficial carbon cycle and its climatic effects depend strongly on the flux rates of carbon into and out of the mantle (Panero and Kabbes, 2008), residence time in deep Earth reservoirs, and partitioning of carbon rich phases between a silicate mantle and metallic core (Dasgupta and Walker, 2008; Sleep and Zahnle, 2001; Wood, 1993). The whole-Earth carbon cycle operates over billion year time scales. A more complete understanding of the Earth’s global carbon cycle over geologic time requires better constraints on carbon flux rates and on understanding possible pathways into and out of the mantle. Therefore, a necessary first step in constraining the highly complex global carbon cycle is determining the mineralogical host(s) of carbon throughout the mantle from the MOHO down to the core-mantle boundary (CMB). Given carbon shows little tendency to be incorporated into mantle silicates (Keppler et al., 2003), it will be stored in the mantle as either diamond or a carbonate such as magnesite (Isshiki et al., 2004; Panero and Kabbes, 2008).
Carbon predominantly enters the mantle through the subduction process as carbonate mineral phases (Yaxley and Green, 1994; Kerrick and Connoly, 2001; Dasgupta et al., 2004). These phases remain stable through the process of sub-arc melting to be later sequestered into the deep mantle through subduction into the transition zone and lower mantle (Yaxley and Brey, 2004; Dasgupta et al., 2004; Furi et al., 2010; Ceron et al., 2000; Keshav and Gudfinasson, 2010). The potential for these carbonate phases to remain stable throughout the mantle depends upon their stability relative to mantle temperature ($T$), pressure ($P$), and oxygen fugacity ($fO_2$). Static compression studies (Biellmann, 1993; Isshiki et al., 2004) and shock studies (Sekine et al., 2006) show MgCO$_3$ to be chemically and thermally stable through the entire depth range of the mantle, suggesting that the major host of carbon throughout most parts of the lower mantle to be magnesite or, at pressures greater than ~100 GPa, magnesite II (Isshiki et al., 2004; Panero and Kabbes, 2008). However, these experiments and calculations are likely not under realistic mantle conditions with regard to oxidation potential. The lower mantle is likely too reducing to allow for carbonate stability, instead reducing C$^{4+}$ in carbonate to C$^0$ (diamond). Diamonds that appear to originate from the lower mantle (McCammon et al., 2004) contain periclase inclusions comprised of approximately 1% ferric iron (Fe$^{3+}$), suggesting reduced carbon is in equilibrium with oxidized iron in the lower mantle. Yet other diamonds originating from the upper mantle (Wang et al., 1996) and the lower mantle (Brenker et al., 2007) contain MgCO$_3$ and CaCO$_3$ inclusions, suggesting that carbonate is present in parts of the mantle in equilibrium with diamond. To resolve these conflicting observations, it is thus necessary to constrain carbon redox potential relative to the redox state of the laterally inhomogeneous lower mantle.
Magnesium silicate perovskite, the most abundant mineral in the lower mantle, plays a key role in governing mantle redox state. Perovskite can incorporate ferrous iron (Fe$^{2+}$) into the Mg sites, and ferric iron (Fe$^{3+}$) in a combination of the Mg and Si sites. As pressure increases with depth through the lower mantle, the perovskite lattice preferentially incorporates high levels of Fe$^{3+}$ to reach a peak Fe$^{3+}$/ΣFe ratio of 0.6, approximately twenty times that of the bulk upper mantle value (O’Neill, et al., 1993; Canil and O’Neill, 1996). Ferric iron can be incorporated into the perovskite lattice by way of a coupled substitution with Al$^{3+}$ for Mg$^{2+}$ and Si$^{4+}$ (Frost et al., 2004), but the presence of aluminum is not necessary, as perovskite has been shown have similar potential for ferric iron incorporation in the absence of aluminum (Auzende et al., 2008). The ferric/ferrous ratio of perovskite is strongly dependent on the volumes of the Fe$^{3+}$ and Fe$^{2+}$ ions relative to their host sited as a function of pressure, both of which dramatically affect the redox state of the mantle and the stability of mantle mineral assemblages. However, at extreme pressures, iron bearing mineral phases undergo several types of pressure induced transitions such as structural, electronic, and magnetic changes that affect chemical reactivity (Hemley et al., 2000). In that volume reduction is a key factor driving these changes, transitions in electronic spin state of iron from high spin to low spin are often energetically favored at pressures above 45 GPa, as they can decrease unit cell volumes by as much as 10% (Matilla et al., 2007). Knowledge of the compressibilities of phases that undergo electron spin transitions is somewhat lacking. Therefore, it is necessary to both thermodynamically model and experimentally determine the phase stability of minerals of interest.
Recent studies have revealed the presence of up to 1 wt% metallic iron in the lower mantle by way of a crystal chemically driven self-reduction of ferrous iron to form iron metal (Fe$^0$) and ferric iron that is incorporated into the perovskite lattice (Frost et al., 2004). As the perovskite lattice is compressed, the Fe$^{3+}$ content increases with pressure. In that this disproportionation of iron is said to be independent of oxygen fugacity, it is likely that the coexistence of reduced iron metal with ferric iron in ferropericlase and perovskite actually buffers mantle redox at or near the iron wüstite buffer (Frost and McCammon, 2008). This should be the case for most of the lower mantle except for the more oxidized regions, such as those near downgoing slabs and the region between D” and the core-mantle boundary. Downgoing slabs introduce surface mineral phases that formed at higher $fO_2$ relative to deep earth phases and, therefore, they buffer the surrounding material to a higher oxidation state. As for the region between D” and the CMB, the effects of pressure and temperature change perovskite to post-perovskite (Murakami, et al., 2004) and the disproportion reaction producing Fe-metal no longer occurs (Auzende et al., 2008), driving redox conditions in this region above those regions containing iron-metal. Therefore, constraining a mineral redox buffer that has both oxidized and reduced forms of carbon relative to mantle redox state will lend insight to what mineral phase carbon will assume, be it oxidized (carbonate) or reduced (diamond). It should be noted that this study does not account for carbonate stability as a function of the total redox state of the lower mantle, as it cannot be represented solely by the coexistence of iron-metal and wüstite. The effects of the downwelling mantle are somewhat neglected, as it contains high levels of majoritic garnet, in which iron can take on a range of valence states.
2. Background

Oxygen fugacity ($fO_2$) of the Earth’s interior is an important variable in deep-Earth crystal chemistry and petrology, as it is responsible for governing mantle mineral assemblages. Several trends in variation of $fO_2$ have been suggested, such as decreasing $fO_2$ with increasing depth (Rohrbach et al., 2007; Wood et al., 1990), based on the self-compression of phases containing reduced iron.

Oxygen fugacity is defined by the expression:

$$fO_2 = \gamma * a_n$$ (1)

where $\gamma$ is partial pressure of oxygen and $a_n$ is the activity coefficient of oxygen. $fO_2$ is a measure of the amount of free oxygen to which a particular system equilibrates. As a result, it is the amount of oxygen available to do work on a system. Oxygen fugacity controls the three valence states of iron, the fourth most abundant element in the Earth’s crust (Frost, 1991). For low $fO_2$, iron has Fe$^0$ valence state, which is referred to as native iron. This valence state is metallic iron, as found in the Earth’s core, where there is low oxidation potential driving the system. As oxygen fugacity increases, iron oxidizes and takes on the higher valence state of Fe$^{2+}$, ferrous iron. This is the most common valence state of iron in upper mantle minerals such as Fe$_2$SiO$_4$ (fayalite). In the highly oxidized crustal region of the Earth, iron is stable in its most oxidized form of Fe$^{3+}$, ferric iron, and resides in Fe$_2$O$_3$ (hematite).
A reaction displaying iron’s change from a reduced metal to a divalent cation by way of oxidation is the following:

$$\text{Fe}^0 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{FeO}$$  \hspace{1cm} (2)

This is an example of a mineral buffer system, the iron- wüstite buffer ($IW$). Another such buffer system, siderite-diamond-iron ($SDI$), can be represented by the reaction:

$$\text{Fe}^0 + \text{C}^0 + \frac{3}{2}\text{O}_2 \leftrightarrow \text{FeCO}_3$$  \hspace{1cm} (3)

The difference in $fO_2$ between a system containing some molar proportion of an oxide and some molar proportion of a reduced species relative to the pure phase buffer can be calculated by the following:

$$\Delta fO_2 = \log \frac{\alpha_{Ox}}{\alpha_M}$$  \hspace{1cm} (4)

where $\alpha_{Ox}$ and $\alpha_M$ are the activities in the oxide and the metal phases, respectively.

Activity, the product of mole fraction ($X$) and activity coefficient ($a_c$), can be represented solely by the mole fraction of the element of interest if activity coefficient is assumed to be 1, and Raoult’s law is obeyed. Making this assumption, eqn. 4 becomes:

$$\Delta fO_2 = \log \frac{X_{Ox}}{X_M}$$  \hspace{1cm} (5)

Oxygen fugacity ($fO_2$) can be expressed in terms of change in the Gibb’s free energy, $\Delta G$, of a particular reaction at a fixed temperature of interest and pressure of 1 bar (Frost, 1991) (eqn. 6):
Expanding eqn. 6 to incorporate fugacity over a range of pressure, \( fO_2 \) is calculated by the following relation of a buffer’s reactants to products:

\[
\log fO_2 = -y \left( \frac{\Delta H + \int_{P_0}^{P} \Delta VdP}{2.303RT} - \frac{\Delta S}{2.303R} \right)
\]  

(7)

where \( y \) is the reciprocal of the coefficient of oxygen in the balanced redox buffer equation, \( \Delta H \) is heat of formation, \( \Delta S \) is entropy of reaction, \( \int_{P_0}^{P} \Delta VdP \) is integrated volume change from reactants to products with respect to pressure, \( T \) is temperature in Kelvin, and \( R \) is the universal gas constant (Siebert et al., 2005). As temperature increases, the buffer moves to higher log units in oxygen fugacity space (Frost, 1991)(Fig. 1). Therefore, a particular assemblage imparts higher levels of oxygen activity at higher temperatures, thus having more potential to oxidize surrounding material. The net effect of increasing temperature is to drive a redox reaction toward oxidation. A similar effect is observed with increasing pressure from a fixed reference point (e.g.: 0.1GPa). As pressure increases, the integrated volume change from the standard pressure to the pressure of interest also increases, thus driving the buffer to higher log units in oxygen fugacity space and creating greater potential to oxidize surrounding material.
3. Methods

3.1 Thermodynamic Model

Using eqn. 7, actual and relative positions of the SDI and IW buffers were modeled thermodynamically at both experimental conditions, and along a representative mantle adiabat (Dziewonski and Anderson, 1981, Turcotte and Schubert, 2002). Pressure range modeled was 5 to 130 GPa. Temperatures were fixed at 2200 K to model experimental conditions, and varied with pressure to model natural conditions. The change in volume term was calculated according to a third order Birch-Murnighan equation of state for each relevant phase (Table 1). Key considerations that went into this model were: spin pairing transition in siderite from high to low spin at 45 GPa (Matilla et al., 2007; Lavina et al., 2009), and a phase change in iron-metal from fcc to hcp at 55 GPa (Shen et al., 1998).

When dealing with \( f_\text{O}_2 \) of a natural system, where elemental substitution often takes place, one must consider how the fugacity will deviate from that of the pure phase buffer. In the lower mantle, for example, Fe\(^{2+}\) often substitutes for Mg in minerals such as wüstite and perovskite. Replacing an element of variable oxidation states with one of fixed valence can cause the fugacity of the new assemblage to deviate from that of the pure phase assemblage. For example, Mg substitution into Fe\(^{2+}\) bearing wüstite can stabilize the phase to higher \( f_\text{O}_2 \), such as in the presence of hematite (Frost, 1991). This is achieved by decreasing the activity of the more reduced phase (wüstite). Conversely,
when ferrous iron is at the oxidizing end of a redox reaction (IW or SDI), Mg substitution will have the opposite effect, lowering the activity on the oxidizing side and thus lowering the fugacity of the assemblage. This effect can be represented by shifts in the IW or SDI buffer (eqn. 8, 9).

\[ \Delta f_{O_2}^{IW} = \log \frac{\alpha_{FeO}}{\alpha_{Fe}} \quad \text{or} \quad \Delta f_{O_2}^{SDI} = \log \frac{\alpha_{FeCO}}{\alpha_{Fe} \cdot \alpha_{Ca}} \]  

(8, 9)

Where \( \alpha \) is the product of mole fraction and activity coefficient, the latter of which is assumed to be 1 (valid when the enthalpy of mixing is 0). Therefore, \( \Delta f_{O_2}^{IW} \) and \( \Delta f_{O_2}^{SDI} \) can simply be represented by log of the mole fraction (\( X \)) of oxidized over reduced species:

\[ \Delta f_{O_2}^{IW} = \log \frac{X_{FeO}}{X_{Fe}} \quad \text{or} \quad \Delta f_{O_2}^{SDI} = \log \frac{X_{FeO} \cdot X_{CO}}{X_{Fe} \cdot X_{Ca}} \]  

(10, 11)

As Mg is a key element in the lower mantle, the effects of Mg substitution into Fe\(^{2+} \) sites of each buffer were investigated. Several hypothetical Mg/(Mg+Fe) ratios of each phase were modeled, as well as the concentration of the natural siderite sample obtained by EDS analysis on a Quanta 200 SEM: \([ (Fe_{74}Mg_{15}Mn_{8}Ca_{3})_{\Sigma=1}CO_3 ] \). All models incorporating Mg partitioning were done at 2200 K, the average temperature for all experimental runs.
3.2 Sample Preparation and Experimental Setup

The laser-heated diamond anvil cell (LHDAC) has recently been proven to be a powerful asset to high pressure works of the petrologic nature (Campbell et al., 2009; Auzende et al., 2010; Frost et al., 2010), allowing for the investigation of petrologic phase relations at pressures unachievable with multi-anvil press (MAP) and other more conventional high pressure techniques. The DAC becomes more useful when coupled with new methods of small scale sample preparation and spot analysis of single sub-micron sized grains, such as focused ion beam milling (FIB) and energy dispersive x-ray spectroscopy (STEM-EDX). However, with new application comes new potential for error that requires consideration. In that grain sizes in DAC experiments are quite small compared to grain sizes in conventional high-pressure techniques, there exists a greater potential for small amounts of contaminated material to influence results. One such factor that carries great potential for error, yet often is overlooked during sample preparation, is the presence of oxygen gas over starting materials. This was of special importance to this study for two reasons: there were highly susceptible iron species in the starting mix, and the carbonate phase had to be buffered as closely as possible to the IW buffer. FeO has a strong tendency to deviate from 1:1 stoichiometry under normal atmospheric conditions. However, the potential for iron-metal to become contaminated by oxygen and eventually alter the buffer system was unknown. To investigate this possibility, I conducted an experiment measuring the degree of oxygen contamination on a clean Fe-metal substrate as a function of time, under normal atmospheric conditions. A 40 micron iron foil was etched in a 10% HCL bath for 20 minutes (to remove previous surface oxygen). After etching, the foil was rinsed in isopropyl alcohol, dried quickly
with an N₂ gas gun, and placed under an ellipsometer, an instrument capable of measuring thin films on a substrate. I observed a thin (~100 nm) oxide layer (hematite) start to form on the metal substrate approximately 1 minute after the acid bath (Fig. 2). The oxide layer continued to grow until it hit a peak thickness of approximately 200 nm at time t=11 minutes. This oxide layer is, no doubt, a very small portion of the relatively thick foil. However, a 200 nm oxide layer can be very significant on a micron-sized spherical grain of iron. A 200 nm (0.2 µm) outer layer on a 1µm spherical grain will produce a contaminated grain 1.2 µm in diameter (Table 2, Fig. 3). The overall volume of the contaminated grain will be 1.44 µm³, 63.5% of which will be hematite. This is most definitely a significant amount of contamination and would skew results of an experiment requiring highly calibrated redox potential of a buffer system. In lieu of this, it was mandatory that all sample loading be done in the absence of oxygen. The volume % of contaminant is much lower for larger iron grain sizes (11.1% for 10 µm iron grain size), which is possibly why this phenomenon has been ignored for piston cylinder and multi anvil press experiments where deleterious effects were relatively undetectable.

To experimentally determine the relative positions of the two buffers, samples were prepared containing metallic iron (Fe), wüstite (FeO), and siderite (FeCO₃) then brought to pressures ranging from 21-62 GPa and temperatures ranging from 2100-2300K. Four samples, NC1, MC2, MC3, and MC6, (Table 3) were prepared for use in the laser-heated diamond anvil cell (DAC) at the OSU Mineral Physics Laboratory. Sample material consisted of metallic iron (Alfa Aesar, 1-3 µm, 98%+ purity), FeO (Alfa Aesar 99.5%+), hereafter referred to as wüstite, and a previously ground natural magnesium bearing siderite [(Fe₇₄Mg₁₅Mn₈Ca₃)Σ=86CO₃]. Before loading, 200µm thick
rhenium gaskets were preindented to approximately 30µm using diamond anvils. 100 µm holes were drilled through the center of each indentation using an EDM. All sample preparation was performed in a glove box saturated with nitrogen gas to minimize oxidation of the starting materials before compression and heating. Oxygen concentration in the loading box was monitored using an AII oxygen analyzer from Analytical Industries Inc. During all sample preparation, oxygen was never detected by the analyzer (detection limit 0.1% by volume). Approximate equal volumes of each phase were ground under agate mortar and pestle, and then compressed into thin plates ≈10 µm thick using tungsten blocks. Samples, accompanied by a small ruby grain, were then loaded into the previously drilled rhenium gaskets, and compressed. The first sample, NC1, was loaded using MgO as a pressure-transmitting medium; all following samples were loaded into argon (Table 3). Sample pressures were determined by the wavelength shift in ruby fluorescence peaks using a 488 nm argon ion laser. Samples MC2, MC6, NC1, and MC3 were compressed to 21, 41, 43, and 62 GPa, respectively. Subsequent laser heating was then conducted at the OSU mineral physics laboratory using a 40W diode-pumped YLF laser. Peak temperatures for each sample were 2,000 to 2,300K. Upon compression and heating, the oxidized phase of carbon (siderite) was buffered by the coexistence of iron and wüstite (IW buffer). Although both iron and wüstite starting materials were quite pure, the buffering potential may have sat slightly off the IW buffer, in that neither phase had 100% purity. The presence or absence of siderite reduction to diamond (accompanied by oxidation of iron and/or wüstite) was, therefore, indicative of the relative position of the SDI buffer to the IW buffer (eqn. 2, 3). Any detection of diamond would be evidence of completion of the reaction in eqn. 3.
3.3 Instrumentation

Bulk phase relations and unit-cell volumes as a function of pressure were determined at the X17C beamline of Brookhaven National Laboratory. The 2 dimensional diffraction patterns were generated by a monochromatic x-ray source of wavelength 0.4066Å and approximate beam dimensions of 25 x 25 µm, with diffraction collected on a 135 mm MAR-CCD. Sample to film distance was calibrated by CeO\textsubscript{2} diffraction. In that diamond was an analyte of interest, but is very insensitive to XRD, further sample analysis was carried out by Raman spectroscopy at the Analytical Spectroscopy Laboratory in the Department of Chemistry at Ohio State University. The instrument used was a Renishaw-Smiths Detection Combined Raman-IR Microprobe with a 633 nm wavelength laser, where the wavelength was chosen to minimize sample fluorescence. The instrument is capable of spot analysis of 2 x 2µm, and excitation volume of approximately 8µm\textsuperscript{3}, making it ideal for small sample area analysis, as well as investigation of possible radial heterogeneities in the experimental product. However, due to the very small excitation volume, this method was almost useless for samples loaded with a solid pressure transmitting medium. Sample NC1, loaded in MgO, required another method for small-scale analysis. Focused Ion Beam Milling (FIB), a powerful method of generating thin foils, was carried out with a Nova 600 at the Campus Electron Optics Facility of Ohio State University (Fig. 4). The foil was milled from the sample directly in the Re gasket, thus eliminating the cumbersome step of transferring the sample material to a TEM grid or other medium. The Ga\textsuperscript{+} ion beam constructed a 10µm wide by 5µm deep cross sectional slice of the sample. The same beam was then used to thin the foil to electron transparency (approximately 100 nm), which is achieved when a
5 keV beam can illuminate the sample. The foil was then lifted out manually with a borosilicate needle and placed onto a TEM grid. STEM-EDS was conducted by a Tecnai F20 in the same facility. Spot size of a few nm made it possible to get EDS information on single grains only 100 nm in diameter. TEM was also performed by the same instrument on several grains of interest, but resulting transmission patterns did not reflect one, but several sets kikuchi lines per grain, suggesting the grains did not penetrate the depth of the entire sample.
4. Results

4.1 Thermodynamic Model Results

Thermodynamic modeling indicates the SDI buffer sits at a higher \( f/O_2 \) than the IW buffer across the entire pressure range of the Earth’s mantle (5 to 130 GPa), both at experimental temperatures (2200K) (Fig. 5a) and along a representative adiabatic gradient (Fig. 5b). For the 2200K model, the buffers are approximately 1.4 log units apart at 5 GPa (Fig. 5c). As pressure increases, the SDI buffer gradually diverges from the IW buffer to a maximum difference of 2.4 log units just before the 45 GPa spin pairing transition in siderite (Matilla et al., 2007; Lavina et al., 2009). At higher pressures, the two buffers re-converge to a difference of 1.5 log units at 130 GPa. This convergence is the result of the 10% volume reduction in siderite across the spin transition, accompanied by a 10% increase in bulk modulus. The increased stiffness of the siderite greatly reduces the \( \int_{P_o}^P \Delta V dP \) term of eqn. (8) for the SDI buffer, thus decreasing its fugacity.

Although a similar transition occurs in magnesiowüstite near 40 GPa (Lin et al., 2007), pure iron wüstite does not undergo the spin pairing transition until 90 GPa (Speziale et al., 2005) with a volume reduction of approximately 3% leading to little effect on the difference between the two buffers. Therefore, the model predicts that at high pressure and temperature, FeCO\(_3\) (siderite) buffered by IW will reduce to diamond at the expense of oxidizing iron or wűstite, with greatest reduction potential near 45 GPa.
Also investigated was the effect of magnesium substitution into the wüstite and siderite phases according to eqn. 10 and eqn. 11, respectively. Whenever Mg substitutes for Fe\(^{2+}\) into a mineral on the oxidizing side of a redox reaction, the buffer’s \(fO_2\) decreased. However, the net effect on the difference between the SDI buffer and the IW buffer is a strong function of Mg partitioning between the siderite and wüstite phases. A magnesium partition coefficient \(D_{Mg}(FeCO_3/FeO)\) of 1 was set to the approximate mantle Mg/(Mg+Fe) ratio of 0.8 for each phase. With equal magnesium partitioning between siderite and wüstite there is no net difference between the two buffers, though each buffer does decrease by 0.51 log units in oxygen fugacity space (Fig. 6a, d). When Mg partitioning into the siderite phase is an order of magnitude greater than in wüstite \(\left(\frac{D_{Mg}(FeCO_3/FeO)}{10}\right)\), giving concentrations of \((Fe_{20}Mg_{40})CO_3\) and \((Fe_{90}Mg_{8})O\), the SDI buffer drops 0.51 log units, while the IW buffer only drops 0.022 log units (Fig. 6b). With these concentrations, the two buffers become approximately 0.5 log units closer (Fig. 6d). When Mg partitioning into the siderite phase is an order of magnitude lower than in wüstite \(\left(\frac{D_{Mg}(FeCO_3/FeO)}{0.1}\right)\), giving concentrations of \((Fe_{90}Mg_{8})CO_3\) and \((Fe_{20}Mg_{80})O\), the SDI buffer drops 0.022 log units, while the IW buffer drops 0.51 log units. With these concentrations, the difference between the SDI buffer and the IW buffer increases by approximately 0.5 log units across the entire pressure range (Fig. 6d).

Also calculated was the fugacity of the SDI buffer according to the cation concentration of the natural siderite sample used in these experiments \[\left(Fe_{74}Mg_{15}Mn_{8}Ca_{3}\right)_{\Sigma=1}CO_3\]. The concentration of the natural siderite sample causes the SDI buffer to drop by only 0.1 log units, as well does the difference between the SDI buffer and IW buffer.
4.2 Experimental Results

All samples show x-ray diffraction patterns of each starting component, as well as run products not present in the starting material (Figure 7). Iron and siderite were detected in each sample in varying proportions. Only small siderite peaks were present in each sample, while iron peaks present were much more intense. X-ray diffraction patterns of those samples loaded in an argon pressure medium show a small peak corresponding to the [111] plane in the diamond lattice (Fig. 4). However, due to the relatively weak reflectance of diamond and a strong overlap with insulating medium, diamond was not detected by x-ray diffraction in sample NC1, loaded in MgO.

Wüstite was detected in all samples through x-ray diffraction. Lattice parameters \( \alpha \) and unit cell volumes of wüstite were calculated according to a least squares fit to the [111], [200], and [220] atomic planes. Iron depletion of the wüstite unit cell was then determined according to the relation of ‘x’ in \( \text{Fe}_x\text{O} \) to \( \alpha \) (McCammon and Liu, 1984) where:

\[
\alpha = 5.656\text{Å} + \frac{0.476\text{Å}}{\text{Fe}_x} \times x
\]

As predicted by the model, all samples show iron depletion of wüstite (Fig. 8). The highest amount of iron depletion was detected in sample MC6, synthesized at 41 GPa and 2200K (7-8.5%), with moderate amounts depleted from samples MC2 (21 GPa and 2100K) (4-6%) and MC3 (62 GPa and 2300K) (5-6%), as predicted by our model. Cell NC1, loaded in MgO and synthesized at 43 GPa and 2200K, shows relatively lower iron
depletion of wüstite (5-6.2%) than cell MC6, synthesized at similar pressure and temperature.

X-ray diffraction patterns of sample MC2 revealed small peaks corresponding to the [002] and [131] atomic planes of the iron-carbide cementite (Fe₃C). Other unidentified peaks exist at 2.22Å (MC3), 2.58Å and 2.88Å (MC2), and 2.95Å (NC1). These are assumed to be another iron-carbide other than cementite. It should be noted that, other than the peak in sample MC3 at 2.22Å, the occurrence of these unidentified peaks were detected in less than half of all spectra of the corresponding sample.

Because the weakly reflected diamond peaks in the x-ray diffraction patterns were very small compared to the other phases (Fig.7), it was necessary to confirm the presence of diamond by other means to ensure its presence in the experimental products. Raman spectroscopy was performed on each sample. Approximately 10 – 15 spectra were taken on each sample. All samples showed diamond Raman shifts at or near 1332 cm⁻¹ (Fig. 9) except for MC3, synthesized at 62 GPa and 2300 K. In this sample, a very intense, broad peak at 1369 cm⁻¹ (R1 ruby) was present and overlapped the diamond peak position at 1332 cm⁻¹. Diamond was detected in samples MC2, MC6, and NC1 (Fig. 9). While most peaks were centered at 1332 cm⁻¹, few appeared at slightly lower wavenumber, the lowest of which was observed in sample MC2 (21 GPa and 2200K), which exhibited a diamond Raman shift at 1325 cm⁻¹. Most diamond peaks in all samples were quite broad, laterally extending as far as +/- 90 cm⁻¹. However, there was occasionally a narrow, intense diamond peak in sample MC6 (41 GPa and 2200K). Of the 14 Raman spectra containing diamond 3 patterns contained both diamond and siderite. One pattern of sample NC1 and two of sample MC6 showed Raman patterns of siderite (1086 and 128 cm⁻¹), as well as
diamond, indicating that either the two phases were in equilibrium under IW conditions or they represent spatially varying temperatures over the depth range of the sample (Panero and Jeanloz, 2001). Also of notable interest was the detection of a recently reported second Raman shift for wüstite at 217 cm⁻¹ (Ovsyannikov et al., 2010).

Sample NC1, loaded in MgO and synthesized at 43 GPa and 2200 K, was not suitable for Raman due to the very small excitation volume of the beam. Almost all attempted runs on the Raman system yielded only insulating medium, with one single spectrum yielding analytes of interest (Fig. 9c). To get better small scale analysis and definite presence/absence of diamond in the run product, focused ion beam (FIB) coupled with STEM-EDS was employed. STEM-EDS analysis on the FIB thin foil section of sample NC1 revealed the presence of several carbon rich grains (>95% C) assumed to be diamond (Fig. 10). Grain sizes ranged in diameter from 50 nm (Fig. 10b) to 500 nm (Fig. 10c), making them too small for characterization by many conventional methods. TEM was performed on these grains, but the resulting pattern appeared polycrystalline, yielding Kikuchi lines unsuitable for proper indexing. This suggests the diamond grains either did not penetrate the entire thickness of the FIB foil, or they are each represent one nucleating grain that quenched to several upon cooling. The Kikuchi patterns were, however, indicative of a cubic lattice. The small sizes of the grains are consistent with the broad diamond Raman shift detected in other samples. Furthermore, the small grains and low diamond abundance lends insight as to why diamond peaks did not dominate the XRD spectra of each cell. This observation illustrates the strength of the FIB-STEM method applied to DAC works of the petrologic nature, where experimental products are usually small and often undetectable by conventional bulk XRD methods.
The STEM-EDS analysis on the foil lifted from sample NC1 (43 GPa and 2200K) also provided an opportunity for estimating the $fO_2$ of this experimental run. According to equations 10 and 11 and assuming activity coefficients of 1 for each phase, spot analysis of grains from the heated area of the foil give a $\Delta fO_2^{IW} = +0.3$ log units and $\Delta fO_2^{SDI} = -0.08$ log units, indicating the system equilibrated above the IW buffer and below the SDI buffer.
5. Discussion

5.1 -Experimental

Either solely by x-ray diffraction or by a combination of x-ray diffraction and other spectroscopic analyses, diamond was detected in all experimental runs, suggesting the SDI buffer to be above the IW buffer at each pressure and temperature studied. Siderite peaks were also observed in most runs; however, it is assumed that this siderite is from cooler, unreacted areas of the sample (Panero and Jeanloz, 2001). In the presence of excess oxygen (from siderite), iron in Fe_xO has a strong tendency to become oxidized to Fe^{3+}, leaving the mineral’s charge unbalanced. In order to neutralize charge, a fraction of iron will vacate the wüstite lattice. Measured zero-pressure wüstite lattice parameters were used to determine the mole fraction iron, x, in Fe_xO according to eqn. 12. Any detection of x<1 indicates the wüstite phase incorporated some Fe^{3+} into its lattice by way of reduction of the siderite. How far the stoichiometry of the Fe_xO phase deviates from a 1:1 ratio of Fe to O can serve as a proxy for the degree of reduction potential between the two buffers. That is, the lower the x in Fe_xO, the farther the buffers are apart from each other in fO_2 space. The model predicts that at 21, 41, and 62 GPa, the SDI buffer will be 1.9, 2.4, and 2.3 log units above the IW buffer, respectively (Fig. 5c). This is supported by the trend of wüstite lattice parameter to pressure quenched (Fig. 8), where iron depletion is lowest at 21 GPa (4-6%), highest at 41 GPa (7-8.5%), and moderate at 62 GPa (5-6%). The lattice parameter of sample NC1 quenched from 43 GPa, however, is
not in agreement with the model. It is possible that the wüstite lattice parameter of this sample does not fit the predicted trend because it was insulated in MgO, rather than inert argon gas compressed to a solid. Apparently, the MgO participated in the assemblage, dampening the redox potential between the IW and SDI buffers, resulting in lower oxygen activity of the siderite phase. It should be noted, however, that it is unlikely that the MgO played a large role in lowering the redox potential of the sample, as a result of low temperatures near the diamond anvil surfaces. More so, a reduction of siderite is evidenced by diamond that was detected by STEM-EDX.

The possible presence of diamond in the x-ray diffraction spectra can be supported by the Raman data. As stated, all samples except MC6 (62 GPa and 2300K) showed diamond at or near 1332 cm\(^{-1}\). Much can be inferred about the physical nature of the diamond grains synthesized in these experiments based on the appearance of their Raman shift. Often, diamond peaks were broad, exhibiting linewidth broadening as high as 90 cm\(^{-1}\). This broadening is indicative of an average Raman shift of several small grains of varying size, similar to Raman shifts observed in chemical vapor deposition (CVD) nanodiamond thin films (Ferreira et al., 2002). Several diamond peaks were not directly on the 1332 cm\(^{-1}\) wavenumber, shifting to wavenumber as low as 1325 cm\(^{-1}\). This shift to lower wavenumber can be interpreted as a result of residual compressive stress on the diamond(s) generating the Raman shift (Ferreira et al., 2002), or as an effect previously observed in Raman spectra of single diamond crystals ranging from 35nm to 90nm in diameter (Sun et al., 2008). In the latter study, the shift to lower wavenumber and associated linewidth broadening was attributed to phonon-confinement effects of the nano-scale single diamond crystals of irregular shape. Both of these scenarios can be
supported by the FIB generated thin foil of sample NC1 (43 GPa and 2200K), as diamond grains ranged in size from 50 to 500 nm, the largest of which was quite irregular in shape (Fig. 10). Of the 14 Raman spectra containing diamond two patterns from sample MC6 (41 GPa and 2200K) and one from NC1 (43 GPa and 2200K) contained both diamond and siderite. Unless the SDI buffer is equal to the IW buffer at these pressures and temperatures, which is inconsistent with the model, it is possible that this area of the sample was depleted in Fe relative to FeCO₃. In this case, siderite reduction was limited by the amount of iron present locally due to heterogeneous loading. It is also possible that the siderite was from a cooler region(s) of the sample, as was the case with x-ray diffraction spectra containing siderite. Fe₂O₃ (hematite) was seen in the Raman pattern from samples MC2 and MC6 (loaded in argon). However, this does not necessarily mean it is present as a run product or from oxygen contamination during sample loading. If that was the case, it would have been detected by x-ray diffraction. It is more likely that this hematite was a result of surface oxidation on the iron and/or wüstite phases that occurred while sitting in the Re gasket in the presence of air for several weeks, as the argon insulating medium evaporated upon pressure quench, exposing the samples.

The thin foil extracted from sample NC1 serves as the hardest piece of evidence for diamond synthesis in these experiments. While EDS is somewhat limited in quantifying elemental concentrations, it is quite useful for qualitative elemental identification. The identification of several grains comprised almost solely of carbon serve to support possible diamond identification in the x-ray and Raman pattern(s) of this cell. In that this foil was lifted from the sample loaded in MgO, where redox potential may have been dampened by the presence of the insulating medium, the detection of
diamond also strengthens results from other samples loaded in argon, where the redox reactions would have been unhindered by the presence of an oxide insulator.

The STEM-EDS spot analysis of several grains in the foil was used to calculate the fugacity to which the system equilibrated at 43 GPa and 2200K. Consistent with the model, chemical analyses indicated SDI resides above IW at these pressure-temperature conditions. However, the model predicts at 43 GPa and 2200K, the natural siderite bearing SDI buffer should reside 2.25 log units above the IW buffer, while the STEM-EDS data suggests they are only 0.38 log units apart. In that eqn. 10 and 11 are based on a log scale, it would require 2 orders of magnitude difference in the ratios of mole fractions from IW and SDI. That is, assuming all activity coefficients are 1, \( \frac{X_{FeO}}{X_{Fe}} \) would have to be approximately 1 and \( \frac{X_{FeO} \cdot X_{CO_2}}{X_{Fe} \cdot X_{C}} \) would have to be 0.01. In that it is highly unlikely that the ratio of \( \frac{X_{FeO} \cdot X_{CO_2}}{X_{Fe} \cdot X_{C}} \) will ever approach 0.01, it is evident that all activity coefficients cannot be assumed to be 1.

5.2 - Model

It has been said that due to the existence of the reduced iron-metal phase, the lower mantle will be too reducing to allow for oxidized carbon to be chemically stable (McCammon et al., 2004). However, there are several conditions that must be accounted for if this question is to be answered with any confidence. A major question is how much does the redox state of the lower mantle vary with position. Another large question is
where the lower mantle sits relative to the SDI buffer and how the physical properties of
the low-spin siderite phase will affect the position of the SDI buffer and, essentially,
determine carbonate stability.

5.2a SDI vs. IW and the effects of the ls-siderite phase

My calculations show that the SDI mineral redox buffer will always reside above
IW, but never by more than 2.5 log units, both at experimental temperatures and along a
representative mantle adiabat. The greatest difference between the two buffers occurs
just before the siderite spin transition (Matilla et al., 2007; Lavina et al., 2009). At
conditions beyond those required for the siderite spin transition, the effects of pressure
drive the two buffers closer together. This can be explained by the physical properties of
the ls-siderite phase. As siderite undergoes the change in spin state, it also undergoes a
10% decrease in unit cell volume (Lavina et al., 2009) and a 10% increase in bulk
modulus. This stiffening of the siderite lattice results in a smaller change in volume with
respect to pressure compared to the weaker high spin siderite, thus lowering the $\Delta V$ term
in eqn. 8. Because the change in volume between reduced and oxidized components of a
redox reaction has great influence on the absolute $fO_2$ of a system (Campbell et al.,
2009), the SDI buffer decreases in $fO_2$ space as the $\Delta V$ term decreases. Essentially, the
stiffening of this carbonate phase across the spin transition has dramatic effects on the
SDI buffer over the pressure range of the mantle. In the lowermost part of the mantle,
where $fO_2$ is above IW, the SDI buffer will reside below mantle oxidation state and
carbonate should be stable.
The 10% volume reduction across the siderite spin transition will also have dramatic effects on the chemistry of the divalent cation population of the siderite crystal lattice, which will, in turn, affect siderite stability with respect to mantle redox. Based on direct measurements of volume reduction across the siderite spin transition (Lavina et al., 2009) and those predicted by first-principles calculations (Shi, et al., 2008), our model shows that a 10% decrease in unit-cell volume brings the volume of the ls-siderite unit cell much closer to that of the previously experimentally determined magnesite unit cell (Fiquet et al., 2002). This will facilitate Mg substitution into the Fe$^{2+}$ sites of the ls-siderite lattice. In that there would now be less ferrous iron requiring some pressure of oxygen holding it as a divalent cation, this substitution should stabilize the ls-siderite phase with respect to redox. It should be noted that our back calculated estimate of $V_0$ for ls-siderite (25.59 cc/mol) is slightly lower than that of Lavina et al., 2009 (26.37 cc/mol). However, both studies agree that the effect of the spin transition drives the volume of the siderite unit cell closer to that of the magnesite unit cell, with the two volumes converging closer as pressure increases.

5.2b Mantle oxidation state and carbonate stability

In a laterally and axially inhomogeneous mantle, there is expected to be variation in several factors that determine the local stable mineralogy, such as oxidation state. One setting that mantle oxidation state should reside well above IW would be near subducted slabs, where relatively oxidized oceanic lithosphere descends deep into the mantle (Hutko et al., 2006). These settings should not be viewed as insignificant to deep mantle
chemistry. Seismic tomography shows that in areas of long lived plate subduction, oceanic slabs can sink all the way to the core-mantle boundary, folding upon themselves and creating huge piles of colder, oxidized material more than 1,000 km wide and 300 km high (Hutko et al., 2006). These slabs have great potential for chemical exchange with the surrounding mantle, thus raising local oxidation state relative to the rest of the mantle at a similar depth. Furthermore, subduction zones are responsible for introducing carbon to the mantle, thus having great significance on deep carbon oxidation state.

Studies have shown that ferrous iron in ferropericlase will self-reduce to form iron-metal and ferric iron, the latter of which is incorporated into the perovskite lattice (Frost et al., 2004). However, more recent studies have proven that this process does not occur in conjunction with the post-perovskite (ppv) phase (Auzende, et al., 2008), which is the likely dominant mantle phase below D” (Hirose, 2006). It can be proposed, then, that the absence of this iron-metal phase will raise the oxygen fugacity of the lowermost mantle above the IW buffer, stabilizing carbonate phases and possibly having dramatic effects on core-mantle exchange of carbon. Auzende et al., 2006 discussed the notion that the formation of the PPv phase and the D” region was the result of the later stage loss of primordial core heat bringing the lowermost mantle into the PPv stability field (Hirose, 2006). This isolated the overlying metal and Pv bearing mantle from the metal-rich iron core, thus limiting iron exchange between the mantle and core and locking in the oxygen fugacity of the mantle. It is possible a similar situation existed for carbon. Early in the Hadean, when the temperature at the base of the mantle was above PPv stability, Pv would have been the dominant phase and the self-oxidation of Pv would have allowed for the existence of iron metal. Under these reducing conditions, it is likely that all carbon,
other than the very small concentration dissolved into mantle silicates (Keppler et al., 2003; Dasgupta and Walker, 2008), would be hosted as diamond and/or iron-carbide (cementite) rather than carbonate. In that carbon in both diamond and cementite is more siderophile than that from a carbonate host, it is logical to propose that there was unhindered carbon exchange between the silicate mantle and the iron-rich core during this period. After the lowermost mantle cooled enough to allow for the formation of PPv, carbon would have taken on the oxidized host of carbonate, likely Mg-siderite or Fe-magnesite. After this point, it is likely that the exchange rate of carbon between the silicate mantle and core was dampened. The larger question is, however, how much carbon was actually present at the CMB before and during this time. Moreover, did the formation of the PPv phase and subsequent oxidation of the lowermost mantle come before, soon after, or much later than the late stage chondritic veneer that brought much carbon to the planet? Any comprehensive attempt to quantify carbon concentration of the core will have to take these conditions into account. Regardless, it appears that if carbon is a major light element of the core with concentrations as high as 6-7 wt.% (Dasgupta and Walker, 2008), it would have to have been sequestered prior to the formation of the PPv phase. It is most likely that carbon alone does not account for the density deficit in the core, but may be a contributor (Hillgren et al., 2000).

Previous attempts to quantify present day carbon content in the core have likely not taken the necessary factors into account. Studies such as those derived from calculations of carbon solubility into mantle silicates vs. iron metal (Dasgupta and Walker, 2008) are not relevant, as carbon saturated dissolution into silicates has already been proven to be too low to account for expected mantle concentrations (Keppler et al.,
2003). In this regard, it is likely that most mantle carbon is in the form of a stable mineral host such as diamond, magnesite, or magnesite II (Panero and Kabbes, 2008). Therefore, any study basing carbon concentration in the core on a calculated $D_{\text{C, silicate/metal}}$ will overestimate sequestration into the core, overlooking the fact that carbon does not necessarily have to dissolve into a silicate phase to reside in the mantle. Experimental studies have also been used to serve as a proxy for C partitioning between mantle and core by extrapolating data from relatively low pressures. However, it is likely that the pressure intervals of the works do not fully represent the high-pressure chemical behavior of elements such as carbon and iron, both of which have multiple hosts with variable spin states that do not exist at near ambient to upper mantle pressures. Any comprehensive attempt at constraining carbon content of the core must take into account the following: carbon concentration at and around the CMB as a function of time, and carbon host(s) over time, as a function of redox state over time. It is likely that the present day scenario at the CMB cannot serve to represent the conditions under which the core and mantle equilibrated with respect to carbon. Several profound events must be chronologically ordered before any sound constraint is reached: core formation, addition of chondritic carbon by the late veneer, initiation of Hadean tectonic process (Hopkins et al., 2008) that would eventually get that carbon near the CMB, and the point at which the lowermost mantle cooled enough to fall into PPv stability (affecting carbon host(s) over time).
6. Conclusions

Experimental results show that when buffered by IW under upper and lower mantle conditions, C in FeCO₃ will reduce to diamond. Thermodynamic calculations show that at 5GPa and 2200 K SDI is approximately 1.4 log units above IW. As pressure increases, the two buffers diverge to a maximum difference of 2.5 log units at 45 GPa and 2200 K. Beyond this pressure, FeCO₃ siderite undergoes a high to low electron spin pairing transition, accompanied by a 10% volume reduction and 10% increase in bulk modulus. After which, the effects of pressure cause the two buffers to gradually converge back to 1.5 log units apart at 130 GPa and 2200 K. This overall trend with pressure is supported by empirical measurements relating reduction in wüstite unit cell volume to oxygen incorporation into the wüstite crystal lattice. Together, these experimental and theoretical results suggests that in a laterally and axially inhomogeneous mantle, where redox state can vary by as many as a few log units in \( f_O^2 \) space, carbonate phases will at times reduce to diamond, and in more oxidizing regions such near subducting slabs and between D” and the core-mantle boundary, carbonate will be the chemically stable host of carbon. In that carbonate phases are less siderophile than diamond, present day carbon exchange between the mantle and core should be relatively limited. If carbon is a major volatile component of the core, it would have to have been sequestered prior to the late stage formation of the post-perovskite phase and the D” region.
Tables

Table 1- Elastic parameters for relevant phases for thermodynamic model of $fO_2$ of the SDI and IW buffers. $V_0$ for ls-siderite was back calculated from spin transition.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$V_0$ (cc/mol)</th>
<th>$K_0$ (GPa)</th>
<th>$K'$</th>
<th>$\Delta H^o_f$ (kJ/mol)</th>
<th>$S^o$ (J/mol · K)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Iron-fcc</td>
<td>6.78</td>
<td>133</td>
<td>5</td>
<td>7.84</td>
<td>35.8</td>
<td>30, 31</td>
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<td>Iron-hcp</td>
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<td>5.33</td>
<td>7.7</td>
<td>34.4</td>
<td>32, 31</td>
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<td>Wüstite</td>
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<td>4</td>
<td>-267.27</td>
<td>57.59</td>
<td>33, 34</td>
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<tr>
<td>Siderite-hs</td>
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<td>117</td>
<td>4</td>
<td>-755</td>
<td>95.47</td>
<td>35, 36</td>
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<tr>
<td>Siderite-ls</td>
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<td>-755</td>
<td>95.47</td>
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<tr>
<td>diamond</td>
<td>3.42</td>
<td>442</td>
<td>4</td>
<td>1.897</td>
<td>2.38</td>
<td>37, 38</td>
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Table 2- Parameters used to calculate effect of 200nm oxide layer on an iron substrate

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<tr>
<th>Grain size Fe (µ)</th>
<th>Radius Fe (µ)</th>
<th>Radius Fe + oxide (µ)</th>
<th>Volume Fe (µ³)</th>
<th>Volume Fe + oxide (µ³)</th>
<th>Volume oxide (µ³)</th>
<th>Volume % oxide/∑volume</th>
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<tr>
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Table 3- Conditions and sample loading configuration for each experiment.

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<tr>
<th>Sample</th>
<th>Starting Material</th>
<th>Insulating Medium</th>
<th>Sample Preparation Atmosphere</th>
<th>Peak Pressure (GPa)</th>
<th>Peak Temperature (K)</th>
<th>Analytic Methods Utilized</th>
<th>Run Products</th>
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</thead>
<tbody>
<tr>
<td>MC2</td>
<td>Fe, FeO, FeCO₃</td>
<td>Argon</td>
<td>Argon gas</td>
<td>21.5</td>
<td>2100</td>
<td>XRD, Raman</td>
<td>Fe, FeO, FeCO₃, C, Fe₃C, unknown</td>
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<tr>
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<td>Fe, FeO, FeCO₃</td>
<td>Argon</td>
<td>Nitrogen gas</td>
<td>41</td>
<td>2200</td>
<td>XRD, Raman, FIB-EDS</td>
<td>Fe, FeO, FeCO₃, C</td>
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<td>MgO</td>
<td>Nitrogen gas</td>
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<td>2200</td>
<td>XRD, Raman, STEM/XRD</td>
<td>Fe, FeO, FeCO₃, C</td>
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<tr>
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<td>Fe, FeO, FeCO₃</td>
<td>Argon</td>
<td>Nitrogen gas</td>
<td>62</td>
<td>2300</td>
<td>XRD, Raman</td>
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**Figure 1**-Log $f_O^2$ as a function of temperature (Frost, 1991). (MH, magnetite-hematite; NiNiO, Nickel-nickel oxide; FMQ, fayalite-magnetite-quartz; WM, wüstite-magnetite; IW, iron-wüstite; QIF, quartz-iron-fayalite).
Figure 2- Ellipsometry data of iron oxide thin film formed on clean iron foil after etching in 10%HCl bath. The peak thin film thickness at time 11 minutes corresponds to an approximate thickness of 200nm.
Figure 3- Volume % of oxide contamination on iron grains as a function of grain size
Figure. 4 SEM images acquired during Focused Ion Beam Milling (FIB) procedure. (a, b) Images looking down the gasket at 56° prior to and 90° after etching (respectively). Sample was milled and lifted directly from gasket, eliminating need to transfer sample to TEM grid. The gallium single isotope ion beam mills out a 20 x 20 µm section above and below the area of interest. (c) Note the differential milling rates of the different phases. The carbonate phase undoubtedly gets milled the fastest, due to its low melting point, low hardness, etc. Each “x” in platinum CVd (white) serves to relocate Ga⁺ beam during milling. (d) 5 kev image taken as the section was being thinned to electron transparency. Notice features become more apparent as thinning progressed. Final thickness is approximately 100 nm. (e, f) Once sample is of desired thickness, tabs are milled away and sample is then lifted out manually.
Figure 4

(a) Image 1
(b) Image 2
(c) Image 3
(d) Image 4
(e) Image 5
(f) Image 6

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Fig. 5. (a) The SDI (red) and IW (blue) buffers in log $f_{O_2}$ as a function of pressure (GPa) at 2200K and (b) the difference between the two buffers as a function of pressure. The two buffers diverge until the 45 GPa siderite spin transition (Matilla et al., ’07, Lavina et al. ’09), then converge as a function of pressure. The discontinuity at 50 GPa represents the high-temperature iron phase transition from fcc to hcp structure (Shen et al., 1998).
**Figure 6** - (a-c) Plots of calculated shifts in $fO_2$ vs. pressure (GPa) for different Mg partition coefficient: $D_{Mg}(\text{FeCO}_3/\text{FeO})$ according to eqn. 11 (IW) and 12 (SDI) and (d) differences between SDI and IW vs. pressure (GPa) for various partition coefficients. Original positions of pure phase buffers are in gray. (a) Mg partition coefficient of 1 yields a Mg/(Mg+Fe) ratio of 0.8 for both siderite and wüstite. There is no change in difference between the two buffers from that of the pure phases (d), but each buffer drops 0.51 log units in $fO_2$ space. (b) Mg partition coefficient of 10 yields a Mg/(Mg+Fe) ratio of 0.8 for siderite and 0.08 for wüstite. This causes the SDI buffer to drop by 0.51 log units, considerably more than the IW buffer which only drops by 0.022 log units. With this $D_{Mg}$ the buffers are approximately 0.5 log units closer than those of the pure phases. (c) Mg partition coefficient of 0.1 yields a Mg/(Mg+Fe) ratio of 0.08 for siderite and 0.8 for wüstite, causing the SDI buffer to drop only 0.022 log units, and the IW buffer to drop 0.51 log units. For this Mg partition coefficient, the difference between the two buffers increases by approximately 0.5 log units compared to the pure phase buffers across the pressure range.
Figure 6 (continued)

b

IW and SDI vs P (GPa) for $D_{Mg}(FeCO_3/FeO)=10$

![Graph showing IW and SDI vs P (GPa) for $D_{Mg}(FeCO_3/FeO)=10$.]

Log $fO_2$ vs Pressure (GPa)

- Log $fO_2$ SDI (2200K)
- Log SDI 2200K (Fe20Mg80)CO3
- Log fO2 IW (2200K)
- Log IW 2200K (Fe92Mg8)O

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c

SDI and IW vs. P (GPa) for $D_{Mg}(FeCO_3/FeO)=0.1$

![Graph showing SDI and IW vs. P (GPa) for $D_{Mg}(FeCO_3/FeO)=0.1$.]

Log $fO_2$ vs Pressure (GPa)

- Log $fO_2$ SDI (2200K)
- Log fO2 SDI 2200K (Fe92Mg8)CO3
- Log fO2 IW (2200K)
- Log fO2 IW 2200K (Fe20Mg80)
Figure 6 (continued)

d

**SDI - IW vs. P (GPa)**

- **SDI-IW DMg(FeCO3/FeO)=0.1**
- **SDI-IW 2200K DMg(FeCO3/FeO)=1**
- **SDI-IW DMg(FeCO3/FeO)=10**

![Graph showing SDI - IW vs. P (GPa)](image-url)
Figure 7—XRD patterns of recovered samples: a.) MC2, b.) MC6, c.) NC1, and d.) MC3. Diamond and Fe$_3$C (cementite) were not in starting material and are, therefore, present as run products (where detected). Unidentified peaks at 2.58 and 2.88Å (a), 2.95Å (c), and 2.22Å (d) are assumed to be an iron carbide other than cementite. Siderite and iron diffraction peaks are assumed to be remnants from relatively cool, unreacted region of the sample chamber, illustrating strong axial temperature gradient across the sample (Panero and Jeanloz, 2001). Samples with 2 representative curves (a and c) contain rare unidentified run products that are not in every pattern. Notably, the upper curve of sample MC2 (red) contains several unidentified peaks and a very weak diamond [111] peak, while the lower curve (black) is lacking the unidentified peaks at 2.58 and 2.88Å, yet has a much more defined diamond [111] peak at 2.06Å.
Figure 7 (continued)

b

Continued
Figure 7 (continued)
Figure. 7 (continued)

d

Cell 3 quench (62 GPa, 2100 K)

Intensity (%) vs D-spacing (Å)

1.0 1.5 2.0 2.5 3.0 3.5 4.0

25 30 35 40 45 50 55 60
Figure 8- $\Delta f_{O_2}$ IW-SDI, ‘X’ in Fe$_x$O and lattice parameter of Fe$_x$O run products as a function of synthesis pressure (black=argon insulating medium; green=MgO insulating medium). ‘X’ in Fe$_x$O was calculated according to a (lattice parameter) = 3.856 + 0.478x (McCammon and Liu, ’84). According to thermodynamic modeling of reduction potential as a function of pressure, (Fig.3b), ‘X’ in Fe$_x$O should be lowest at and around 45 GPa, steadily increasing at higher and lower pressures as reduction potential decreases at pressures above and below 45GPa. At 21 GPa iron depletion in Fe$_x$O is low to moderate (4-6%), high at 41 GPa (7-9%), then moderate again at 62 GPa (5-6%). The sample loaded in MgO (green) is unusually low in iron depletion (5-6%), suggesting dampening of redox potential by the insulating medium.
Figure 9- Raman spectra of recovered samples: a.) MC2, b.) MC6, and c.) NC1. All spectra show diamond near 1332 cm$^{-1}$. Raman shift of diamond in sample MC2 (21 GPa and 2100K) gives a peak center at 1325 cm$^{-1}$, indicative of residual compressive on the diamond grain(s) (Ferreira et al., 2002). Fe$_2$O$_3$ (hematite) was formed by surface oxidation of FeO (wüstite).
Figure. 9 (continued)

B

![Graph showing Raman shift against intensity for different compounds.](Image)

Cell 8 (quench from 41 GPa 2100K)

Continued
Figure. 9 (continued)
**Figure 10**- SEM images of thin foil lifted from sample NC1 (43 GPa and 2200K). (a) Image of entire foil showing cooler region on top half and peak T region near bottom. Foil dimensions are 10 x 5 x 0.1µm. (b, c) Dark black grains are diamond, dark grey wüstite, and light grey siderite. Diamond grain sizes range from 500 to less than 100 nm. STEM-EDX spot analysis of grains indicated system equilibrated at $f_O^{inw} = +0.3$ log units and $f_O^{SDI} = -0.08$ log units.
Work Cited:


Mao, H.K., et al., (1990), Static compression of iron to 300 GPa and Fe0.8Ni0.2 alloy to 260 GPa – Implications for composition of the core, *Journal of Geophysical Research-Solid Earth and Planets*, 95, 21737-21742.


