INTRODUCTION

The mantle is the largest identified reservoir for carbon stable within a variety of CO$_2$-bearing melts and fluids. Owing to the low solubility in mineral phases (Shcheka et al., 2006) the residence time of carbon and its flux out of the mantle will depend crucially on the conditions under which it is stable within melts or fluids, compared with conditions under which it forms solid phases, such as graphite or diamond, that linger in the convective mantle. Numerous studies have been performed to understand decarbonation and the onset of melting in CO$_2$-bearing mantle systems (Gudfinnsson & Presnall, 2005; Dasgupta & Hirschmann, 2010 and references therein). For many years it has been recognized that carbonated lherzolite systems will produce carbonate melts at pressures above 2.5 GPa and temperatures above approximately 1200 °C. However, it is possible that small degree carbonate-rich melts are the first liquids produced during adiabatic mantle up-welling beneath mid-ocean ridges at 300 km in depth as recently demonstrated by experimental studies (Dasgupta & Hirschmann, 2006) and geophysical evidences (Gaillard et al., 2008) with implications for the origin of basalts and the trace element signature in erupted MORBs. Although extensive work has been performed to determine the effect of pressure on the melting temperature of carbonated peridotite very little attention has been paid to the stability of oxidized carbon (carbonate minerals and melts) with respect to reduced carbon (diamond and graphite), both of which are known to be present under certain conditions in the mantle. The stability of elemental carbon with respect to the carbonate end-member MgCO$_3$ in peridotitic assemblages is described by the equilibrium,

$$
\text{MgSiO}_3 + \text{MgCO}_3 = \text{Mg}_2\text{SiO}_4 + \text{C} + \text{O}_2
$$

which assumes the acronym EMOG (or EMOD in the diamond stability field), and was calibrated by Eggler & Baker (1982) at a pressure of 2.9 GPa. They determined that the oxygen fugacity buffered by this equilibrium was approximately 1 log unit below the FMQ oxygen buffer. In mantle lherzolite assemblages at pressures below 4 GPa dolomite is the stable carbonate phase at temperatures below the solidus, where the governing carbonate-carbon reaction is,

$$
2\text{Mg}_2\text{Si}_2\text{O}_6 + \text{CaMg(CO}_3)_2 = \text{CaMgSi}_2\text{O}_6 + 2\text{Mg}_2\text{SiO}_4 + 2\text{C} + 2\text{O}_2
$$

This equilibrium, which assumes the acronym EDDOG, was also calculated by Eggler & Baker (1982) to buffer oxygen fugacities at values almost identical to equilibrium (1).

However, the knowledge of the oxygen fugacities buffered by equilibria (1) and (2) is only useful if they can be compared with the likely oxygen fugacity of the mantle to determine the conditions under which elemental carbon or carbonate phases are stable. Oxygen thermobarometry has been applied extensively on mantle xenoliths to infer the oxygen fugacity of the mantle. Gudmundsson & Wood (1995) calibrated the equilibrium,

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2\text{Fe}_2\text{Fe}^{3+}\text{Si}_3\text{O}_{12} = 4\text{Fe}_2\text{SiO}_4 + 2\text{FeSiO}_3 + \text{O}_2
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which allows estimates to be made for the oxygen fugacity at which garnet peridotite rocks equilibrated using mineral chemical analyses. Fig. 1 shows oxygen fugacities determined for xenoliths from various cratons as a function of equilibration depth. With increasing depth the determined oxygen fugacities decrease, which is mainly due to the effect of pressure on equilibrium (3). The volume change of this reaction favours the formation of the Fe₃Fe³⁺Si₃O₁₂ garnet component (skiagite) with increasing pressure, which drives down the oxygen fugacity (Frost & McCammon, 2008). An extrapolated EMOG(D) buffer at high pressure is also shown and indicates that at pressures greater than 3 GPa most cratonic lithosphere xenoliths record oxygen fugacities below the EMOD(G) buffer and therefore should be in the graphite/diamond stability field.

However, a number of issues concerning the redox state of carbon in the mantle, the possibility of carbon-mediated redox melting and the oxygen fugacity of the mantle in general remain to be resolved. In particular, 1) the oxygen fugacity at which elemental carbon (graphite or diamond) is oxidized to produce solid carbonate or CO₂-bearing melts is undetermined at pressures above 3 GPa. Understanding the origin of deep mantle melts requires the knowledge of the redox conditions at which carbonate melts become stable with respect to elemental carbon phases. 2) Although equilibrium (3) has been calibrated to pressures of 3 GPa (Gudmundsson & Wood, 1995) for determining the oxygen fugacity of garnet peridotite rocks, this equilibrium must be extrapolated for use at high pressures and has not been tested. The relationship between the oxygen fugacity of the mantle and the Fe³⁺/ΣFe is therefore poorly constrained at high pressures.

METHODS

High-pressure experiments

In this study oxygen fugacities, buffered by assemblages containing both elemental carbon (graphite or diamond) and carbonate minerals or melts, were determined using presses available at the Bayerisches Geoinstitut (BGI, Bayreuth) capable of producing loads of 500, 1000 and 1200 tons to generate pressures up to 25 GPa (Keppeler & Frost, 2005), corresponding to pressures in the upper part of the Earth’s lower mantle and temperatures at and above the carbonated peridotite solidus. Two starting materials were initially employed. A simplified carbonated harzburgite in the system Fe-Mg-Si-O-C was assembled from a mineral mixture of natural San Carlos olivine, (Mg, Fe)SiO₂ enstatite, MgCO₃ magnesite, and graphite. A simplified lherzolitic composition in the system Fe-Ca-Mg-Si-O-C was made from a similar assemblage. In all experiments 3% iridium metal powder was added to the starting materials to act as a redox sensor (Taylor et al., 1992). Starting materials were
loaded into graphite capsules that were enclosed in a rhenium foil. After pressurization experiments were generally heated for 24 hours.

During this study it was also possible to perform experiments at pressure and temperature conditions of the Earth’s mid lower mantle (~ 1200 km in depth) using a DIA-type multi anvil guide block system at the Geodynamic Research Centre (Ehime, Japan). High-pressure cell assemblies were optimized for use with sintered diamond anvils and employed an MgO pressure medium doped with 5 wt. % chromium.

**Analytical techniques**

All the recovered run products were mounted in epoxy resin and then ground and polished using ethanol to preserve the carbonate phases (solid and melt) for analytical investigations. In the case of graphite containers employed at P > 6 GPa, the capsule material transformed to diamond. The preparation of suitable samples for analytical investigations required the use of diamond polishing plates. Textural observations of the recovered run products were performed using a LEO Gemini 1530 equipped with a Schottky emitter scanning electron microscope. The chemical compositions of liquid and mineral phases were obtained using a Jeol JXA-8200 electron microprobe equipped with five wavelength-dispersive spectrometers. A LABRAM Raman spectrometer with a He-Ne laser with the 632 nm red line excitation was used to confirm the presence of diamond, clinopyroxene, wadsleyite and ringwoodite in some samples relative to the low pressure polymorphs. The determination of the iron oxidation state in garnets equilibrated with carbon and carbonate-bearing mantle assemblages was a key topic of this study to better understand the conditions at which carbon oxidizes to carbonate and infer the likely redox profile applicable to the Earth’s mantle. The Fe\(^{3+}/\Sigma\)Fe ratio in garnets recovered from high-pressure experiments was, therefore, investigated using Mössbauer spectroscopy. Samples were double polished to account for about 5 mg Fe/cm\(^2\) absorber thickness and avoid saturation effects. Mössbauer spectra were recorded at room temperature (298 K) in transmission mode on a constant acceleration Mössbauer spectrometer (McCammon, 1994).

Finally, a QUANTA 3D FEG focused ion beam was used in this study to prepare samples for TEM analysis and for the study of the iron valence state using EELS (Electron Energy-Loss Spectroscopy) in a perovskite sample recovered from 45 GPa and 1700 °C. ELNES spectra were collected using an energy-loss spectrometer (Gatan PEELS 666).

**RESULTS**

**Oxygen fugacity measurements of carbon-carbonate assemblages**

In the first part of this study experiments were performed to measure the oxygen fugacity at which carbon (graphite or diamond) oxidizes to carbonate minerals or melts in synthetic lherzolitic and harzburgitic assemblages representative of equilibria (1) and (2) between 2.5 and 11 GPa at 1100-1600 °C. The experiments were performed up to temperatures where carbonate melts evolve towards more silicate-rich compositions, such as kimberlitic melts. Samples containing clino- and orthopyroxene, olivine and either carbonate minerals or melts (carbonatitic or kimberlitic) were recovered, and with graphite (or diamond) being dispersed throughout the material as a redox sensor. During the experiments the oxygen fugacity was internally fixed by the coexistence of carbon and solid carbonates and this oxygen fugacity was experimentally measured using the equilibrium,

\[
\text{Fe}_2\text{SiO}_4 = \text{SiO}_2 + 2\text{Fe} + \text{O}_2
\]

in particular the proportion of Fe in the Ir-Fe alloy with the appropriate activity-composition model for the Fe-bearing phases and the silica activity, which is determined from the equilibrium between olivine and enstatite. During the experiments iron (contained in the phase assemblage) is reduced to metal and alloys with Ir.
metal to shift the oxygen fugacity of the Fe and FeO bearing equilibrium to that imposed by the presence of carbonate melt and graphite (or diamond). The resultant lowering of the activity of the Ir metal component is consequence of the redox conditions imposed by the carbon-carbonate equilibrium as function of pressure and temperature and the evolving melt composition.

At temperatures corresponding to the carbonated solidus, the determined oxygen fugacity is very similar to that calculated by Eggler & Baker (1982). However, as temperature increases the activity of the carbonate component in the melt decreases, which drives the equilibrium oxygen fugacity down compared to previous extrapolations. In Fig. 2 oxygen fugacities determined using equation (4) are plotted as a function of inverse temperature for experiments performed between 3 and 11 GPa and 1100-1600 °C and compared with the EMOG/D equation of Eggler & Baker (1982). The parameterization of all the results gives the following equation,

$$\log_{10} f_{O_2} = 5.44 - 21380/T + 0.078(P-1)/T + \log(\chi_{CO_2})$$

(5)

where P is the pressure (bars), T is temperature (Kelvin) and \(\chi_{CO_2}\) is the mole fraction of CO\(_2\) dissolved in the melt. This parameterization reproduces the experimental results to within 0.3 log units and can be used to determine the \(f_{O_2}\) of any peridotitic assemblage where elemental carbon coexists with a CO\(_2\)-bearing melt between 2.5-11 GPa.

These results have implications for the onset of melting within upwelling mantle material. Several studies have indicated that the mantle may become more reduced with depth (Frost & McCammon, 2008 and references therein). This means that the oxidation of elemental carbon (graphite or diamond) may occur in upwelling rocks where the oxidized product is a carbonate-bearing magma. When the experimental data are compared with current estimates for the \(f_{O_2}\) of mantle rocks the implication is that peridotitic mantle will remain in the diamond stability field up to at least 100-150 km depth (Fig. 3). Only at depths shallower than 150 km would Fe\(^{3+}\) in mantle silicates react with graphite to produce carbonate-rich melts in a redox melting process (Stagno & Frost, 2010). If melting occurs at greater depths it must occur in a mantle that is more oxidized (i.e. contains more Fe\(^{3+}\)) than the most oxidized garnet peridotite samples.
The stability of magnesite in the transition zone and the lower mantle as function of oxygen fugacity

Further experiments were performed to determine the $f_{O_2}$ at which diamond oxidizes to carbonate at conditions of the transition zone and lower mantle. Similar experiments than those described above were performed between 15 GPa and 22 GPa, where wadsleyite first, and then ringwoodite are stable with respect to the low-pressure polymorph, olivine. Experiments at 25 and 45 GPa examined the stability of magnesite with respect to diamond coexisting with (Fe,Mg)O magnesiowüstite and Al-Fe bearing perovskite of a composition similar to that expected in the lower mantle (Irifune et al., 2010).

The measured oxygen fugacity using Ir redox sensor was found to be approximately 3 log units above the iron-wüstite oxygen buffer ($\Delta IW+3$). As the oxygen fugacity of the transition zone and lower mantle is most likely at or below the IW buffer this confines the stability of solid carbonate to the upper mantle or to unusually oxidized regions of the deeper mantle (Brenker et al., 2007). The oxygen fugacity at which magnesite and diamond coexist showed a slight decrease with pressure; however, implying the possibility that magnesite may become the stable host for carbon at the very base of the lower mantle (Stagno et al., 2011). Ferric iron contents in wadsleyite, ferropericlase and perovskite (Fig. 4) equilibrated with carbon and carbonate were measured using both Mössbauer and EELS spectroscopy. Experimental results show that to raise the $f_{O_2}$ to levels where carbonate can be stable would require wadsleyite Fe$^{3+}$/∑Fe ratios of about 5%, while perovskite and
ferropericlase $\text{Fe}^{3+}/\sum\text{Fe}$ ratios of approximately 0.7 and 0.02 similar to values found for inclusions in natural diamonds.

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**Fe$^{3+}$/Fe$_{\text{tot}}$ measurements of garnets equilibrated with carbon and carbonate in a peridotite assemblage**

Garnet-peridotite oxy-thermometry predicts that the range of $f_0^2$ in the asthenospheric mantle should become more reduced with depth as a result of the volume change of the governing ferric/ferrous equilibrium in the silicate assemblage. If correct, this means that carbonate melting will only commence in adiabatically up-welling asthenospheric mantle, once the plausible range of mantle $f_0^2$ crosses the $f_0^2$ constrained by the equilibrium between carbonate melt and graphite (or diamond). Our experimental results on the carbon/carbonate equilibria, combined with calculations on the redox state of the upper mantle, indicated a depth interval for the onset of carbonate-rich redox melting of 100-150 km (Fig. 3), with the deepest value corresponding to a highly oxidized mantle assemblage. However, predictions of redox melting processes and the depth interval over which carbonate-rich melts can form beneath mid-ocean ridges would be dramatically affected by erroneous extrapolation of the currently used equilibrium (3). Although this oxy-thermobarometer has been calibrated at pressures of 3-3.5 GPa, the predicted oxygen fugacities have not been experimentally confirmed at higher pressures, where the volume change of the equilibrium is predicted to significantly lower the mantle $f_0^2$ to values at which Ni-Fe alloy will precipitate (Woodland & Koch, 2003; Frost & McCammon, 2008).

In this study a series of experiments were performed to determine the Fe$^{3+}$ content of garnet at an oxygen fugacity buffered by carbon-carbonate equilibria. Starting assemblages were identical to the previous experiments except that a layer of garnet was placed inside the graphite capsules, sandwiched between layers of the buffering carbon-carbonate assemblage, either lherzolitic or harzburgitic (Fig. 5). Mg, Fe- and Ca, Fe, Mg- bearing garnets were both synthetic and natural. The ferric iron contents of the garnet layers in the run products were determined by $^{57}$Mössbauer spectroscopy.

The results from these experiments allow the redox conditions for the stability of elemental carbon and carbonate to be compared directly to the Fe$^{3+}/\sum\text{Fe}$ ratio of the peridotite and therefore with measurements on mantle samples. The oxy-thermobarometer used for determining the oxygen fugacity of
garnet-bearing assemblages was also tested at pressures where they have not been calibrated to date. The Fe$^{3+}$/\sum Fe ratios measured for Ca-bearing garnets in these experiments (~ 6-12%) are similar to values found in natural garnets of mantle xenoliths equilibrated at similar pressures (Luth et al., 1990). However, our oxygen fugacities fixed by the carbon-carbonate equilibrium and measured using Ir redox sensor are approximately 1 log unit higher than we determined using equilibrium (3) on our mineral assemblage (Fig. 6). These results indicate that the pressure dependence of this oxy-barometer may be in error and a preliminary recalibration implies that cratonic lithosphere may not be as reduced as previously considered.

**Fig. 6** - Blue and pink symbols indicate oxygen fugacity of natural mantle xenoliths calculated as function of pressure before and after recalibration of equilibrium (3). The grey curve is calculated using the EMOG/D buffer modified by Stagno and Frost (2010) along an adiabat at a potential temperature (T_P) of 1300 °C. Dotted line indicates the transition from graphite to diamond.

**REFERENCES**


