EXPERIMENTAL DETERMINATION OF MELTING IN THE SYSTEMS ENSTATITE-MAGNESITE AND

MAGNESITE-CALCITE FROM 15 TO 80 GPa

Revision 1

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ABSTRACT

Pressure-temperature melting curves in two carbonate bearing systems of relevance to Earth’s mantle have been determined using the laser-heated diamond anvil cell (LH-DAC). The solidus along the MgSiO\textsubscript{3}-MgCO\textsubscript{3} join in the MgO-SiO\textsubscript{2}-CO\textsubscript{2} system (MS-CO\textsubscript{2}) was defined from 15 to 80 GPa using \textit{in-situ} melting criteria, reaching a maximum temperature of \(\sim 2340\) K at 80 GPa. The occurrence of melting has been confirmed with \textit{ex-situ} textural and chemical analysis of recovered samples. The melting curve has a negative \(dT/dP\) slope at pressures between \(\sim 15\) and 23 GPa resulting from the subsolidus phase transition of ilmenite- to perovskite-structured MgSiO\textsubscript{3}. The shallow slope of the melting curve at pressures higher than this transition indicate that for plausible mantle geotherms carbonate-bearing silicate lithologies will melt throughout the lower mantle. The solidus of a mixture
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along the MgCO$_3$-CaCO$_3$ join was determined as a proxy for alkali-free carbonate lithologies. Melting temperatures increase from 1860 K at 16 GPa to ~2100K above 35 GPa, where the melting curve flattens. The melting reaction magnesite + post-aragonite (high-pressure CaCO$_3$) = melt was confirmed using an in-situ experiment. We conclude that crystalline Mg and Ca carbonate mixtures are unstable with respect to molten carbonate at conditions of the convective lower mantle. The flat melting curves at high pressures in both systems suggests that subducted carbonates will undergo melting at lower mantle conditions, a process that may be important for superdeep diamond formation and carbon storage in the deep mantle.

Keywords: deep carbon, diamond anvil cell, magnesite, melting

1. INTRODUCTION

Carbon is a key component of Earth’s atmosphere and biosphere and is essential for the preservation of a habitable climate throughout geological time. The atmospheric carbon budget is maintained by exchange with mantle reservoirs through subducting material and volcanic degassing (Sleep and Zhanle, 2001). The overall mantle carbon budget is not well constrained due to uncertainties in the primary bulk earth carbon budget and incoming/outgoing fluxes, but its massive size makes it a large potential carbon storage reservoir (Dasgupta and Hirschmann, 2010). Hirschmann and Dasgupta (2009) estimate that the H/C ratio of the mantle is superchondritic, an observation inconsistent with a chondritic Earth or one where the late veneer dominates the volatile budget, and the presence of a hidden carbon-rich reservoir in the deep Earth is one possible explanation. The fate of subducted carbon has been the subject of many studies in recent decades, and its presence can have large effects on the chemical, physical and redox behaviour of the mantle (Frost and McCammon 2008; Gaillard et
The activity of oxygen is the critical factor in determining the form of carbon that exists in the mantle, as it fixes the distribution of oxidised and reduced carbon species. Peridotitic mantle with constant oxygen content should become more reducing with depth as a consequence of increased ferric iron solubility in deep mantle phases like majorite and perovskite. There is evidence for this in samples of cratonic lithosphere and some inclusions in diamonds originating in the lower mantle (McCammon et al., 1997; Woodland and Koch, 2003; Frost and McCammon, 2008; Rohrbach and Schmidt, 2011).

However, the exact oxygen content of the majority of the mantle is not constrained by samples. The redox state of carbon within slabs as they subduct into the mantle is also not well known. Initially the majority of carbon introduced into the mantle is in oxidised forms, mostly carbonates added to ocean-floor material during alteration by hydrothermal fluids and seawater interaction (Shilobreeva et al., 2011). Thermodynamic models and petrological experiments indicate that carbonates can remain stable in slabs as they undergo metamorphism and dehydration in the sub-arc mantle (Connolly, 2005; Gorman et al., 2006; Molina and Poli, 2000; Poli et al., 2009), and carbonate phases are known to have stability fields that extend throughout the mantle depth range (Isshiki et al., 2004). There is now significant tomographic and geodynamic evidence that subducting slabs can penetrate into the lower mantle (van der Meer et al., 2010; Steinberger et al., 2012). It is therefore important to understand what happens to the carbon cargo carried by slabs into the deep mantle.

Previous work on the effect of carbonate on silicate phase relations at upper mantle pressures is extensive (e.g. Katsura and Ito, 1990; Luth, 1993; Hammouda, 2003; Dasgupta et al., 2004; Yaxley and
At pressures relevant to the lower mantle, the stability of carbonate minerals coexisting with mantle silicates is much more uncertain, and it is possible that decarbonation reactions, which produce free CO_2 or other carbon phases, can occur. Recent work shows that at lower mantle pressures and temperatures CO_2 should be a liquid or may even dissociate into C + O_2 (Litasov et al., 2011; Boates et al., 2012; Teweldeberhan et al., 2013). In contrast, the stability of magnesite at 85 GPa and 3000 K (Isshiki et al., 2004) suggests that the decarbonation of carbonate minerals does not occur under mantle conditions. This view is further supported by the observation that MgO and CO_2 react to form MgCO_3 at 5-40 GPa and 1400-1800 K (Scott et al., 2013). Seto et al. (2008) investigated the reaction of MgCO_3 and SiO_2 at lower mantle pressures to address the potential decarbonation of subducting materials that contain free SiO_2. It was observed that MgSiO_3 and CO_2 were formed by a decarbonation reaction above ~ 2400 K from 30 – 80 GPa. However, thermodynamic modelling of this reaction was found to be inconsistent with the experimental data (Litasov et al., 2008).

Carbonate suppresses the silicate solidus considerably at upper mantle conditions, so carbonated-melt is potentially the most important deep mantle carbon-bearing phase. Experimental studies on carbonated materials, both peridotitic and eclogitic, at upper mantle pressures have shown that low degree melts are carbonate-rich, often containing < 1wt.% SiO_2 (Dalton and Presnall, 1998; Hammouda, 2003; Dasgupta et al., 2004; Kiseeva et al., 2013 etc.). Therefore the melting temperature of all such carbonated (anhydrous) materials can be estimated from the melting curves of pure carbonate systems (Buob et al., 2006, Franzolin et al., 2011). The melting behaviour of simple carbonate systems is a suitable proxy for many alkali-free carbonate-bearing lithologies. For example they can be used to understand the behaviour of slab material that has undergone sub-arc melting (and...
hence contains low residual concentrations of alkali components) or the melting of carbonated peridotite.

Previously, Katsura and Ito (1990) investigated the MgSiO$_3$-MgCO$_3$ binary system, observing that at 8 and 15 GPa a eutectic melt is formed at ~ 2050 – 2100 K. Despite its potential relevance throughout the mantle, this eutectic melting reaction has not been explored further. In this study we extend the melting curve to ~ 80 GPa in the MgSiO$_3$-MgCO$_3$ system using laser-heated diamond anvil cell (LH-DAC) experiments. In addition, we determine the melting curve in the system MgCO$_3$-CaCO$_3$ to ~ 80 GPa. These experiments provide new information regarding the maximum temperature stability of carbonate phases within the convecting mantle.

### 2. METHODS

This study consists of experiments in two separate chemical systems, MgSiO$_3$-MgCO$_3$ and MgCO$_3$-CaCO$_3$. Melting curves were determined using experiments performed in the LH-DAC at the School of Earth Sciences, University of Bristol (described in section 2.1). One subsolidus run was performed in the MgSiO$_3$-MgCO$_3$ system. Additionally a single experiment was conducted with in-situ X-ray diffraction (XRD) in the LH-DAC at beamline ID-27 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France (described in section 2.2).

The starting materials were made by mixing equal masses of natural magnesite with either synthetic MgSiO$_3$ glass or reagent grade CaCO$_3$ (>99.99% purity). Before weighing, the individual components were dried at 220°C for more than 24 hours. After a minimum of 30 minutes grinding under ethanol in an agate mortar, ~ 10 wt.% platinum black was added to each mix as a laser absorber. Subsequently,
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mixes were ground for a further 2-3 hours to ensure homogeneity and to reduce the grainsize of the Pt black; particles are observed to be predominantly sub-micron, but with the occasional grain in the one to ten micron range that are avoided. In order to ensure that the systems remain iron-free the crucibles and agate mortars had never previously been used with iron-bearing compositions. EDS analysis revealed that the MgCO$_3$-CaCO$_3$ starting mix contains minor contamination of up to 0.5 wt% SiO$_2$ in the bulk.

2.1 Off-line LH-DAC experiments on MgSiO$_3$-MgCO$_3$ and MgCO$_3$-CaCO$_3$

Experiments were performed in Princeton-type symmetric DACs using anvils with standard 250µm culets (200µm culet diamonds were used in the highest pressure MgCO$_3$-CaCO$_3$ experiment). Rhenium was used as the gasket material, pre-indentated to ~25 GPa. Three or four 30-40µm sized holes were drilled in the central portion of each gasket using an UV laser ablation unit (New Wave research, LUV series, operating wavelength 266 nm) creating multiple, physically separated sample chambers (see figure 1a). A single starting mix, either MgSiO$_3$-MgCO$_3$ or MgCO$_3$-CaCO$_3$, was loaded into all the sample chambers, to eliminate the possibility of cross-contamination. A single ruby grain (< 2-3µm) was added to one of the sample chambers. Each loaded cell was heated at 125°C for 1 hour prior to sealing in order to eliminate any adsorbed water contamination acquired during loading.

Pressure was monitored in one chamber during compression using the shift in the R1 ruby fluorescence peak as calibrated by Mao et al. (1986). Pressure was measured at room temperature after the experiment in all chambers using two different methods. Firstly, the ruby scale pressure was determined in the ruby-bearing chamber. Then, pressure in all sample chambers was measured using the shift of the 1332 cm$^{-1}$ Raman peak of diamond at the culet surface measured with a custom-built...
confocal Raman system. The Raman peak shift, $\Delta \nu$, was converted to sample chamber pressure using a calibration curve specific to the materials used as pressure media (e.g. the sample mixes). The calibration was made by plotting the ruby pressure vs. $\Delta \nu$ for the ruby-bearing chambers in all experiments, as shown in Fig. 2. A highly correlated linear relation exists between ruby pressure and $\Delta \nu$, with a measurement precision in each reported pressure of ± 1.9 GPa at one standard error; pressure accuracy is tied to the ruby scale. This method of pressure measurement is preferred as it avoids possible contamination with ruby (Al$_2$O$_3$) during laser heating, and allows pressure to be measured directly adjacent to the heated region thereby minimising the effects of pressure gradients. Reported pressures are those recorded post-heating. Thermal pressure during heating was estimated in one experiment as described below.

Samples were laser heated in a double-sided configuration using a pair of 100 W diode-pumped fibre lasers (TEM$_{00}$) emitting at 1070 nm. The Gaussian energy distribution of the lasers can generate strong temperature gradients in the sample. Such gradients are undesirable as they exacerbate errors in temperature measurement related to chromatic aberration (Walter and Koga, 2004), can lead to Soret diffusion, and increase the sensitivity of measured temperature to system alignment. Therefore, we have employed beam shaping optics combined with variable beam expanders to create a flat-topped energy profile at the sample surface of up to ~30 µm diameter. This setup can yield a nearly isothermal temperature at the surface of uniformly absorbing samples. In the experiments reported here, the temperature distribution across the sample is observed to depend considerably on the distribution of the Pt absorber within the flat-topped energy profile. Laser power was increased automatically (after an initial temperature of 1600-1700 K was reached) in linear steps with intervals of 7 seconds with a temperature measured at each interval. Experiments lasted 3-10 minutes in total duration.
Temperature was measured along a vertical profile located centrally across the heated region on both sides of the sample simultaneously, using standard imaging spectroradiometry techniques. Details of the optical configuration, procedures and calibrations are presented in full elsewhere (Lord et al., submitted; 2010; 2009; Walter and Koga, 2004), but a brief description of salient points is presented here. We focus the lasers and image the sample using a 20 mm focal length Mitotoyu apochromatic lens designed for radiation in the near-infrared. The light from the sample is focused at the spectrometer slit (image plane) using a 1 metre f achromatic doublet, which in combination with the objective yields a magnification of 50x. On the basis of the magnification and detector pixel size, our system has an ideal resolution of ~ 0.5 μm. However, the diffraction limit at 700 nm, which is the nominal central wavelength used in the spectral fitting, is ~ 1.3 μm, defining the maximum spatial resolution that can practically be achieved. Optical aberrations can further reduce the resolution. Based on measurements using a resolution target the diffraction limit is achieved in our system for a flat-field illumination. However, chromatic aberrations can further limit the effective spectroradiometric resolution if a temperature gradient is present (Boehler and Chopelas, 1991; Walter and Koga, 2004; Benedetti et al., 2009). On the basis of the measured focal deviations of our system (maximum of ± 5 μm at the image plane over the 200 nm spectral window), we calculate a worst-case spectroradiometric resolution of ~ 3 μm at the sample surface (object plane). Errors associated with chromatic aberration can be deduced from the precision of the spectral fits to the ideal greybody Wien function, and are a function of the temperature gradient (Walter and Koga, 2004). The precision of the spectral fits reported here are typically less than 5 K, and in all cases < 10 K, indicating that chromatic effects are not a significant component of the fits. All things considered, we make a conservative estimate of error in calculated temperatures associated with optical aberrations of less than 50 K, and likely less than 25
K. The accuracy of the temperature measurement system has previously been tested at ambient pressure against the known melting points of a range of metals (Lord et al., 2009; 2010) and is estimated at 50-200 K. The source of this inaccuracy is likely the unknown emissivity of the samples used in calibration, a parameter that is both material specific and dependent on temperature and pressure. Because we have very little information regarding the emissivity of our samples, we choose not to include this error in our reported uncertainties, but simply acknowledge that it exists. It is also noteworthy that where our data overlap with those of previous multi-anvil experiments we find a very good consistency in melting temperature (see below).

2.2 In-situ LH-DAC experiment on MgCO3-CaCO3

Unlike the off-line experiments (§2.1), this experiment employed a single, 100µm diameter sample chamber. The sample chamber was filled with a foil of sample material containing platinum black sandwiched between foils of the same composition without platinum black, which act as both pressure medium and thermal insulation. The foils were created by compressing powder between diamond anvils and pieces of appropriate size were chosen for loading. A single ruby grain was placed on the edge of the sample chamber to allow the pressure to be monitored during compression. Laser heating was performed using a double-sided, off-axis geometry generating a heated spot of ~ 30 µm diameter. The incandescent light is collected using reflective optics and a 2 x 2 µm region at the centre of the heated spot is selected for temperature measurement. Temperatures on both sides are equalised before the experiment, but only measured on the upstream side during the experiment to allow simultaneous XRD. For further details see Schultz et al. (2005). The 33 keV X-ray beam (λ = 0.3738 Å) had a FWHM of 4 µm and was aligned with the centre of the heated spot using the X-ray induced fluorescence of the sample. Diffraction patterns were collected on a MAR345 CCD using an exposure...
time of 15 seconds. The distance between sample and detector was calibrated using a LaB₆ standard. X-ray diffraction patterns were taken before, periodically throughout and after sample heating. 2-D XRD patterns were masked and integrated into 1-D patterns using Fit2D (Hammersley, 1997). These patterns were in turn fitted and analysed using the Le Bail method (Le Bail et al., 1988) as implemented in the GSAS suite of programmes (Larson and Von Dreele, 2000; Toby, 2001). The pressure in this experiment was calculated from the measured unit cell volume of the platinum laser absorber and the measured temperature using the Mie-Grüneisen-Debye P-V-T equation of state (EOS) for platinum of Zha et al. (2008).

2.3 Melt Detection

We use multiple criteria to deduce the temperature at which the sample melts during laser heating, of which the primary criterion is a discontinuity in the temperature vs. laser power curve generated during the heating ramp. The key perturbation is the development of a temperature plateau, where over some range of increasing power, temperature remains essentially constant or oscillates around some value. Temperature plateaux have been used extensively as a melting criterion in the LH-DAC (e.g. Lord et al., 2009; 2010; submitted; Fischer et al., 2013; Asanuma et al., 2010), and are well correlated with independent observations of melting using in situ X-ray diffraction techniques (Fischer et al., 2013; Lord et al., submitted). The exact causes of the perturbations are difficult to assess fully, but are likely related to a combination of differences in the thermal properties of the co-existing solid and liquid phases during melting and changes in sample absorption properties (Lord et al., submitted; 2010; Geballe and Jeanloz, 2012). In the experiments reported here where an extrinsic absorber (Pt black) is used, mechanical changes in the sample upon melting and subsequent redistribution of the Pt grains also contributes to the perturbation, and can be recognized by variations in the shape of the temperature
profile that occur once a plateau is reached. Finally, using a variable neutral density filter and a CCD camera we can visually observe movement in the sample (mechanical or convective) that occurs once the temperature plateau is reached. After melting begins, during the temperature plateau, we observe that the Pt absorbers often migrate away from the melted-region and often form a bright doughnut shape that expands as the experiment continues.

In experiments on the MgSiO$_3$-MgCO$_3$ system the discontinuities that define melting are flat plateaux and are also extremely stable, remaining at constant temperature until the end of the experiment (figure 3). In this case the melting temperature is defined as the average of all temperatures within the plateau. The uncertainty associated with the melting temperature is reported as twice the standard deviation of all the temperature measurements in the plateau ($2\sigma$).

MgCO$_3$-CaCO$_3$ experiments display a slightly different behaviour. Discontinuities in this system do not typically appear as long, stable plateaux, but instead as a short plateau followed by rising temperatures (figure 4). On close inspection of individual temperature profiles collected throughout the heating ramp it can be seen that increasing temperatures after the short plateau are caused by the presence of localised hotspots of platinum-rich material at temperatures above the liquidus of the sample. As this superheating continues, often the entire sample becomes heated to super-liquidus temperatures, during which time convection is observed to be vigorous. During the subsolidus heating ramp, samples can display considerable temperature topographies depending on the initial distribution of platinum within the sample chamber (Fig. 1). When the melting temperature is reached the temperature profile across the sample becomes flatter as convection begins to occur. Once the temperature across the entire sample has equalised, the platinum-rich hotspots begin to form. A schematic illustration of this process
can be seen in figure 1b and an example of real data can be seen in figure 1c. Due to the presence of
this behaviour the definition of the melting temperature in MgCO₃-CaCO₃ experiments is based on a
combination of three criteria, not all of which are always observed in each experiment. These are a) the
observation of a limited plateau, b) visible convective motion of the sample and c) the loss of any
subsolidus topography in temperature profiles as the melting temperature is reached. It is also worth
noting that in all cases a break in slope of the temperature-power curve is seen at the point of initial
melt generation (see figures 3 and 4) and that all three criteria provide the same result. As the plateaux
in this system are much shorter the uncertainty in the melting temperature has often been
conservatively estimated, instead of reporting a standard deviation value based on fewer than 10 data
points.

In some experiments there was a significant difference between temperatures measured on each side of
the DAC throughout heating. As chromatic aberration is insignificant (see above) it is suggested that
this is caused either by poor laser coupling or by misalignment of the emitted light with the
spectrometer entrance slit on one side of the system. This is likely due to the difficulties in perfectly
aligning the system at low temperatures, when the emitted light is weak. When this occurs only the
higher temperature side is used to determine melting temperatures (e.g. fig 3c), as misalignment will
cause an underestimation, and never an overestimation, of true temperature.

2.4 Ex-situ Sample Analysis

After complete pressure release samples were recovered from the DAC and selected MgSiO₃-MgCO₃
experiments mounted in epoxy to permit ex-situ analysis. Samples were polished by hand using 0.3 μm
alumina-impregnated Mylar sheets prior to Ar-ion polishing using a Technoorg Linda ion mill.
Textural and chemical analyses were performed using the JEOL JXA8530F Field Emission Gun Electron Microprobe at the University of Bristol operated at 5-9 keV and 20 nA over three analytical sessions. The system was calibrated using St John’s Island olivine and platinum metal as primary standards and was verified with diopside as a secondary standard.

3. Results

3.1 Enstatite-Magnesite

All melting experiments in the enstatite-magnesite system produced clearly defined plateaux in temperature vs. laser power that were used to define the eutectic melting temperature (figure 3). Previous work (Newton et al., 1975; Katsura and Ito, 1990; Koziol and Newton, 1998) has shown that this system becomes a simple binary above ~5 GPa and up to 15 GPa, producing a eutectic melt at 2073 - 2173 K at 15 GPa. As there are no known phases with intermediate compositions we assume that the system continues to behave similarly throughout all the high pressures experiments of this study. The measured eutectic temperatures and associated errors are listed in Table 1 and plotted as a function of pressure in figure 5a.

The lowest pressure experiment in this study was conducted at 16 ± 2 GPa and was found to melt at 2080 ± 40 K. This is within the temperature bracket for eutectic melting of previous experiments determined from ex-situ analysis of multi-anvil press experiments (Katsura and Ito, 1990), providing further credibility for the accuracy of both our temperature measurement and melting criteria. With increasing pressure the eutectic temperatures decrease, reaching a minimum at ~ 23 GPa. It is clearly not possible to fit a single melting curve to the entire dataset, as there is a change in melting slope at ~ 23 GPa. This pressure corresponds to the location of the phase change from ilmenite- to perovskite-
structured MgSiO$_3$ (Ono et al., 2001) at the solidus. The melting curve in the interval 5 – 23 GPa marks
the reaction ilmenite MgSiO$_3$ + magnesite = melt and is defined by a polynomial with coefficients
reported in table 2; all data collected at pressure < 24.5 GPa are used in this fit.

At pressures above ~ 23 GPa, the eutectic temperature rises consistently to 2350 ± 75 K (2σ) at 80 GPa.

The experiments above 22 GPa were fitted using a damped Simon-Glatzel melting equation

$$(T_m = T_c \left( \frac{P}{P_c} + 1 \right)^{\frac{1}{n}} \exp (-cP)),$$

Simon and Glatzel, 1929; Kechin, 2002) with coefficients reported in table 2. This defines the eutectic melting curve where the reaction perovskite MgSiO$_3$ + magnesite = melt. The intersection of the two fitted curves at ~ 23 GPa represents the triple point corresponding to

the assemblage magnesite + ilmenite + perovskite + liquid. Figure 5a shows that this point falls almost

exactly upon the ilmenite + perovskite phase boundary in the MgSiO$_3$ system previously determined

using in-situ experiments (Ono et al., 2001). With increasing pressure dT/dP decreases such that the

estimated melting temperature at the core mantle boundary (135 GPa), assuming no further phase

changes occur, is 2522 ± 131 K (2σ).

Ex-situ analysis of subsolidus runs performed at ~ 100 and 300 K below the melting point at ~ 35 GPa

($T_m^{35} = 2104 ± 69$ K) reveal experimental products consisting only of coexisting crystals of perovskite

and magnesite approximately 1 - 3µm in size (figure 6a). Crystal compositions were confirmed as

stoichiometric MgSiO$_3$ and MgCO$_3$ (CO$_2$ by difference) using multiple quantitative analyses and WDS

element maps. In these experiments the platinum laser absorber remains evenly distributed as small (<

1µm) grains throughout the sample chamber. A third experiment in the same gasket (31.5 GPa, $T_{max} =

2040$ K) was quenched within 15 seconds of achieving the melting temperature. This experiment also

has a larger grain size (up to ~ 10 µm) in one portion of the experiment, assumed to correspond to the
location of heating. No phases other than perovskite, magnesite or Pt metal were observed in this
experiment. The textural and chemical features observed in the recovered experiments that were interpreted as
having partially melted (using the plateau and other criteria described above) are significantly different
than the subsolidus runs. The location of the centre of the heated spot is clearly defined either by the
small grain size in the central region due to quench crystallisation or the annular distribution of phases
in the experiments (e.g. figure 6b and c). We observe that phase separation occurred in the molten
region, with grains of MgO, SiO₂ and diamond identified. It is also observed that the platinum absorber
has migrated away from the centre of this region and often formed clumps at the boundary with
surrounding material (figure 6c). Outside this central area the samples consist of MgSiO₃ and MgCO₃
with well-dispersed Pt, as seen in subsolidus runs. Within the hotspot region MgO grains are most
commonly found in areas near the sample surfaces, adjacent to the diamond culets (figure 6b), whilst
SiO₂ is only observed in the central region of the sample (figure 6c). This axial phase distribution was
confirmed by analysing the same experiments at two different levels during subsequent analysis
sessions (e.g. figure 6b and c) and has been confirmed in experiments conducted at ~ 18, 27 and 36
GPa. The phase distribution corresponds to SiO₂ migration towards the hotter regions and MgO
migration towards the cooler regions of the sample, a feature that results from Soret diffusion in LH-
DAC experiments (Sinmyo and Hirose, 2010). The changes observed in the textural and chemical
features between subsolidus and molten conditions provide further confirmation that our in-situ criteria
are reliable indicators of melting. However, the estimation of melt compositions is prevented by phase
separation occurring after melting and is beyond the scope of this study.
3.2 Magnesite-Calcite

Previously, the minimum melting point in the MgCO$_3$-CaCO$_3$ system had been defined at 1, 2.7 and 6 GPa (Byrnes and Wyllie, 1981; Irving and Wyllie, 1975; Buob et al., 2006 respectively), corresponding to the reaction dolomite$\rightarrow$ melt. Our experimental data points range from 16 – 80 GPa (table 1 and figure 5b) and corresponds to the reaction magnesite + aragonite = melt (confirmed by in-situ experiment and the previous study of Luth, 2001). We observe that the melting temperature increases as pressure rises to above ~ 35 GPa, above which the melting temperature is nearly constant at ~ 2100 K and possibly decreases with continued pressure increase. The fitting coefficients corresponding to the parameterised melting curve in figure 5b and 7 are presented in table 2. The melting temperature at 135 GPa, again assuming no phase changes occur in the intervening pressure interval, is 1994 ± 239 K (2σ).

The single in situ experiment undertaken at ESRF was used to confirm that the melting temperatures determined from the off-line experiments do indeed represent a eutectic melting reaction, rather than a subsolidus phase change. The post-heating pressure of the experiment, calculated from the room temperature EoS of platinum (Zha et al., 2008), was 45.7 GPa. The pressure during melting (2030 K) was 52.4 GPa, implying a thermal pressure of 6.7 GPa (~15%). This experiment avoided the effect of hotspot growth as temperature was only measured in a single spot aligned with the x-ray beam within the centre of the melt pool. The maximum temperature reached in this experiment was 2066 K and the melting temperature is estimated as 1990 ± 90 K from a clearly defined plateau. Dynamic recrystallisation, indicated by the appearance of saturated spots that move between consecutive diffraction patterns, was observed throughout the temperature plateau. The melting temperature is slightly lower than (but within error of) the melting curve defined by the off-line experiments. The same three-component phase assemblage was present before, during (figure 7) and after heating:
magnesite, post-aragonite structured CaCO₃ (Ono et al., 2005) and platinum. There is one peak that cannot be fitted at a d-spacing of ~ 2.65Å that was present before, during and after the experiment, so is not thought to be involved in a reaction. It does not match the position of any expected peaks from materials that might be expected to be present, such as Re, Al₂O₃, MgO or diamond. This experiment confirms that there is no chemical reaction or subsolidus phase change occurring, but rather, plateaux correspond to the eutectic melting of MgCO₃-CaCO₃ at lower mantle pressures.

3.3 Effect of thermal pressure

In our study we have reported all pressures as post-heating pressures, without any correction for the possible effect of thermal pressure. The thermal pressure was determined in the single in-situ experiment as ~ 15% of the post-heating pressure. However, as the sample geometry employed during the in-situ experiment was significantly different from that during all off-line experiments there is no reason to believe this thermal pressure should apply to all experiments. Furthermore, the proximity of the known ilmenite/perovskite phase boundary and the pressure at which we observe the cusp in the MgSiO₃-MgCO₃ melting curve suggests that thermal pressure is negligible.

4. DISCUSSION

The occurrence of carbonated melting in the deep mantle depends on whether carbonates are stable at high pressure. As suggested in the introduction, there is significant uncertainty about whether carbon is present in oxidized or reduced forms throughout the mantle. The oxygen fugacity required to reduce carbonate to diamond is thought to be 2-3 orders of magnitude above the iron-wüstite buffer (Stagno et al., 2011), and would be reached for ferric/ferrous ratios typical of the lithospheric mantle at depths in excess of ~ 200 km. The extent to which lithospheric mantle is representative of the ambient mantle is
unclear, but it suggests that melting curves of carbonated lithologies might only be applicable to abnormally oxidised regions of the mantle where carbonates remain stable.

If we assume that redox conditions allow carbonate stability then the system MgSiO$_3$-MgCO$_3$ is a proxy for the behaviour of carbonated silica-poor mantle material, i.e. the peridotitic mantle or lowermost portions of subducting assemblages. The results of this study imply that a model magnesite + enstatite/perovskite mantle would be subsolidus along a mantle adiabat (e.g. Katsura, 2010) in the upper mantle and transition zone. However, due to the cusp along the solidus associated with the ilmenite-perovskite transition, this model carbonated mantle would begin melting at pressures in excess of ~ 35 GPa (figure 8). The addition of other chemical components, especially alkalis, would be expected to reduce the solidus and smear out the cusp, but a solidus depression, even a deep one, might still be expected in a natural carbonated peridotite system; previous experimental data are consistent with this interpretation. Ghosh et al. (2009) bracketed the solidus of carbonated peridotite from 10-20 GPa using multi-anvil experiments, and data from their study are plotted in figure 9 alongside the melting curves of carbonated peridotite from natural and model systems. Ghosh et al. (2009) suggest a flat melting curve above ~ 14 GPa, but a negative $\partial P/\partial T$ slope from 16 – 20 GPa as indicated by our data in the simple MgO-SiO$_2$-CO$_2$ system is also consistent with their experimental data. Ghosh et al. (2009) suggested that the close relationship of the mantle geotherm with the carbonated peridotite solidus could lead to a region of melting at the top of the lower mantle. Our new data showing a cusp along the solidus related to the subsolidus transition to a perovskite-bearing lower mantle strengthens this interpretation considerably, and indicates that the upper/lower mantle boundary could be a potential location where carbonate melts are produced.
Slab materials undergo hydrous melting at sub-arc pressures, causing loss of alkali and water components (Yaxley and Green, 1994; Molina and Poli, 2000; Kerrick and Connolly, 2001; Connolly, 2005; Poli et al., 2009), but are thought to retain the majority of their carbon. It is also likely that redox conditions in the remnants of subducted materials are more oxidising than the ambient mantle, and thus carbonates are the dominant carbon species. In this situation the system MgCO₃-CaCO₃ is an appropriate proxy for carbonate-rich components of subducting assemblages whereas the MgSiO₃-MgCO₃ system is relevant to peridotitic (or SiO₂ undersaturated) portions. Based on subduction geotherms from Syracuse et al. (2010) and the shallow or flat solidi defined in this study, it is expected that these portions of subducted assemblages will experience melting within the lower mantle (figure 8). It is uncertain whether carbonated eclogite material will experience a similar fate as the study of Seto et al. (2008) suggests that silica-rich compositions experience a different behaviour at lower mantle pressures.

Carbonate melts have been shown to be highly mobile in the upper mantle (Hammouda and Laporte, 2000) and would be expected to rapidly percolate into surrounding mantle regions. Upon reaching a reduced mantle domain (normal ambient mantle) it has been experimentally shown that they will undergo ‘redox-freezing’ reactions to form diamond and other minerals (Rohrbach and Schmidt, 2011). As this study suggests that carbonated melting occurs in the upper/lower mantle boundary region it is also implied that a significant amount of diamond formation might occur in this region, provided that carbonate melts remain mobile at these pressures. Diamonds from the transition zone and lower mantle that have been discovered worldwide may share a common origin related to melting of carbonated protoliths and redox driven crystallization (see Harte, 2010 for a review of sub-lithospheric diamonds).
5. IMPLICATIONS

Our study implies that, if conditions are sufficiently oxidising, carbonate phases will melt along a geotherm throughout the lower mantle. The Clausius-Clapeyron slope of both melting curves indicate that low-degree melting of subducted carbonated lithologies is expected to be widespread at lower mantle depths. Extrapolation of our melting curves suggest that the maximum temperature of carbonate stability in the mantle is ~ 2500 K. The initiation of carbonated melting near the upper/lower mantle boundary that is predicted by our data can help explain the widespread discovery of ‘superdeep’ diamonds from this depth interval.

A further possible consequence of our results relates to the observation that the slopes of both melting curves presented (dT/dP) approach zero, or become negative, at high pressures. Given the relationship dT/dP = \Delta V/\Delta S it is implied, assuming that \Delta S is positive for the melting reaction, that the density of the melt approaches, or possibly becomes greater than that of the residual solid with increasing pressure. Therefore, if any carbonated material does survive to lower mantle depths the melts they eventually produce may be neutrally, or even negatively, buoyant allowing them to become trapped in the lower mantle. This would allow the creation of a carbon-rich reservoir hidden from materials sampled at the Earth’s surface. This hidden reservoir could balance the superchondritic H/C composition of the bulk Earth (Hirschmann and Dasgupta, 2009), thus removing the reliance on either carbon storage in the core, removal of a CO₂ atmosphere or a non-chondritic late-veneer to explain the bulk earth’s volatile budget.

6. ACKNOWLEDGEMENTS
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7. REFERENCES


Thomson et al. (2014) Melting curves of MgSiO₃-MgCO₃ and MgCO₃-CaCO₃


Thomson et al. (2014) Melting curves of MgSiO$_3$-MgCO$_3$ and MgCO$_3$-CaCO$_3$


Thomson et al. (2014) Melting curves of MgSiO₃-MgCO₃ and MgCO₃-CaCO₃


Thomson et al. (2014) Melting curves of MgSiO$_3$-MgCO$_3$ and MgCO$_3$-CaCO$_3$ pressure-high temperature monochromatic X-ray diffraction at the ESRF. High Pressure Research, 25, 71-83.


FIGURE CAPTIONS

Figure 1: (a) Photograph of the experiment #21 taken whilst pressurised at ~ 80 GPa. Three (or four in the case of other experiments) ~ 40 µm sample chambers were drilled into a rhenium gasket that had been pre-indentated using 200 or 250 µm diamond culets. Ruby was placed in one sample chamber only. The laser spot filled almost all of one sample chamber. (b) Illustrative cartoon showing how the temperature profiles across the heated spot change throughout each experiment. Any ‘topography’ in the temperature profile is maintained through the heating ramp until the melting temperature is reached, at which point the sample becomes isothermal. Further heating causes platinum migration and super-heating, generating hotspots in some experiments. If these develop, local peaks in temperature are observed that develop until the entire sample is at super-liquidus temperatures. (c) An example of the behaviour described in (b) with real data from the right-hand side of an experiment at 59.6 GPa with a melting point at 2080 ± 50 K (plateau shown in figure 4c). Even numbered profiles are shown as solid lines, odd as dashed lines. The first and last profile are labelled with the total laser power.

Figure 2: Calibration curve for pressure determination using the shift in the 1332 cm⁻¹ Raman peak for diamond. The pressure measured by ruby fluorescence (one chamber in each experiment contained ruby) is plotted against the shift in Raman frequency (Δν = measured Raman shift – 1332.4 cm⁻¹).

Figure 3: Three examples of temperature vs. laser power plateaux observed in enstatite-magnesite experiments and used to define eutectic melting temperatures. Temperatures marked are maximum temperatures observed within profiles measured on each side of the DAC. (a) 22.6 GPa, (b) 37.3 GPa, (c) 76.1 GPa (right hand side only used to define plateau). Open symbols show temperatures measured on the right hand side of the DAC, closed symbols are from the left hand side. The downward pointing
arrow marks the first observation of visible convection within the sample chamber. The error of each individual temperature measurement is < 10 K. The temperatures used to define the melting temperatures (grey bars) and uncertainties (2σ) are those between the two vertical black lines.

**Figure 4:** As figure 3, but for experiments in the magnesite-calcite system. (a) 19.6 GPa (b) 45.7 GPa (in-situ experiment) (c) 59.6 GPa. Unlike enstatite-magnesite experiments plateaux appear short-lived, due to the formation of platinum hotspots that become superheated relative to the melting temperature (see text). The melting point is identified by examining individual temperature spectra in combination with the presence of plateaux in temperature-power curves.

**Figure 5:** (a) Melting curve for MgSiO$_3$-MgCO$_3$ system to 80 GPa. Open (ruby-bearing) and grey-filled (ruby-free) circles are experiments from this study. Black squares are the eutectic melting temperature at lower pressure defined in multi-anvil experiments by Katsura and Ito (1990). The known transition of ilmenite to perovskite structured MgSiO$_3$ is plotted as a long dashed line (Ono *et al.*, 2001). The melting curve is kinked at a pressure corresponding to this transition. The short dashed line, open and grey squares indicates the location of the decarbonation reaction MgSiO$_3$ + MgCO$_3$ = Mg$_3$SiO$_4$ + CO$_2$ at low pressure (Newton and Sharp, 1975; Koziol and Newton, 1998). The coefficients defining the melting curve equations are presented in table 2. (b) Eutectic melting curve for the MgCO$_3$-CaCO$_3$ system to 80 GPa. Open (ruby-bearing) and grey-filled (ruby-free) circles are experiments from this study. The minimum melting temperature at low pressure corresponding to the reaction dolomite$_{ss} = $ melt are shown as square symbols and taken from Irving and Wyllie (1975), Byrnes and Wyllie (1981) and Buob *et al.* (2006). The triangular symbols represent data from Luth
(2001) defining the reaction dolomite_{ss} = aragonite + magnesite, and this reaction has been extrapolated with a dashed line. The in-situ experiment performed at ESRF is shown as a black diamond.

Figure 6: Field-emission gun EPMA mages of recovered products from a subsolidus (a) and a partially melted (b and c) experiment. The column at the left shows backscattered electron images, the centre (SiO2) and right (MgO) columns show X-ray maps calibrated to show approximate composition (in weight %) by greyscale. Labels correspond to crystalline phases: Pp = perovskite, Mag = magnesite and Di = diamond and the location of the laser spot during heating is defined by a white circle in (b) and (c). (a) Subsolidus experiment conducted at 33.9 ± 1.9 GPa and a maximum temperature of 1950 K. Experiment consists of perovskite (with beam damage), magnesite and platinum (the white phase in BSE images) of uniform grainsize evenly distributed throughout the charge. (b) A surface section, adjacent to the culet, of experiment #07a conducted at 36.3 GPa. Inside this heated region the grain size is significantly smaller than the surrounding material and consists of a phase assemblage of MgO, perovskite and magnesite (seen in the MgO map). The colder surrounding region has the same phase assemblage as (a). (c) A central section of the same experiment after further polishing. In the centre of this heated region grains of SiO2 and diamond (dark phase in BSE; confirmed with Raman spectroscopy) have been identified. The central region of this experiment is essentially devoid of MgO. The heterogeneity observed in (b) and (c) is a consequence of partial melting and Soret diffusion in the melt (see text). The observations provide independent supporting evidence for the location of the solidus and a verification of the methods used here to determine melting temperatures in in-situ DAC experiments.
**Figure 7:** XRD data (black dots) collected at 2030K and 52.7 GPa during the in-situ experiment in the magnesite-calcite system and fitted using the Le Bail method (solid black curve). The background (grey dashed line) and residual (lowermost grey line) are also shown. The sample consists of the assemblage MgCO$_3$ + CaCO$_3$ in the post-aragonite structure.

**Figure 8:** The experimentally determined melting curves from this study for MgSiO$_3$-MgCO$_3$ and MgCO$_3$-CaCO$_3$ systems (solid black lines), with associated 95% confidence intervals (grey dotted lines), extrapolated to the pressure of the core-mantle boundary (135 GPa). The light grey field represents the Earth’s adiabat from Katsura (2010) while the geotherm of a hot subducting slab is indicated by the grey arrow (Syracuse et al., 2010).

**Figure 9:** A comparison of the melting curve of carbonated peridotite defined in a simple system (MgSiO$_3$-MgCO$_3$, this study) and in a natural carbonated peridotite system with 5 wt% CO$_2$ (labelled G-09, Ghosh et al., 2009). Squares represent experimental runs from Ghosh et al. (2009); closed squares are subsolidus conditions (all carbonate as magnesite solid), open squares are experiments containing a carbonated melt and split squares are charges containing both solid and liquid carbonate. In the two experiments at 20 GPa with split symbols magnesite was only found at the cold end of the capsule estimated by the authors to be 40 – 70 °C colder than the quoted run temperature. It is suggested that the solidus of natural carbonated peridotite will also have a cusp, as observed in the simple system; a potential solidus that is consistent with the experimental data of Ghosh et al. (2009) is shown as a dashed curve.

**Table 1:** Summary of experimental results from this study
Table 1: Fitting parameters for the melting curves defined in this study. Polynomial equations take the form $T = k_0 P^2 + k_1 P + k_2$. The damped Simon-Glatzel equation is $T_{rm} = T_c \left( \frac{\xi}{\alpha} + 1 \right)^{\frac{1}{\alpha}} \exp \left( -\epsilon P \right)$. 

(a) 

(b) 

(c) 

ruby Re gasket
sample chambers

T (K)

laser power

2075 ± 50 K
59.6 GPa

RHS

12 - 43.8 W
36 - 56.2 W

100 µm
\[ P = 0.4908 \times \Delta \nu \]
\[ R^2 = 0.98959 \]
(a) $1885 \pm 25 \text{ K}$
$19.6 \text{ GPa}$

(b) $1986 \pm 86 \text{ K}$
$45.7 \text{ GPa}$

(c) $2075 \pm 50 \text{ K}$
$59.6 \text{ GPa}$

Temperature RHS
Temperature LHS
first convection

Total Laser Power
This study

Ilmenite/perovskite MgSiO$_3$ transition (Ono et al., 2001)

MgSiO$_3$ - MgCO$_3$

Newton et al. (1975)

Katsura & Ito (1990)


This study

This study (with ruby)

MgCO$_3$ - CaCO$_3$

Byrnes & Wyllie (1981)

Buob et al. (2006)

Irving & Wyllie (1975)

Arag + Mag (Luth, 2001)

Dolss (Luth, 2001)

This study

This study (with ruby)

This study (in-situ experiment)

Arag + Mag (Luth, 2001)

Dolss (Luth, 2001)
(a) subsolidus

(b) sample surface

(c) sample interior

BSE

SiO$_2$ (wt%) MgO (wt%)

fig6
Pressure (GPa) vs Temperature (K)

- mantle adiabat - Katsura (2010)
- MgSiO$_3$ + MgCO$_3$ melt
- MgCO$_3$ + CaCO$_3$ melt

Hot slab
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*post-heating pressure from Pt MGD EoS (Zha et al., 2008)

In-situ experiment

$\Delta v$ (cm$^{-1}$) represents the change in wavenumber, P (GPa) is pressure, $T_m$ (K) is the melting temperature, $2\sigma$ (K) is the standard deviation of the melting temperature, and ruby P (GPa) is the pressure from ruby experiment.
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<tr>
<td>MgSiO$_3$ - MgCO$_3$</td>
<td></td>
<td></td>
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<tr>
<td>5-23 GPa</td>
<td>-1.305</td>
<td>38.32</td>
<td>1806</td>
</tr>
<tr>
<td>±</td>
<td>0.7976</td>
<td>27.56</td>
<td>231</td>
</tr>
<tr>
<td>$T_m^0$</td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>&gt; 23 GPa</td>
<td>1039</td>
<td>0.1848</td>
<td>7.44</td>
</tr>
<tr>
<td>±</td>
<td>2.06E+04</td>
<td>28.1152</td>
<td>5.32</td>
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<tr>
<td>MgCO$_3$ - CaCO$_3$</td>
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<tr>
<td>&gt; 12 GPa</td>
<td>994.05</td>
<td>0.67003</td>
<td>4.8058</td>
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<tr>
<td>±</td>
<td>1.08E+04</td>
<td>40.8</td>
<td>10.58</td>
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</tbody>
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