CHEMISTRY AND MINERALOGY OF EARTH’S MANTLE

Experimental determination of melting in the systems enstatite-magnesite and magnesite-calcite from 15 to 80 GPa†

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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 MgSiO3-MgCO3 join in the MgO-SiO2-CO2 system (MS-CO2) was defined from 15 to 80 GPa using in situ melting criteria, reaching a maximum temperature of ~2340 K at 80 GPa. The occurrence of melting has been confirmed with ex-situ textural and chemical analysis of recovered samples. The melting curve has a negative dT/dP slope at pressures between ~15 and 23 GPa resulting from the subsolidus phase transition of ilmenite- to perovskite-structured MgSiO3. The shallow slope of the melting curve at pressures higher than this transition indicates that for plausible mantle geotherms carbonate-bearing silicate lithologies will melt throughout the lower mantle. The solidus of a mixture along the MgCO3-CaCO3 join was determined as a proxy for alkali-free carbonate lithologies. Melting temperatures increase from 1860 K at 16 GPa to ~2100 K above 35 GPa, where the melting curve flattens. The melting reaction magnesite + post-aragonite (high-pressure CaCO3) = 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

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 Zhang 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 behavior of the mantle (Frost and McCammon 2008; Gaillard et al. 2008; Stango and Frost 2010; Rohrbach and Schmidt 2011; Walter et al. 2011; Dasgupta et al. 2013; Dasgupta 2013; Shirey et al. 2013).

The activity of oxygen is the critical factor in determining the form of carbon that exists in the mantle, because it fixes the distribution of oxidized 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 such as 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 oxidized 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 subduct into the mantle and are also not well known. Initially the majority of carbon introduced into the mantle is in oxidized 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 (Ishikawa 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 and Torsvik