Thermal equation of state and spin transition of magnesiosiderite at high pressure and temperature

**JIN LIU**\(^1\), **JUNG-FU LIN**\(^1\), **ZHU MAO**\(^1\) and **VITALI B. PRAKAPENKA**\(^2\)

\(^1\)Department of Geological Science, Jackson School of Geosciences, The University of Texas at Austin, Austin, Texas 78712, U.S.A.
\(^2\)Consortium for Advanced Radiation Sources, The University of Chicago, Chicago, Illinois 60637, U.S.A.

**ABSTRACT**

In situ synchrotron X-ray diffraction experiments on natural magnesiosiderite \([\text{(Mg}_{0.35}\text{Fe}_{0.65})\text{CO}_3]\) were conducted using resistive and laser-heated diamond-anvil cells (DACs) up to 78 GPa and 1200 K. Based on thermal elastic modeling of the measured pressure-volume curves at given temperatures, we have derived thermal equation of state (EoS) parameters and the spin-crossover diagram of magnesiosiderite across the spin transition. These results show the spin crossover broadened and shifted toward higher pressures at elevated temperatures. Low-spin magnesiosiderite is 6% denser and 8% more incompressible than the high-spin phase at 1200 K and high pressures. Within the spin crossover from 53 to 63 GPa at 1200 K, magnesiosiderite exhibits anomalous thermal elastic behaviors, including a dramatic increase in the thermal expansion coefficient by a factor of 20 and a drop in the isothermal bulk modulus by approximately 75 and 50%, respectively. Compared with the end-member magnesite \([\text{MgCO}_3]\) at relevant pressure-temperature conditions of the subducted slabs, the high-spin magnesiosiderite with 65 mol% \text{FeCO}_3 is approximately 21–23% denser and its unit-cell volume is 2–4% larger, whereas the low-spin state is 28–29% denser and 2% smaller than the end-member magnesite. Since ferromagnesite with 20 mol% of iron has been proposed to be a potential deep-carbon carrier, our results here indicate that the dense low-spin ferromagnesite can become more stable than high-spin ferromagnesite at pressures above approximately 50 GPa, providing a mechanism for \((\text{MgFe})\)-bearing carbonate to be a major carbon host in the deeper lower mantle.

**Keywords:** Fe-rich carbonate, thermal equation of state, spin transition, ferromagnesite, diamond-anvil cell

**INTRODUCTION**

The existence of oxidized carbon in the Earth’s deep interior can significantly affect several geophysical and geochemical properties of the planet \(\text{(e.g., Gaillard et al. 2008; Dasgupta and Hirschmann 2010). Due to the nominally low solubility of carbon in the main minerals of the mantle (Kepler et al. 2003; Dasgupta et al. 2013), carbon from primordial origins or altered ocean crusts is expected to be present as accessory phases in the deep mantle, such as carbonates, carbonate melts, carbonate-bearing fluids, diamond, and/or iron carbides (e.g., Berg 1986; Alt and Teagle 1999; Pal’yanov et al. 1999). Laboratory studies of carbon-bearing minerals at high pressures and temperatures \((P-T)\) can provide crucial constraints on the role and behavior of deep carbon in the geochemistry and geophysics of the Earth’s mantle, and therefore the mantle’s role in the global carbon cycle (Hazen et al. 2012). Magnesite \([\text{MgCO}_3]\) has been reported to be stable at relevant \(P-T\) conditions of the Earth’s lower mantle \(\text{(Isshiki et al. 2004; Oganov et al. 2008). High \(P-T\) experiments on carbonated peridotite and eclogite further showed that approximately 20 mol% siderite \([\text{FeCO}_3]\) can be dissolved in magnesite, forming an Fe-bearing \([\text{(MgFe)}\text{CO}_3]\) solid solution with rhombohedral structure (Dasgupta et al. 2004). This form, called ferromagnesite for the Mg-rich part of the system and magnesiosiderite for the Fe-rich part of the system, could be a stable major deep-carbon host in the lower mantle. Iron as a transition metal is known to play an important role in the physical, chemical, and transport properties of the mantle minerals due to the various electronic spin and valence states exhibited by the 3d electrons of iron at high \(P-T\) conditions \(\text{(e.g., Lin and Tsuchiya 2008). An electronic high-spin (HS) to low-spin (LS) transition of iron in the magnesite-siderite system has been recently observed to occur at approximately 45 GPa using several experimental and theoretical techniques including high-pressure X-ray emission spectroscopy, X-ray diffraction, laser Raman spectroscopy, and first-principles calculations (Mattila et al. 2007; Shi et al. 2008; Lavina et al. 2009, 2010a, 2010b; Nagai et al. 2010; Farfan et al. 2012; Lin et al. 2012). This transition is associated with a 6–10% reduction in the unit-cell volume, making the LS state denser and more incompressible than the HS counterpart (Lavina et al. 2009, 2010b; Nagai et al. 2010; Farfan et al. 2012; Lin et al. 2012). It has been suggested that iron may preferentially partition into the LS ferromagnesite, which would make it a stable deep-carbon host in the lower mantle (Lavina et al. 2009, 2010a, 2010b; Nagai et al. 2010; Farfan et al. 2012; Lin et al. 2012). On the other hand, iron-bearing magnesite and siderite have been reported to transform into an assemblage of magnetite, nano-diamonds, and a new high-pressure phase with three-membered rings of corner-sharing \([\text{CO}_3]\) tetrahedra at pressures exceeding 40 GPa and high temperatures (Boulard et al. 2011, 2012). Furthermore, the electronic spin-pairing transi-