



Siderite at lower mantle conditions and the effects of the pressure-induced spin-pairing transition

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[1] Siderite (FeCO_3) forms a complete solid solution with magnesite (MgCO_3), the most likely candidate for a mantle carbonate. Our experiments with natural siderite reveal spin pairing of d -orbital electrons of Fe^{2+} at 43 GPa, as evidenced by a sharp volume collapse of about 10%. The initially colorless crystals assume an intense green color after the transition, which progressively turns to red above 60 GPa. We present clear evidence for the instability of an intermediate spin state in siderite at ambient temperature. At the transition pressure, domains of high and low spin siderite coexist. The unit cell volume difference between magnesite and siderite is significantly decreased by the spin transition, enhancing the solubility between the two calcite-type minerals. A siderite component in magnesite at lower mantle pressure would significantly increase its density and slightly increase the carbonate bulk modulus.

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1. Introduction

[2] Cosmochemical abundance arguments suggest that a large amount of Earth's carbon, one of the more fundamental elements for the nature of our planet and its life, is stored in the deep interior [*Sleep and Zahnle*, 2001]. Given the very low solubility of carbon in mantle phases [*Shcheka et al.*, 2006; *Panero and Kabbes*, 2008] carbon should be found segregated into separate accessory minerals of widely variable properties, spanning from hard diamond, to conductive graphite, and to the many forms of CO_2 [e.g., *Downs and Somayazulu*, 1998; *Tschauner et al.*, 2001; *Iota and Yoo*, 2001; *Sun et al.*, 2009] that might buffer the mantle oxidation state. These phases can be generated after partial breakdown of subducted carbonates, when CO_2 is released during arc volcanism [*Sano and Williams*, 1996]. The most likely carbonate phase at mantle conditions, according to experimental [*Isshiki et al.*, 2004] and theoretical studies [*Dorogokupets*, 2007; *Panero and Kabbes*, 2008], is magnesite (MgCO_3 , Mgs). The stability of magnesite in association with silicates is, however, controversial, probably confined to the cold geotherm of subducting slabs [*Katsura*

and *Ito*, 1990; *Biellmann et al.*, 1993; *Seto et al.*, 2008]. The discovery of carbonate inclusions in diamonds [*Wang et al.*, 1996; *Brenker et al.*, 2007] is direct evidence of the existence of carbonates in the mantle.

[3] Given the abundance of iron in the mantle, it is likely that deep carbonates are solid solutions of magnesite and siderite (Sd). The high-spin (HS) to low-spin (LS) magnetic transition in siderite measured by means of x-ray emission spectroscopy (XES) has been recently reported to occur at ~ 50 GPa [*Mattila et al.*, 2007] and later modeled by means of first principle calculations [*Shi et al.*, 2008]. This electronic transition is of fundamental importance to mantle physics, affecting density, seismic velocities and electronic properties of major mantle minerals [e.g., *Lin and Tsuchiya*, 2008]. The volume-driven electronic transition in mantle minerals has been predicted since the early 1960s [*Fyfe*, 1960], but only recently has it been experimentally observed [*Badro et al.*, 2003, 2004]. Siderite is among the few minerals to reject mixed valence substitutions, is unlikely to contain vacancies and has a simple structure wherein Fe^{2+} is 6-fold coordinated, located on an inversion center in a slightly distorted trigonal octahedron, and therefore presents an ideal model to study the spin-pairing transition.

2. Experiment

[4] Two experiments, covering different pressure ranges, have been conducted on the same specimen; the sample is a natural Mg-bearing siderite, [$\text{Fe}_{0.72}\text{Mg}_{0.24}\text{Mn}_{0.03}\text{Ca}_{0.01}\text{CO}_3$], from Příbram, Czech Republic that was obtained from the RRUFF Project collection (ID number is <http://rruff.info/R040034>). In both experiments, a cleavage rhombohedron about $10\ \mu\text{m}$ thick, with $20\ \mu\text{m}$ edge, was loaded in a symmetric diamond anvil cell (DAC) together with fine gold powder. The sample chamber between the anvils was obtained by drilling a hole ($130\ \mu\text{m}$ diameter for $300\ \mu\text{m}$ anvil culets and $80\ \mu\text{m}$ diameter for $150\ \mu\text{m}$ anvils culets) in Re gaskets pre-indented to $30\ \mu\text{m}$ (Figure 1). The sample chamber was loaded at pressure (172 MPa) with Ne [*Rivers et al.*, 2008] in order to ensure a quasi-hydrostatic stress field around the crystal. Single crystal diffraction data were collected at the bending magnet and the undulator stations (13BMD and 13IDD) at the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) at the Advanced Photon Source (APS) of the Argonne National Laboratory. Monochromatic radiation of 37 keV, focused to a spot of less than $10\ \mu\text{m}$ in diameter, was used to probe the structure at pressure. Omega scan patterns were collected with a CCD (MAR-165, 13IDD station) and an image plate (MAR-345, 13BMD station). Peak coordinates in reciprocal space were used to index the peak list and cell parameters

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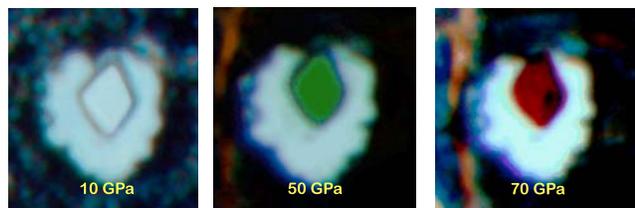


Figure 1. Optical image of the siderite crystal in the diamond anvil cell showing the change in color from clear (10 GPa) to green (50 GPa) to red (70 GPa) as pressure is increased.

were obtained by least square refinement of the d -spacing of 30 to 70 peaks (see auxiliary material).¹ The restricted access to reciprocal space and other limitations on the measurements of integrated intensities introduced by the DAC prevented stable structural refinements. Measurements were performed at ambient temperature in the range 0–90 GPa, about 30 data points, more finely spaced around and after the spin transition, were collected. Pressure was estimated using the diffraction pattern from gold as an internal pressure standard [Fei *et al.*, 2007a, 2007b].

3. Results and Discussion

3.1. Volume and Compressibility

[5] In siderite, the spin transition is marked by a sharp volume decrease at 43 GPa (Figure 2), no evidence of structural phase transitions was detected. The pressure of the transition is in good agreement with the XES study [Mattila *et al.*, 2007] where the transition was shown to occur between 46 and 56 GPa, and where the pressure stability was around 3 GPa. The investigated sample is a solid solution between siderite, magnesite, rhodochrosite and calcite ($\text{Mgs}_{24}\text{Sd}_{72}\text{Rh}_3\text{Cc}_1$). In order to estimate the volume of the siderite end-member, the rhodochrosite and calcite components have been ignored as negligible, the Vegard's law has been assumed [$V(\text{Sd}_{75}) = 0.75 V(\text{Sd}) + 0.25 V(\text{Mgs})$] and the volume of magnesite was calculated using EOS parameters [Litasov *et al.*, 2008]. The volume decrease at the spin transition is 9%, in very good agreement with a theoretically predicted value of 10% [Shi *et al.*, 2008]. The pressure dependence of the volume of HS-Sd is in fairly good agreement with the EOS parameters proposed for this phase [Zhang *et al.*, 1998]. Assuming $K'_0 = 5.0$, a 3rd order Birch Murnaghan equation of state has been fit to the P-V data of LS-Sd, resulting in a zero pressure volume of LS-Sd and bulk modulus: $V_0(\text{LS-Sd}) = 263(3) \text{ \AA}^3$ and $K_0(\text{LS-Sd}) = 148(12) \text{ GPa}$, respectively. The choice of K'_0 is particularly arbitrary in rhombohedral carbonates, where values close to 5 are most commonly reported; however values in the range 4–5.4 have been recently proposed [Zhang *et al.*, 1998; Fiquet *et al.*, 2002; Litasov *et al.*, 2008; Dorogokupets, 2007]. The fitted V_0 and K_0 are almost fully correlated, it follows that the absolute values of the EOS parameters are poorly constrained, however, the relative values are useful in comparing the compression curves of the LS-Sd with the magnesite one [Fiquet *et al.*, 2002]. The

comparison is particularly important because the Mg-Fe²⁺ substitution is likely the most common in mantle carbonates as well as in major mantle minerals. At the spin crossover, the volume of LS-Sd is significantly lower than the volume of magnesite, so that, at the transition pressure, the effective ionic radius of iron in the low spin configuration is smaller than the radius of magnesium. The volume mismatch between siderite and magnesite decreases with pressure, LS-Sd being less compressible than magnesite, and the volumes of the two calcite-type carbonates converge at about 80 GPa.

3.2. Sharpness of the Electronic Transition

[6] The diffraction pattern collected at the transition pressure (Figure 3) differs intriguingly from the diffraction patterns that were collected immediately below and above the transition: all peaks are split, the smaller the d -spacing, the larger the splitting. We interpret the pattern as the result of the coexistence of two lattices with the same symmetry and orientation but different size. Two volumes were calculated for siderite at 43 GPa matching the compression curves of HS-Sd and LS-Sd. To our knowledge, this phenomenon has not been observed in other phases undergoing the spin pairing transition. The coexistence of distinct domains of HS-Sd and of LS-Sd might be generated by small differences in pressure within the sample which nevertheless would imply a sharp transition. A narrow range of coexistence of the two spin states might be intrinsic to the pairing transition in the investigated phase. The diffraction pattern at 43 GPa, with no trace of an intermediate volume, is evidence for the lack of an intermediate state in siderite at ambient temperature, both in terms of a statistical distribution of HS-Fe²⁺ and LS-Fe²⁺ in a relaxed lattice or of an intermediate distribution of paired electrons in the 3d orbitals.

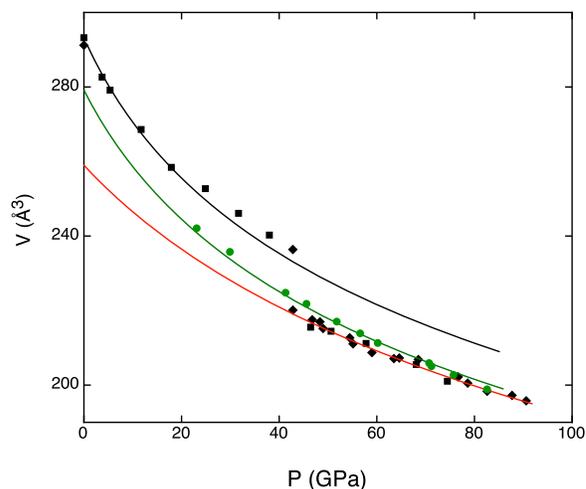


Figure 2. Volume of Mg-bearing siderite as a function of pressure from ambient to 90 GPa (all measurements at ambient temperature). The discontinuity at 43 GPa marks the high spin-low spin magnetic transition. Squares: data collected at Station 13BMD, diamonds: data collected at the Station 13IDD, green circles: magnesite data [Fiquet *et al.*, 2002]. Solid black curve: EOS for HS-Sd from the literature. Solid red curve: EOS of LS-Sd, this work. Solid green curve: magnesite EOS [Fiquet *et al.*, 2002].

¹Auxiliary materials are available in the HTML. doi:10.1029/2009GL039652.

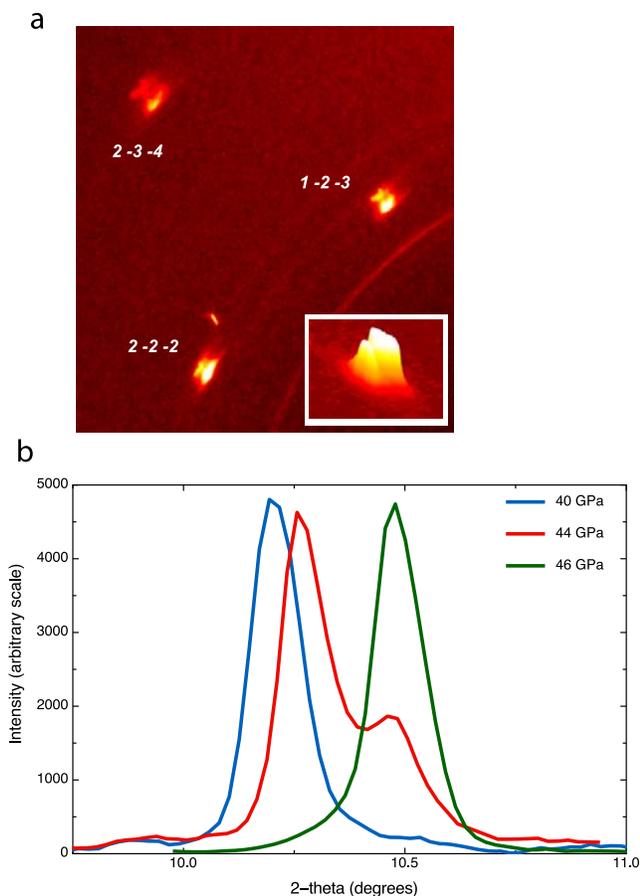


Figure 3. (a) Diffraction pattern at the transition pressure, 43 GPa, with split peaks suggesting the coexistence of HS-Sd and LS-Sd domains with distinct volumes. The 3-D plot of the peak in the inset emphasize the splitting of the peaks in two distinct maxima. (b) The profile of the peak (2-2-2) at the spin transition is clearly split in two components matching the values for the LS-Sd and HS-Sd at 43 GPa. Immediately after the transition the peak width is comparable to the peak width before the transition.

[7] The P-T range over which the spin transition occurs at extreme conditions is difficult to determine. Experiments and theoretical predictions suggest for ferropericlase and perovskite a broad pressure range at mantle temperatures while for ambient temperature a general agreement has not been reached. In fact, in contrast to the results of the present study, most experiments conducted at ambient temperature show a gradual variation with changing pressure of the parameters related to the spin state (see *Li* [2007] for a review) which are, however, not necessarily interpreted as a result of a gradual spin transition. The fact that experiments on annealed samples tend to show sharper transitions than others [cf. *Badro et al.*, 2003, 2004; *Li et al.*, 2004; *Jackson et al.*, 2005] supports the hypothesis that large differential stress in the diamond anvil cell might be responsible for broadening the transition [*Li et al.*, 2005]. Spin pairing is expected to occur at different pressures for different site geometries, different valences and different iron concentrations; the more diverse the iron bonding in a mineral, the more complicated the spin pairing dependence on pressure is expected to be.

3.3. Color

[8] Macroscopic fresh specimens of siderite are transparent yellow-green, whereas surface alteration, inclusions and exsolution products can give siderite a red or black color. Microscopic samples appear colorless. The perfectly transparent and colorless siderite crystals loaded in the diamond anvil cell assumed a green color at the spin transition, becoming progressively deeper green with pressure. Upon further compression the mineral color changed to grey and finally to bright red at ~ 60 GPa (Figure 1). Even though small pressure variations cause appreciable color changes, no variation in color within the crystals was observed, further suggesting minimal pressure gradients within the sample chamber. The color changes, which are reversible, are likely due to a gain in absorption in the visible range accompanying the spin transition, which has also been described in ferropericlase and perovskite, and has implications for the radiative properties of the mantle [*Goncharov et al.*, 2006, 2008]. The change in color is not an unexpected pressure effect [*Burns*, 1993; *Taran et al.*, 2008], as bond shortening and increase of the energy of the bands cause a blue-shift of the absorption bands.

4. Conclusions

[9] This study presents definitive evidence for the sharpness of the spin crossover in siderite at ambient temperature, which is reasonable considering that all iron is divalent and is located in a slightly distorted octahedral site with six identical bond distances. We also show that domains in the high and low spin states coexist at the crossover. Whether or not this heterogeneity is caused by small pressure gradients, this multiphase behavior should be taken into account when interpreting experimental results since intermediate values of the properties probed as a measure of the spin state may result from different proportions of high and low spin state domains rather than intermediate spin states. The volume change, increase in the bulk modulus and visible light absorption associated with the spin transition in siderite are comparable to what has been observed in ferropericlase where iron is also mostly divalent and six-coordinated.

[10] The spin transition drastically reduces the volume mismatch between the iron and magnesium rhombohedral carbonates and should favor solubility of iron in magnesite in the lower mantle. Since a smaller radius of the metallic ion is expected to stabilize the calcite structure at high pressure [*Santillan and Williams*, 2004], the stability of Fe-bearing magnesite should be lower than pure magnesite at low pressures where Fe^{2+} is in the high spin state and the opposite should be true at higher pressures after the spin pairing. If the scheme for the P-T dependence of the number of unpaired electrons described for Fe^{2+} in ferropericlase [*Sturhahn et al.*, 2005] is assumed, the transition would be shifted to higher pressure and broadened over a wide range (~ 70 – 100 GPa) along the mantle geotherm. In the bottom part of the lower mantle, most of *d*-orbital electrons of Fe^{2+} in siderite should be paired.

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