

Effect of temperature on the pressure-induced spin transition in siderite and iron-bearing magnesite: a Raman spectroscopy study

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Abstract: High-pressure and high-temperature Raman spectra of synthetic FeCO_3 siderite and $\text{Mg}_{0.76}\text{Fe}_{0.24}\text{CO}_3$ magnesite were measured across the spin transition up to nearly 60 GPa and 700 K. In pure siderite the spin transition is sharp and observed between 44 and 46 GPa, with no discernible temperature dependence up to 700 K. The spin transition in Fe-bearing magnesite (“ferromagnesite”) is also sharp and takes place between 45 and 47 GPa at ambient temperature, whereas the transition pressure range broadens significantly at about 600 K (45–52 GPa). Our results suggest that the *onset* pressure of the spin transition in the siderite–magnesite solid solution series is independent of temperature and composition up to 700 K, whereas the broadening of the spin transition range at higher temperature is driven by the Mg content of the sample. Finally, comparison of the $(\text{Mg,Fe})\text{CO}_3$ and the $(\text{Mg,Fe})\text{O}$ systems indicates that the onset pressure of the spin transition is temperature-independent in both cases, which is rationalized in terms of the FeO_6 octahedral compression.

Key-words: high pressure; high temperature; siderite; magnesite; iron spin transition; Raman spectroscopy; carbonates.

1. Introduction

One of the most active fields of current research in mineral physics are the pressure-induced spin state transitions observed in various Fe-bearing minerals, such as “ferropericlase”¹ (e.g. Badro *et al.*, 2003; Lin *et al.*, 2012a) and siderite (e.g. Matilla *et al.*, 2007; Lavina *et al.*, 2010a), at conditions of the Earth’s lower mantle. In these minerals, the Fe^{2+} cations, with six electrons in their 3d orbitals ($3d^6$), exhibit an octahedral coordination with respect to their oxygen neighbors. Due to the octahedral crystal field, the Fe^{2+} 3d orbitals split into a low-energy triplet t_{2g} and a high-energy doublet e_g (e.g. Burns, 1993). The energy difference between the t_{2g} and e_g states is called crystal-field splitting Δ . Increase of the external pressure leads to the enhancement of Δ via the shortening of the Fe–O bond lengths (Burns, 1993). Upon sufficient compression, Δ will eventually overcome the spin pairing energy, thus leading to a change in the spin state of Fe^{2+} from the starting high-spin (HS) to a low-spin (LS) configuration. These HS to LS transitions are accompanied by *isostructural* transitions with sizeable volume changes,

which primarily result from the reduction of the Fe^{2+} ionic radius [$r_{\text{VI}}^{\text{HS}}(\text{Fe}^{2+}) = 0.78 \text{ \AA}$, $r_{\text{VI}}^{\text{LS}}(\text{Fe}^{2+}) = 0.61 \text{ \AA}$ (Shannon & Prewitt, 1969)]. These accompanying structural effects allow for the (indirect) detection of the HS to LS transitions by various experimental probes, such as X-ray diffraction (XRD) and Raman spectroscopy.

The pressure-induced spin transitions are known to affect many important physical and chemical mineral properties, such as seismic velocities, electrical conductivity, and element partitioning (e.g. Badro, 2014), which in turn strongly influence the properties of the lower mantle. Despite the high abundance of Fe-bearing minerals in the mantle (e.g. ferropericlase or bridgmanite), clear evidence of such a spin transition has not been detected by seismologic observations (e.g. Lin *et al.*, 2007; Cammarano *et al.*, 2010; Antonangeli *et al.*, 2011). A plausible explanation might be that the range of the spin transition at high pressure (P) and high temperature (T) is significantly broadened, which would smear out any discontinuous changes in the physical properties of the respective mantle phase. Therefore, unraveling the P , T and compositional (X) dependence of the HS to LS transitions is of fundamental importance for understanding the respective mineral properties under mantle conditions, as well as to better constrain the range of spin transitions in the lower mantle.

In this work, we focus on the high-pressure and high-temperature vibrational behavior of $(\text{Fe,Mg})\text{CO}_3$ carbonates by means of Raman spectroscopy. For all compositions, the

¹ Expressions like “ferropericlase” and “magnesiowüstite”, or “ferromagnesite” and “magnesiosiderite”, are not proper mineral names but are used in the high-pressure community to refer to, e.g., an Fe-bearing periclase or Mg-bearing wüstite. For simplicity they are used without quotes in the following, but are not meant as mineral names.

solid solution adopts a calcite-type structure at ambient conditions (space group $R\bar{3}c$, $Z=6$), with the Fe^{2+}O_6 octahedra stacked along the c -axis and separated by triangular planar CO_3 -groups (e.g. Lavina *et al.*, 2010a). These carbonate minerals have attracted recent interest as they are considered potential candidates for transporting carbon into the deep mantle (e.g. Isshiki *et al.*, 2004). Hence, the understanding of their high-pressure behavior is also important for advancing our comprehension of the deep carbon cycle (e.g. Dasgupta & Hirschmann, 2010).

Recent literature on FeCO_3 siderite reports a pressure-induced spin transition between 40 and 50 GPa (Matilla *et al.*, 2007; Lavina *et al.*, 2009, 2010a and b; Spivak *et al.*, 2014; Cerantola *et al.*, 2015; Lobanov *et al.*, 2015, 2016; Taran *et al.*, 2017), depending on the experimental method and the composition of the starting material (Table S1, freely available online as Supplementary Material linked to this article on the GSW website of the journal, <http://eurjmin.geoscienceworld.org/>). Spivak *et al.* (2014) and Cerantola *et al.* (2015) performed high-pressure Raman spectroscopic investigations on a synthetic FeCO_3 sample at room- T . They detected a change of the Raman spectra, *i.e.* discontinuous frequency shifts for all of the observed siderite Raman-active modes and, most importantly, the occurrence of two distinct ν_1 -modes between 40 and 47 GPa, which was interpreted as the signature of the HS to LS transition. The broad transition range was attributed to the coexistence of the HS and LS phases. On the contrary, Raman, XRD, and optical absorption studies conducted on natural siderite samples with slightly lower Fe^{2+} content revealed a relatively sharp transition between 43 and 46 GPa (Farfan *et al.*, 2012; Lavina *et al.*, 2010a; Lin *et al.*, 2012; Lobanov *et al.*, 2015; Fu *et al.*, 2017). By means of high-pressure Raman spectroscopy, Müller *et al.* (2016) showed recently that the spin transition in natural siderite is instantaneous at room- T , and that the broad HS to LS transition range is caused by stress gradients on the sample. On the other hand, Lavina *et al.* (2010b) reported that in the $(\text{Mg,Fe})\text{CO}_3$ solid-solution series the HS to LS transition pressure shifts to slightly higher pressures with increasing Mg content. In addition, combined high- P and high- T investigations on magnesiosiderite revealed the upshift of the HS to LS transition pressure, as well as a further broadening of the transition range with increasing temperature (Liu *et al.*, 2014). These studies are recapitulated in Table S1.

The following questions arise from the present state of knowledge: (1) Are the differences in the HS to LS transition pressure between natural and synthetic siderite, as well as the respective coexistence range, dependent on the composition of the studied sample? (2) What is the effect of temperature on the HS to LS transition for the siderite end-member? In order to address these questions, we have conducted combined high- P and high- T Raman spectroscopic measurements on both a siderite and a ferromagnesite sample. Our results indicate that, at room- T , the HS to LS transition in both compounds is sharp and, within error, occurs at the same pressure. In addition, we did not observe any apparent temperature dependence of

the spin transition in pure siderite, *i.e.* the transition remains sharp up to 700 K. On the contrary, the HS to LS transition range in ferromagnesite exhibits a broadening upon temperature increase, whereas the onset transition pressure remains unaffected by temperature.

2. Materials and methods

2.1. High-pressure experiments

The high-pressure Raman experiments were performed with synthetic siderite (FeCO_3) and synthetic ferromagnesite ($\text{Mg}_{0.76}\text{Fe}_{0.24}\text{CO}_3$) in order to investigate the compositional effects on the spin transition. In order to reduce the stress gradient and obtain signal from the whole sample, we used small crystals of 10–20 μm edge length in all of our experiments. Details of the sample synthesis can be found in Cerantola *et al.* (2015).

Siderite and ferromagnesite at ambient temperature were measured in Boehler-Almax diamond-anvil cells (DAC) (Boehler, 2006), which were loaded cryogenically with argon (siderite) and helium (ferromagnesite) as pressure transmitting media (PTM). The combined high- P and high- T experiments were performed with a Diacell DAC-HT, equipped with an internal heater. Pressure in this cell is induced via a gas membrane, with NaCl serving as PTM.

All DACs were equipped with diamonds of 300 μm culet and rhenium gaskets, which were preindented to 30–40 μm thickness. The holes in the gaskets were about 100–150 μm in diameter. Small ruby crystals were loaded in each cell in order to determine the pressure using the ruby fluorescence method after Mao *et al.* (1986). Since the shift of the ruby fluorescence lines is dependent on pressure and temperature, $\text{SrB}_4\text{O}_7\text{:Sm}^{2+}$ was added in the combined high- P high- T experiments. $\text{SrB}_4\text{O}_7\text{:Sm}^{2+}$ has a fluorescence line at 685.4 nm, which shifts with pressure but is almost independent of temperature in the T -range of interest (Datchi *et al.*, 2007; Raju *et al.*, 2011). With the help of the ruby and the $\text{SrB}_4\text{O}_7\text{:Sm}^{2+}$ fluorescence peak shifts we were able to calculate the temperature inside the DAC; we note that the thermocouple measures T only in the periphery of the sample chamber. Following Koch-Müller *et al.* (2016) and Efthimiopoulos *et al.* (2017), the pressure obtained from the $\text{SrB}_4\text{O}_7\text{:Sm}^{2+}$ was used to calculate the position of the ruby R_1 peak at room- T . A subtraction between this calculated R_1 peak room- T value and the measured R_1 position at any temperature yields the temperature-induced shift of the ruby R_1 peak, from which we calculate the temperature in the sample chamber (Datchi *et al.*, 2007). Note that the temperature measured by the thermocouple outside the sample chamber is always higher than the ruby-extracted value (Fig. S1).²

² Note that in Koch-Müller *et al.* (2016, p. 549) the temperature reading of the thermocouple was given erroneously. It should read “The temperature outside the gasket hole was always higher than inside, ...”.

Klotz *et al.* (2009) determined pressure from various ruby spheres in the same experiment and studied the effects of the PTM on the pressure determination. For argon at *ca.* 40 GPa the obtained pressures are within 1.2 GPa (Klotz *et al.*, 2009), which we use as the error in our pressure determination. In NaCl deviatoric stress at 40 GPa and ambient temperature is 4 GPa, but can be strongly reduced when heated (*e.g.* Dubrovinsky *et al.*, 1998; Dorfman *et al.*, 2010). At high temperature we assume an error of the pressure determination of ± 1.5 GPa at 40 GPa. Since the calculated temperature relies on the pressure determination, the error of the ruby-determined temperature is mainly determined by the pressure uncertainty. From this, we estimate an average temperature error of ± 50 K.

2.2. Raman spectroscopy

The Raman spectroscopic measurements were performed with a HORIBA Jobin Yvon LabRAM HR800 VIS spectrometer equipped with a blue 473 nm diode-pumped solid-state laser. All measurements were done with a 20 $\times$ lens, with the obtained Raman spectra collected between 200 and 1250 cm⁻¹ frequency range for 15–20 s and 5–10 accumulations.

3. Results

The Raman spectrum of siderite at ambient conditions shows four distinct peaks between 150 and 1250 cm⁻¹ (Fig. S2), in agreement with literature data (*e.g.* Rutt & Nicola, 1974). The most prominent Raman feature is the internal symmetric stretching mode (ν_1) located at 1085 cm⁻¹. At the HS to LS transition pressure, a new mode appears close to the ν_1 -mode at lower wavenumbers, which is assigned to the ν_1 -mode of the LS siderite phase (Spivak *et al.*, 2014; Cerantola *et al.*, 2015; Müller *et al.*, 2016). Thus, the monitoring of this mode suffices for the identification of the HS to LS transition. Given that at high-*P* and high-*T* only the ν_1 -mode was clearly observable (Fig. S2), we restrict the following discussion to this mode alone.

Our high-pressure Raman measurements at room-*T* on FeCO₃ evidence the change of the ν_1 -mode between 44.4 and 48 GPa (Fig. 1). However, at 45.2 GPa the crystal has almost completely adopted the LS state. Müller *et al.* (2016) showed that the apparent coexistence of HS and LS is only an effect of the stress gradient on the sample and due to the limited spatial resolution of the measuring system. Therefore, we consider the spin transition within the range of 44.4–45.2 GPa at room-*T* as sharp. Our result for the synthetic FeCO₃ is in excellent agreement with our recent observation on a natural siderite sample (Fe_{0.89}Mn_{0.07}Mg_{0.03}Ca_{0.01}CO₃, Müller *et al.*, 2016), suggesting that the exact composition of the siderite sample under study neither influenced the onset pressure nor the pressure range of the spin transition in this material. Furthermore, for synthetic FeCO₃ at *ca.* 700 K, this transition is also manifested within a narrow pressure

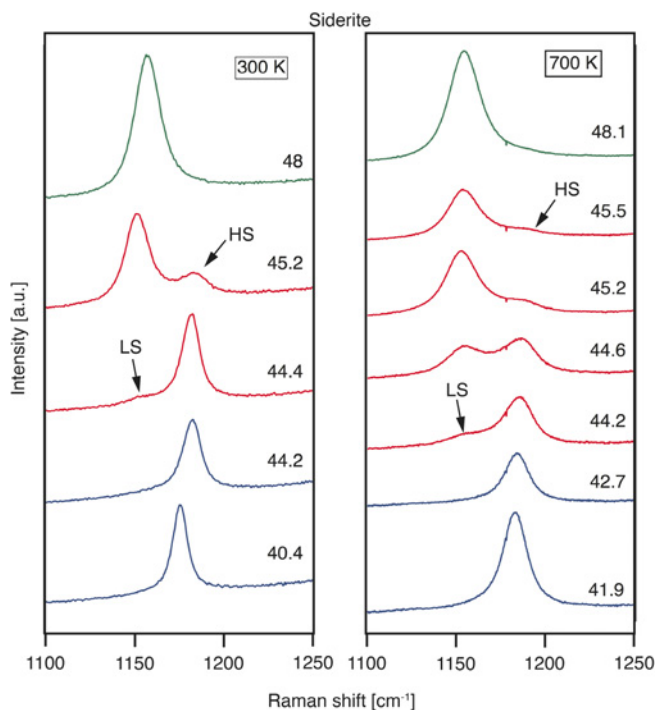


Fig. 1. Raman spectra of the ν_1 -mode of synthetic siderite from the experiments at 300 and at 700 K. Numbers above each spectrum refer to the respective pressure (GPa). The spin transition could be narrowed down to a pressure range of 44 and 46 GPa, as indicated by the change of the ν_1 -mode. (Online version in color.)

range, 44.2–45.5 GPa, which is the same as at room-*T* for this compound (Fig. 1). Hence, we conclude that the HS to LS transition in the FeCO₃ end-member is sharp, with a negligible effect of temperature (at least up to 700 K).

Upon completing the 700 K high-pressure cycle, the sample was quenched to room-*T* and pressure was decreased to ~ 29 GPa. Then the crystal was heated again up to about 550 K, and by isothermally increasing pressure, we observed the spin transition between 42.6 and 47.2 GPa. This transition range is broader compared to the room-*T* and 700 K compression cycles. We tend to attribute this transition-pressure broadening, as well as the lower onset pressure, to the fracturing of the crystal during the quenching and decompression process. Such fracturing is expected to result in internal stress maxima and minima, resulting in a large stress gradient on the sample (*e.g.* Takemura, 2001), which in turn can account for both this extended HS to LS transition-pressure range and the lower onset transition pressures.

Turning now to ferromagnesite, a shift to lower wavenumbers and a significant broadening of the ν_1 -mode is evidenced between 45 and 47 GPa at room-*T* (Fig. 2). In analogy to siderite, we assign these observations to the signature of the spin transition. Beyond 47 GPa, the ν_1 -mode remains broad and highly asymmetric. This line shape change in the LS state may indicate either a tendency of the ν_1 -mode to split into (at least) two components, *i.e.* a local structural distortion accompanying the HS to LS transition, or significant phonon anharmonic effects inherent of the LS state (Foster *et al.*, 1993). We note that by assuming two

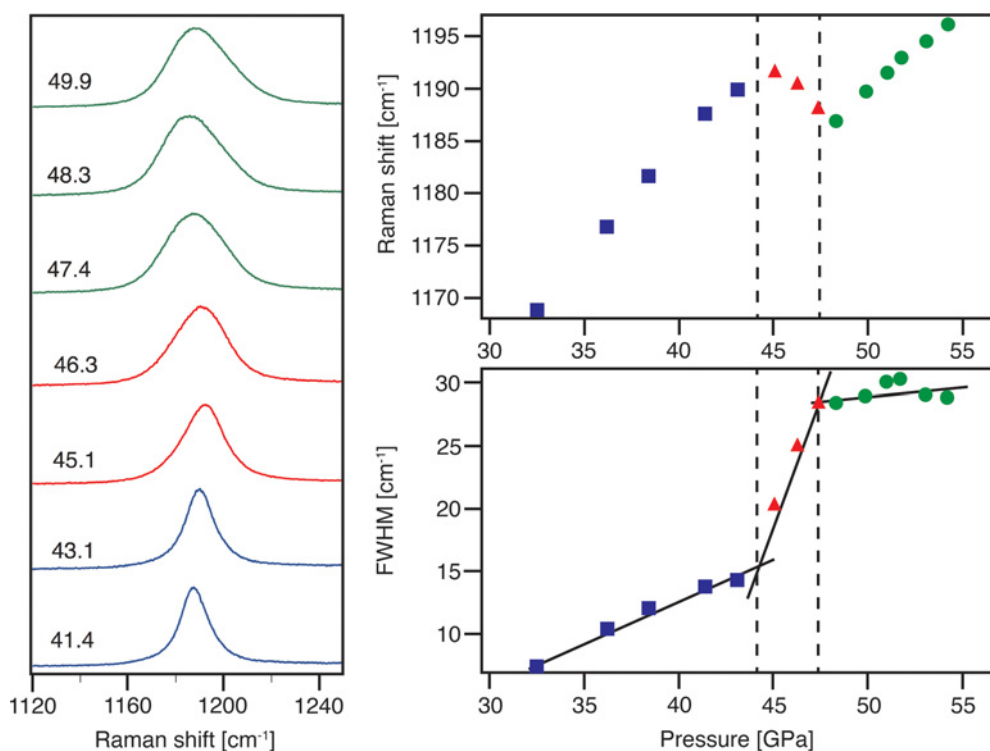


Fig. 2. High-pressure and ambient-temperature Raman spectra of the ν_1 -mode of synthetic ferromagnesite ($\text{Mg}_{0.74}\text{Fe}_{0.26}\text{CO}_3$) across the spin transition (left). Numbers above each spectrum refer to the respective pressure (GPa). Between 45 and 47 GPa the spin transition is indicated by a shift of the ν_1 -mode to lower wavenumbers (right top), combined with a significant increase of the full width at half maximum (FWHM) (right bottom). The error bars for the Raman shift and the FWHM lie within the symbols. (Online version in color.)

constituents for fitting the asymmetric LS ν_1 -mode, the respective relative intensities of the two components remain pressure-independent throughout the whole LS stability range (47–55 GPa) explored in this study.

On the other hand, the respective ν_1 -mode frequency downshift at higher temperatures is not as obvious as at ambient temperature (Fig. 3). Consequently, we used the pressure-induced evolution of the ν_1 -mode's full width at half maximum (FWHM) for identifying the spin transition in ferromagnesite at higher temperatures. At the onset pressure of the spin transition the ν_1 -mode starts to broaden continuously. Although the ν_1 -mode apparently splits into two components in the LS phase, we have fitted the LS ν_1 -mode assuming only one Gaussian peak in order to be consistent with the fits of the HS spectra. The onset and the end of the spin transition are marked by a change of the pressure slopes of both the ν_1 Raman mode frequency and its FWHM (Fig. 3). Ambient- and high-temperature deconvolution examples of ν_1 -mode of HS and LS ferromagnesite components can be found in Fig. S3.

In the high- P - T experiments on ferromagnesite, we observed the spin transition in a broader range, between 45 and 52 GPa at *ca.* 550–600 K (Fig. 3). At 400 K we observed the onset of the spin transition at *ca.* 45 GPa, but we largely overstepped the end of the transition and we were not able to monitor the HS and LS coexistence range in this case. Nevertheless, the onset pressure of the transition is the same for both siderite and ferromagnesite and it appears to be independent of temperature in both cases. The results are summarized in Fig. 4 in the form of P - T phase diagrams.

4. Discussion and conclusions

The observations of this study confirm that the spin transition in siderite is sharp and takes place between 44 and 46 GPa at room- T . In addition, our high-pressure room- T Raman study on ferromagnesite showed that the spin transition is also sharp with (roughly) the same onset pressure as for siderite. Thus, within experimental uncertainty, the composition of the solid solution seems to have a minor effect on the spin transition (Fig. 5). The latter observation is consistent with recent studies on $(\text{Mg}_x\text{Fe}_{1-x})\text{CO}_3$ solid solutions, which did not detect any compositional dependence of either the onset transition pressure, or the pressure range of the spin transition at room- T (Liu *et al.*, 2014; Hsu & Huang, 2016). We note though that these results are in contrast to the data of Lavina *et al.* (2010b), who observed a compositional dependence of the onset pressure of the spin transition.

A possible reason for this absence of compositional dependence in the spin transition pressure may be the similar structural response of calcite-type carbonates under pressure. In particular, the room- T bulk moduli values of siderite, magnesiosiderite, magnesite, and rhodochrosite are very similar (Zhang *et al.*, 1998; Fiquet *et al.*, 2002; Lavina *et al.*, 2010a; Liu *et al.*, 2014; Merlini *et al.*, 2015; Table S2). Since the compressibility of the calcite-type structure depends mainly on the metal-oxygen octahedra, the similarity of the bulk moduli values is expected to reflect the similarity in the pressure dependence of the octahedral volumes or, equivalently, the

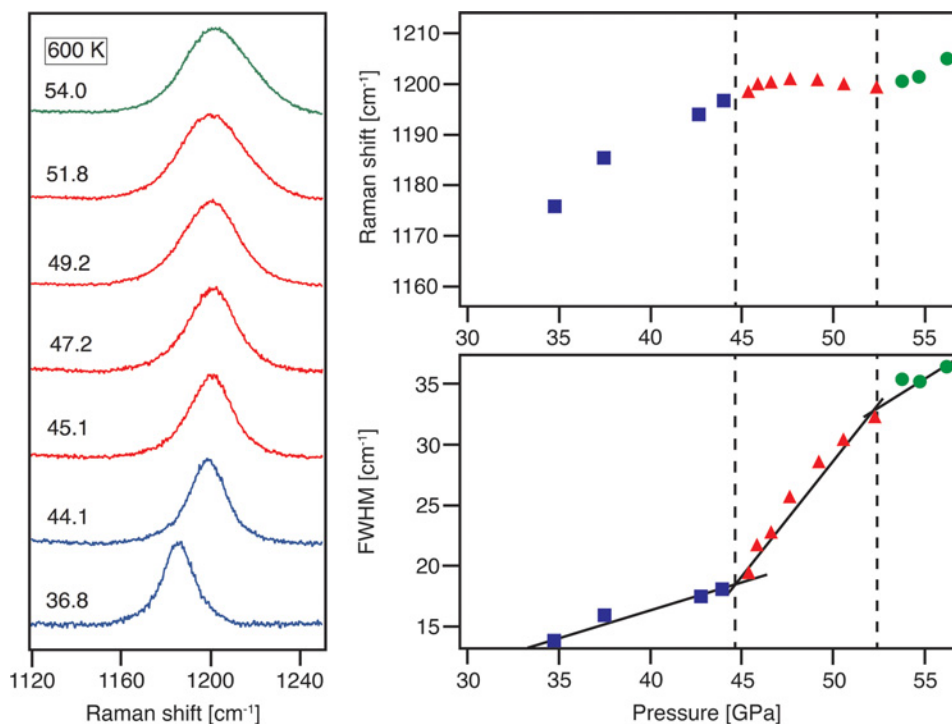


Fig. 3. Raman spectra of the ν_1 -mode of ferromagnesite at different pressures and 600 K (left), and pressure-dependence of the Raman shift and the FWHM at 600 K (right). Numbers above each spectrum refer to the respective pressure (GPa). The changes in the slopes of both the Raman shift and the FWHM narrow down the spin transition range in ferromagnesite at 600 K between 44 and 52 GPa. The error bars for the Raman shift and the FWHM lie within the symbols. (Online version in color.)

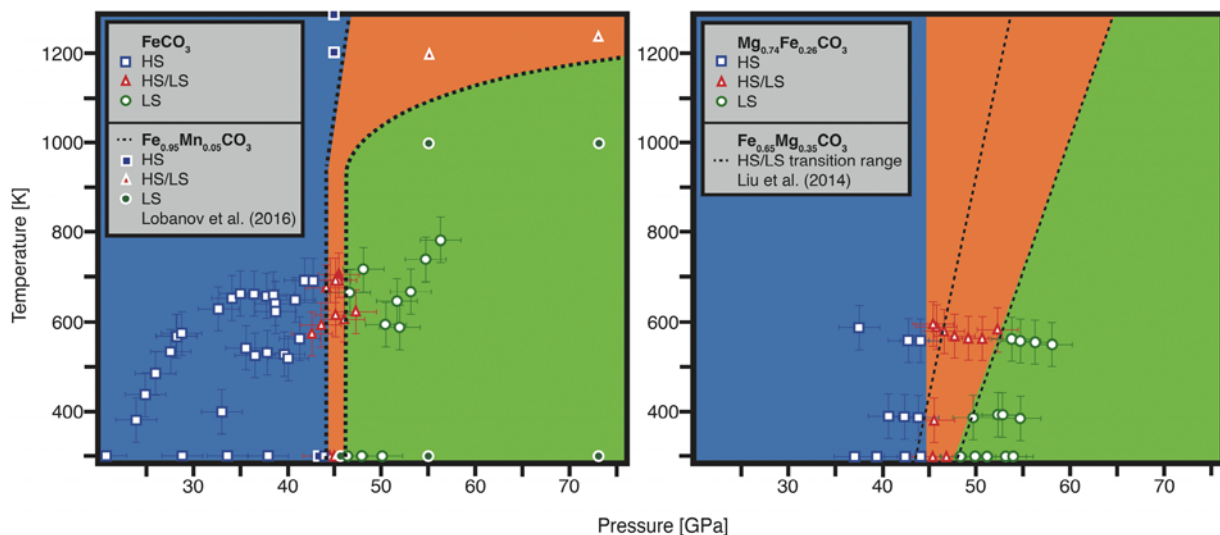


Fig. 4. Phase diagrams of siderite (left) and ferromagnesite (right). Blue squares represent Fe²⁺ in the HS configuration, red triangles stand for the HS and LS phases in coexistence, and green circles denote the LS configuration from the present study. The siderite data by Lobanov *et al.* (2016) are plotted for comparison (left). We note that the orange area in the siderite phase diagram (left) mark the HS/LS mixed state. The orange area is extrapolated from the HS to LS transition range from the data of Lobanov *et al.* (2016) and this study. In the ferromagnesite phase diagram (right) the dashed lines indicate the spin transition range of magnesiosiderite determined by Liu *et al.* (2014), whereas the orange area is an extrapolation of the ferromagnesite data of this study. (Online version in color.)

metal–oxygen bond distances. Indeed, close comparison of the metal–oxygen distances from different calcite-type carbonates (FeCO₃, MgCO₃, MnCO₃, and CdCO₃) under room-*T* compression reveals approximately the same (relative) compressibility (Fiquet *et al.*, 2002; Lavina *et al.*, 2010; Minch *et al.*, 2010; Merlini *et al.*, 2015; Fig.

S4). Since the metal–oxygen bond distance is inversely proportional to Δ , which is the cause behind the HS to LS transition (Marfunin, 1979; Burns, 1993), and given the similar bond compressibilities, the spin transition pressure at room-*T* should not depend heavily on the composition of the Fe-bearing carbonate under study.

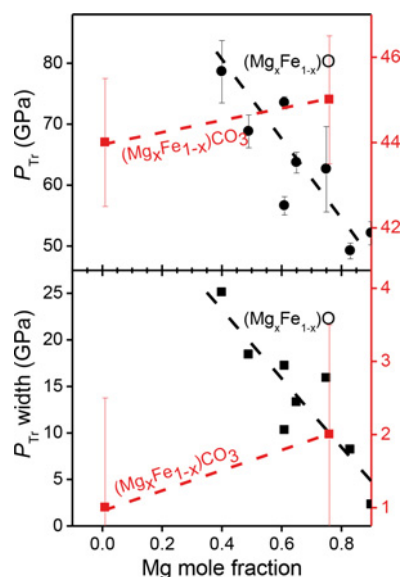


Fig. 5. Effect of Mg content on the onset pressure (top) and the width (bottom) of the spin transition in the periclase–wüstite (black, left axis) and the magnesite–siderite (red, right axis) solid solutions at ambient temperature. Data for periclase–wüstite are taken from Solomatova *et al.* (2016). (Online version in color.)

Another interesting aspect of our observations is that the spin transition in siderite remains sharp up to 700 K, whereas the onset transition pressure is (within error) the same in siderite and ferromagnesite at ambient and high temperature; the main high-*P* and high-*T* difference between the two compounds is that the transition range in ferromagnesite broadens significantly with temperature (Fig. 4).

In the case of siderite, a temperature-induced change of the spin transition pressure range has been reported (Hsu & Huang, 2016; Lobanov *et al.*, 2016; Torchio *et al.*, 2016). Lobanov *et al.* (2016) studied the spin transition in siderite above 1000 K, *i.e.* conditions that are relatively close to the *P*–*T* range of this study. Combining our results with those of Lobanov *et al.* (2016), the following picture emerges. Up to 700 K the spin transition range is sharp and the transition pressure does not depend significantly on temperature. Between 700 and 1000 K the pressure range of the spin transition broadens considerably and the onset pressure of the spin transition increases (Fig. 4, left). We should note here that siderite undergoes a structural phase transition to the orthorhombic siderite-II/magnesiosiderite-II structure above 50 GPa and 1300 K (Liu *et al.*, 2015), which is exactly in the range where Lobanov *et al.* (2016) observe the mixed spin state of HS/LS siderite. So far, the exact structural details and the spin state of the siderite-II and magnesiosiderite-II are not known and thus all high-temperature data, including those of Torchio *et al.* (2016), may not be directly comparable to our study. In a computational study, Hsu & Huang (2016) confirmed the general trend of a shift of the transition pressure and a broadening of the spin transition range between 300 and 3000 K, but they did not study the subtle changes in the temperature range below 1000 K, which is of interest here.

To our knowledge, high-*T* data do not yet exist for ferromagnesite. The closest match to our sample is a magnesiosiderite ($\text{Mg}_{0.35}\text{Fe}_{0.65}\text{CO}_3$) sample studied by Liu *et al.* (2014) and the computational study of ($\text{Mg}_{0.5}\text{Fe}_{0.5}\text{CO}_3$) by Hsu & Huang (2016). Both studies show that the spin transition range in Mg-bearing siderite broadens with increasing temperature. At 600 K the onset pressure of the spin transition in magnesiosiderite is only slightly shifted to higher pressure (Liu *et al.*, 2014) and, within error, is in agreement with our data (Fig. 4, right); with further temperature increase, however, the onset pressure of magnesiosiderite moves to even higher pressures. As in the previous discussion on siderite, this suggests a change of the behavior of the spin transition above 600 K.

Due to the sparse data on the spin transition in siderite and ferromagnesite at high temperature, the interpretation of the present results in conjunction with previous studies still needs to be critically assessed. The different temperature dependence of the onset pressure and the transition pressure range may also have been influenced by other experimental factors. This includes (a) the different samples (synthetic *vs.* natural), (b) the heating methods used (resistive heating *vs.* laser heating), (c) the different PTM, and (d) the different sensitivity of the analytical methods used (Raman spectroscopy *vs.* optical absorption spectroscopy *vs.* XRD *vs.* EXAFS). Dedicated future studies addressing these issues would be extremely useful.

To rationalize our results regarding the temperature-independent spin transition in siderite we consider again the high-*P* and high-*T* behavior of the metal–oxygen distances. Increasing temperature at ambient pressure does not lead to significant thermal expansion of the metal–oxygen distances in calcite-type carbonates, at least up to 700 K (Markgraf & Reeder, 1985; Ballirano, 2016; Fig. S4). Given that temperature does not induce any structural distortion in the HS-state of either siderite or ferromagnesite in the pressure range of interest (Liu *et al.*, 2014), it can be stated that the Fe–O distances, hence Δ , are only slightly affected by temperature at either ambient or high pressures (Lobanov *et al.*, 2015, 2016). On the other hand, the combined effects of heating and increasing content of Mg in ($\text{Mg,Fe}\text{CO}_3$) appear to broaden the width of the spin transition range substantially (Fig. 4).

Given the similar FeO_6 building blocks, a comparison of results on the ($\text{Mg,Fe}\text{CO}_3$) solid solution with the relevant studies conducted on the ($\text{Mg,Fe}\text{O}$) solid solution is appealing. Systematic studies on ($\text{Mg,Fe}\text{O}$) reveal a broad spin transition range over several GPa, with the onset pressure and the transition width strongly increasing proportionally to the Fe-content (*e.g.* Speziale *et al.*, 2005; Fei *et al.*, 2007; Solomatova *et al.*, 2016) (Fig. 5). This behavior is clearly different from the ($\text{Mg,Fe}\text{CO}_3$) solid solution. Regarding the diverse behavior in the HS to LS transition onset pressure we speculate that it arises due to the different compressibility mechanisms between the two structures. The compression of the FeO_6 octahedra in the ($\text{Mg,Fe}\text{O}$) structure is isotropic (or slightly anisotropic due to the rhombohedral distortion in certain cases, *e.g.*

Kantor, 2007). On the other hand, the carbonate structure consists of both FeO₆ octahedral and CO₃ triangular units, which leads to an anisotropic structural response under pressure as follows: compression of the long *c*-axis results in the compression of octahedral units alone, whereas compression in the *a*–*b* plane takes place through the compression of both the octahedral and the nearly incompressible carbonate groups. Such diverse compressibility mechanism may account for the different HS to LS transition pressure between the two phases. On the other hand, a plausible explanation behind the different effect of Mg content on the width of the transition might come from the reduced Fe–Fe interaction pathways in the carbonate structures with respect to the (Mg,Fe)O system (Lavina *et al.*, 2010b; Lin *et al.*, 2012b; Hsu & Huang, 2016).

Similar to (Mg,Fe)CO₃, increasing temperature results in a significant broadening of the spin transition pressure range in the (Mg,Fe)O solid solution. For example Lin *et al.* (2007) observed the spin transition in (Mg_{0.75}Fe_{0.25})O at ambient temperature in a range between 50 and 65 GPa, which broadens to a range of 50–90 GPa at 2000 K. The exact reasons behind this broadening are unknown. Ideally, the study of pure Fe²⁺O wüstite would contribute to solve the effect of composition on the broadening, but such measurements are not possible due to incorporation of Fe³⁺ (e.g. Hazen & Jeanloz, 1984). Therefore, siderite constitutes a good model-system material for the study of the spin transition in a pure Fe²⁺-end-member material.

Despite a few studies, it is not clear whether the onset pressure of the spin transition in (Mg,Fe)O is affected by temperature. Lin *et al.* (2007) and Lyubutin *et al.* (2013) both did not observe any temperature dependence on the onset pressure in a (Mg,Fe)O crystal. In addition, optical absorption measurements on a (Mg,Fe)O crystal did not reveal any changes of the crystal-field splitting up to 60 GPa and 800 K (Goncharov *et al.*, 2008). Considering also that the thermal expansion of the Mg–O bond in periclase ($12.4 \times 10^{-6} \text{ °C}^{-1}$, Hazen, 1976) is comparable to that in magnesite ($15.8 \times 10^{-6} \text{ °C}^{-1}$, Markgraf & Reeder, 1985), the structural explanation for the temperature independence of the onset transition pressure put forward for ferromagnesite could be applied in the case of (Mg,Fe)O as well. However, Komabayashi *et al.* (2010) report a clear temperature dependence on the onset pressure in (Mg,Fe)O in a similar temperature and composition range as Lin *et al.* (2007).

In conclusion, we found a temperature-independent onset pressure of the spin transition in (Mg,Fe)CO₃ at temperatures below 700 K and for two different compositions, which seems to be different from the behavior at higher temperatures. This observation can be rationalized by the compression mechanisms of Fe²⁺O₆ octahedra and seems similar to some extent to results from the (Mg,Fe)O system. Despite previous studies of both solid solutions, there are still too few data available to derive a conclusive model of the apparently changing temperature and composition dependence of the spin transition. More experiments with a better temperature

resolution, especially in the temperature range up to 1000 K, are necessary to obtain a more systematic understanding of the thermodynamic parameters that control the spin transition in (Mg,Fe)CO₃ and (Mg,Fe)O. If this temperature-independent onset of the spin transition is verified in further studies, theoretical models derived from *ab initio* simulations (e.g. Holmström & Stixrude, 2015; Hsu & Huang, 2016) may have to be revised in terms of the underlying electronic and molecular processes driving the spin transition.

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