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Effect of temperature on the pressure-induced spin transition in siderite and ferromagnesite derived from Raman spectroscopy

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Iron is the most prominent transition metal on Earth and due to its electronic structure iron bearing phases may undergo a pressure-induced electronic high-spin (HS) to low-spin (LS) transitions at lower mantle conditions [1]. Such HS to LS transitions are widely known for prominent lower mantle phases such as ferropericlase, and affect many mineral/mantle properties (e.g. seismic velocities or magnetic properties) [1]. The exact mechanisms of such transitions, however, are not fully understood, including the effects of temperature, mineral composition and/or change in the Fe oxidation state. The siderite-magnesite solid solution series can serve as model system for answering several open questions, since (a) it undergoes a pressure-induced HS to LS transition [e.g. 2; 3] and (b) it enables the study of an Fe-endmember that contains ferrous iron only.

In this study high-pressure and high-temperature Raman spectra of synthetic siderite ($FeCO_3$) and synthetic ferromagnesite ($Mg_{0.76}Fe_{0.24}CO_3$) were measured across the spin transition up to nearly 60 GPa and 700 K. In siderite the spin transition is sharp and observed between about 44 and 46 GPa, with no discernible temperature dependence up to 700 K. The spin transition in ferromagnesite is also sharp and takes place between 45 and 47 GPa at ambient temperature, whereas it broadens significantly at about 600 K in a pressure range between 45 and 52 GPa. Interestingly, the onset pressure of the spin transition was essentially the same for both samples at all temperatures. We conclude that the onset pressure of the spin transition in the siderite-magnesite solid solution series is independent of temperature and composition up to at least 700 K. The broadening of the spin transition on the other hand appears to be a combined effect of temperature and composition.

[1] Lin et al. (2013) *Rev. Geophys.* **51,** 244-275. [2] Müller et al. (2016) *Am. Mineral.* **101**, 2638-2644. (3) Lavina et al. (2010) *Phys. Rev. B* **82,** 064110.