

# **In situ Raman vibrational spectra of siderite (FeCO<sub>3</sub>) and rhodochrosite (MnCO<sub>3</sub>) up to 47 GPa and 1100 K**

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## **ABSTRACT**

Siderite (FeCO<sub>3</sub>) and rhodochrosite (MnCO<sub>3</sub>) are two interesting carbonate minerals, which normally occur in hydrothermal deposits on deep-sea altered oceanic crust. Despite the ubiquity of carbonates in the slab, little is known of the physicochemical behavior of siderite and rhodochrosite at high-pressure ( $P$ ) and high-temperature ( $T$ ) conditions during slab subduction. In this study, we characterized the Raman vibrational spectra of natural siderite and rhodochrosite up to 47 GPa and 1100 K in an externally heated diamond-anvil cell (DAC). Experimental results show that the Raman frequency shifts ( $\nu_i$ ) for siderite and rhodochrosite are a function of both  $P$  and  $T$ , and the effect of the  $P$ - $T$  cross derivative term cannot be neglected, especially at high- $P$  and high- $T$  conditions. Based on the functional relationship of  $\nu_i$ - $P$ - $T$ , the  $P$ - $T$  calibrants of siderite and rhodochrosite are developed, respectively. This is significant for studying the water-carbonate interaction at high  $P$ - $T$  conditions in a DAC because the undesired change of the experimental system from traditional pressure sensors (e.g., ruby, quartz) in a reaction chamber can be avoided. Like previous studies, we observed a sharp spin transition at  $\sim$ 45 GPa in siderite and a phase transition from MnCO<sub>3</sub>-I to MnCO<sub>3</sub>-II at  $\sim$ 46 GPa for rhodochrosite at room temperature. Furthermore, we determined the isobaric and isothermal equivalents of the mode Grüneisen parameter ( $\gamma_{iP}$ ,  $\gamma_{iT}$ ) and the anharmonic parameter ( $a_i$ ) for each Raman mode of siderite and rhodochrosite. The  $\delta\nu_i/\delta P$ ,  $\delta\nu_i/\delta T$ ,  $\gamma_{iP}$ ,  $\gamma_{iT}$  and  $a_i$  span a much larger value range for the external lattice modes ( $T$ ,  $L$ ) than internal modes ( $\nu_4$ ,  $\nu_1$ ) in both siderite and rhodochrosite. Combining Raman frequency shifts and the first-order Murnaghan equation of state, we also developed a method to calculate the temperature dependence of the bulk modulus ( $K_T$ ) for siderite and rhodochrosite, respectively.

**Keywords:** Siderite, rhodochrosite, Raman spectroscopy, high- $P$  and high- $T$ ,  $P$ - $T$  sensor, thermodynamical parameters