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In situ Raman vibrational spectra of siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) up to 47 GPa and 1100 K

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Abstract

Siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) 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 (ν_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 ν_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 ~45 GPa in siderite and a phase transition from $MnCO_3$-I to $MnCO_3$-II at ~46 GPa for rhodochrosite at room temperature. Furthermore, we determined the isobaric and isothermal equivalents of the mode Grüneisen parameter (γ_{iT}, γ_{iP}) and the anharmonic parameter (a_i) for each Raman mode of siderite and rhodochrosite. The $\delta\nu_i/\delta P$, $\delta\nu_i/\delta T$, γ_{iT}, γ_{iP}, and a_i span a much larger value range for the external lattice modes (T, L) than internal modes (ν_4, ν_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