Goldschmidt 2022 Abstract
https://doi.org/10.46427/gold2022.10308

High-pressure and high-temperature vibrational properties and anharmonicity of siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) up to 47 GPa and 1100 K by Raman spectroscopy

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Siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) are two interesting carbonate gangues, 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 physiochemical behavior of siderite and rhodochrosite at high-pressure (P) and high-temperature (T) conditions during 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 (Fig. 1). 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. We found that 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 high P-T Raman frequency shifts and the first-order Murnaghan equation of state, the temperature dependence of the bulk modulus (K_T) for siderite and rhodochrosite can be derived (Eq. 1, Where T is in °C).

$$K_T(FeCO_3) = 117 - 0.02961 \times (T - 20); \quad (1a)$$

$$K_T(MnCO_3) = 110 - 0.01735 \times (T - 20) \quad (1b)$$

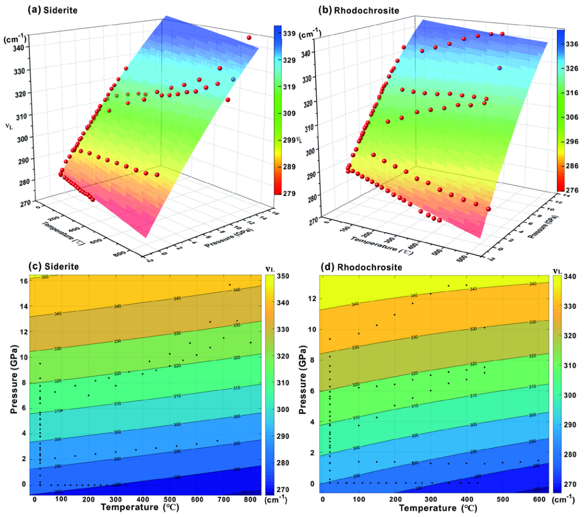

Figure 1: (a-b) Frequency shift of the traced L mode of siderite (a) and rhodochrosite (b) as a coupled function of P and T and their polynomial fitting surface. (c-d) P-T diagrams showing contours of the L mode Raman band of siderite (c) and rhodochrosite (d).