In situ Raman vibrational spectra of siderite (FeCO₃) and rhodochrosite (MnCO₃) up to 47 GPa and 1100 K

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Abstract

Siderite (FeCO₃) and rhodochrosite (MnCO₃) 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 MnCO₃-I to MnCO₃-II at ~46 GPa for rhodochrosite at room temperature. Furthermore, we determined the isobaric and isothermal equivalents of the mode Grüneisen parameter (γ_iP, γ_iT) and the anharmonic parameter (α_i) for each Raman mode of siderite and rhodochrosite. The δν/δP, δν/δT, γ_iP, γ_iT, and α_i span a much larger value range for the external lattice modes (T, L) than internal modes (ν_i, ν_i) 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_b) for siderite and rhodochrosite, respectively.

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

Introduction

Carbonates are the major carbon reservoir on the Earth’s surface. Previous studies estimate that more than 6.5 × 10^10 Gt carbon have been stored in carbonate sediments and carbonated oceanic/continental crusts (DePaolo 2015). These carbonates can be transported into deep mantle through the subduction of oceanic and continental slabs (Javoy 1997; Dasgupta and Hirschmann 2006; Seto et al. 2008). With increasing depth in the Earth’s interior, some carbon may return to Earth’s surface by decarbonation processes from subducted slabs through the magmatic processes (Stewart et al. 2019). The stability of carbonates at high-P and high-T conditions controls the extent and rate of carbon recycling to the Earth’s surface. Therefore, knowing the physicochemical (e.g., thermodynamic) properties of carbonates at high P-T conditions relevant to subduction zones is particularly important for understanding the deep carbon cycle process (Dasgupta and Hirschmann 2010; Tao et al. 2013; Plank and Manning 2019; Farsang et al. 2021).

Siderite (FeCO₃) and rhodochrosite (MnCO₃) occur as common carbonate minerals in many hydrothermal deposits in the altered oceanic crust (Robie et al. 1984). Subduction of siderite and rhodochrosite may therefore play an important role in the geochemical cycles of key elements (e.g., Fe, Mn, and C) between Earth’s surface and deep interior (Sherman 2009). On the other hand, previous studies have suggested magnesite (MgCO₃) is the most important carbonate mineral in the deep Earth mantle, which could be stable up to the P-T conditions of core-mantle boundary (Fiquet et al. 2002; Ishihiki et al. 2004; Dasgupta and Hirschmann 2010). Considering the average Fe/Mg molar ratio of ~0.12 in the bulk composition of Earth’s mantle (McDonough and Sun 1995), and the commonly occurring Fe-Mg exchange between carbonates and Fe-bearing silicates at high-P and high-T conditions (Boullard et al. 2015), it is believed that siderite (FeCO₃) should be a significant component in solid solution with magnesite in the subducted slab and deep mantle (Anovitz and Essene 1987; Wood et al. 1996; Lin et al. 2012; Tao et al. 2013; Kang et al. 2015). Similarly, divalent Mn has a cation size between that of Mg²⁺ and Ca²⁺, which could make rhodochrosite (MnCO₃) a non-trivial end-member component in aragonite...