High-pressure and high-temperature vibrational properties and anharmonicity of carbonate minerals up to 6 GPa and 500 °C by Raman spectroscopy

STEFAN FARSANG1,*, REMO N. WIDMER2, AND SIMON A.T. REDFERN3†

1Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, U.K.
2EMPA, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, Thun, 3602, Switzerland
3Asian School of the Environment, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798, Singapore

ABSTRACT

Carbonate minerals play a dominant role in the deep carbon cycle. Determining the high-pressure and high-temperature vibrational properties of carbonates is essential to understand their anharmonicity and their thermodynamic properties under crustal and upper mantle conditions. Building on our previous study on aragonite, calcite (both CaCO₃ polymorphs), dolomite [CaMg(CO₃)₂], magnesite (MgCO₃), rhodochrosite (MnCO₃), and siderite (FeCO₃) (Farsang et al. 2018), we have measured the pressure- and temperature-induced frequency shifts of Raman-active vibrational modes up to 6 GPa and 500 °C for all naturally occurring aragonite- and calcite-group carbonate minerals, including cerussite (PbCO₃), strontianite (SrCO₃), watherite (BaCO₃), gaspeite (NiCO₃), otavite (CdCO₃), smithsonite (ZnCO₃), and spherocobaltite (CoCO₃). Our Raman and XRD measurements show that cerussite decomposes to a mixture of PbO₂ and tetragonal PbO between 225 and 250 °C, smithsonite breaks down to hexagonal ZnO between 325 and 400 °C, and gaspeite to NiO between 375 and 400 °C. Spherocobaltite breaks down between 425 and 450 °C and otavite between 375 and 450 °C. Due to their thermal stability, carbonates may serve as potential reservoirs for several metals (e.g., Co, Ni, Zn, Cd) in a range of crustal and upper mantle environments (e.g., subduction zones). We have determined the isobaric and isothermal equivalents of the mode Grüneisen parameter and the anharmonic parameter for each Raman mode and compare trends in vibrational properties as a function of pressure, temperature, and chemical composition with concomitant changes in structural properties. Finally, we use the anharmonic parameter to calculate the thermal contribution to the internal energy and entropy, as well as the isochoric and isobaric heat capacity of certain carbonates.

Keywords: Anharmonicity, cerussite, diamond-anvil cell, gaspeite, high pressure, high temperature, otavite, pressure sensor, Raman spectroscopy, smithsonite, spherocobaltite, strontianite, watherite

INTRODUCTION

Carbonate minerals play a dominant role in the deep carbon cycle that includes the transport of carbon in subducting slabs to the deep Earth, their devolatilization, melting, and dissolution in slab fluids, the transport of liberated CO₂, followed by volcanic outgassing (e.g., Dasgupta and Hirschmann 2010; Ague and Nicolescu 2014; Manning 2014; Kelemen and Manning 2015; Plank and Manning 2019). Carbonates transport carbon into the deep Earth in three distinct lithologies: oceanic sediments, igneous crust, and lithospheric mantle. Their behavior as a function of pressure (P), temperature (T), and composition of adjacent phases determines the extent and rate of carbon recycling to the atmosphere and oceans. Modeling the deep carbon cycle, therefore, requires an understanding of numerous geologic processes involving carbonate minerals, which in turn depends on the thermodynamic properties of carbonates under crustal and upper mantle conditions. In all high-temperature environments (e.g., deep Earth), key thermodynamic properties of phases are dependent upon their anharmonicity. To obtain meaningful values for thermodynamic properties, anharmonicity and anharmonic corrections must be quantified.

The vibrational properties of a mineral control several of its thermodynamic properties. Raman spectroscopy provides a route, therefore, to determine thermodynamic properties at the P-T conditions of measurement. As abundant CO₂-bearing minerals, the thermodynamic properties of carbonates are of particular importance. A significant number of Raman studies of the high-pressure behavior of carbonate minerals have been reported, including aragonite, calcite, vaterite, and other high-pressure CaCO₃ polymorphs (Fong and Nicoll 1971; Nicoll and Ellenson 1972; Salje and Viswanathan 1976; Liu and Mernagh 1990; Hess et al. 1991; Kraft et al. 1991; Biellmann and Gillet 1992; Gillet et al. 1993; Suito et al. 2001; Shi et al. 2012; Pipping et al. 2015; Koch-Müller et al. 2016; Liu et al. 2017; Lobanov et al. 2017; Murayama et al. 2017; Gavryushkin et al. 2017; Bayarjargal et al. 2018; Farsang et al. 2018; Yuan et al. 2019), azurite (Xu et al. 2015), cerussite (Lin and Liu 1997b, 1997c; Minch et al. 2010b; Zhang et al. 2013; Gao et al. 2016), dolomite (Kraft et al. 1991; Biellmann and Gillet 1992; Gillet et al. 1993; Efthimiopoulos et al. 2017, 2018; Farsang et al. 2018; Vennari and Williams 2018), ikaite (Shahar et al. 2005), magnesite (Williams et al. 1992; Gillet 1993; Gillet et al. 1993; Spivak et al. 2014; Müller et al. 2017; Farsang et al. 2018; Liang et al. 2018; Vennari and Williams 2018).