High-temperature and high-pressure behavior of carbonates in the ternary diagram $CaCO_3$-$MgCO_3$-$FeCO_3$

Marco Merlini[1,*], Francesca Sapelli[1], Patrizia Fumagalli[1], G. Diego Gatta[1],
Paolo Lotti[1,2], Simone Tumiati[1], Mahmoud Abdellatief[2,§], Andrea Lausi[2], Jasper Plaisier[2],
Michael Hanfland[3], Wilson Crichton[3], Julien Chantel[3,†], Jeremy Guignard[3,‡],
Carlo Meneghini[4], Alessandro Pavese[1], and Stefano Poli[1]

[1]Università degli Studi di Milano, Dipartimento di Scienze della Terra, Via Botticelli, 23, 20133 Milano, Italy
[2]Elettra Sincrotrone Trieste S.c.P.A., Strada Statale 14, km 163.5, 34149 Basovizza, Trieste, Italy
[3]European Synchrotron Radiation Facility, 6 Rue Jules Horowitz, 38043 Grenoble Cedex, France
[4]Dipartimento di Scienze, Università Degli Studi Roma TRE, Via della Vasca Navale 84-00146 Roma, Italy

Abstract

We report the thermal expansion and the compressibility of carbonates in the ternary compositional diagram $CaCO_3$-$MgCO_3$-$FeCO_3$, determined by in situ X-ray powder and single-crystal diffraction. High-temperature experiments were performed by high-resolution X-ray synchrotron powder diffraction from ambient to decarbonation temperatures (25–850 °C). Single-crystal synchrotron X-ray diffraction experiments were performed in a variable pressure range (0–100 GPa), depending on the stability field of the rhombohedral structure at ambient temperature, which is a function of the carbonate composition. The thermal expansion increases from calcite, $CaCO_3$, $\alpha_0 = 4.10(7) \times 10^{-5}$ K^{-1}, to magnesite, $MgCO_3$, $\alpha_0 = 7.04(2) \times 10^{-5}$ K^{-1}. In the magnesite-siderite ($FeCO_3$) join, the thermal expansion decreases as iron content increases, with an experimental value of $\alpha_0 = 6.44(4) \times 10^{-5}$ K^{-1} for siderite. The compressibility in the ternary join is higher (i.e., lower bulk modulus) in calcite and Mg-calcite [$K_0 = 77(3)$ GPa for $Ca_{0.91}Mg_{0.06}Fe_{0.03}(CO_3)$] than in magnesite, $K_0 = 113(1)$ GPa, and siderite, $K_0 = 125(1)$ GPa. The analysis of thermal expansion and compressibility variation in calcite-magnesite and calcite-iron-magnesite joins clearly shows that the structural changes associated to the order-disorder transitions [i.e., $R\bar{3}c$ calcite-type structure vs. $R\bar{3}$ $CaMg(CO_3)_2$ dolomite-type structure] do not affect significantly the thermal expansion and compressibility of carbonate. On the contrary, the chemical compositions of carbonates play a major role on their thermo-elastic properties. Finally, we use our P-V-T equation of state data to calculate the unit-cell volume of a natural ternary carbonate, and we compare the calculated volumes to experimental observations, measured in situ at elevated pressure and temperatures, using a multi-anvil device. The experimental and calculated data are in good agreement demonstrating that the equation of state here reported can describe the volume behavior with the accuracy needed, for example, for a direct chemical estimation of carbonates based on experimental unit-cell volume data of carbonates at high pressures and temperatures.

Keywords: Carbonates, high temperature, high pressure, equation of state