High-temperature and high-pressure behavior of carbonates in the ternary diagram 
CaCO₃-MgCO₃-FeCO₃

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ABSTRACT

We report the thermal expansion and the compressibility of carbonates in the ternary compositional diagram CaCO₃-MgCO₃-FeCO₃, 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, CaCO₃, α₀ = 4.10(7) ×10⁻⁵ K⁻¹, to magnesite, MgCO₃, α₀ = 7.04(2) ×10⁻⁵ K⁻¹. In the magnesite-siderite (FeCO₃) join, the thermal expansion decreases as iron content increases, with an experimental value of α₀ = 6.44(4) ×10⁻⁵ K⁻¹ for siderite. The compressibility in the ternary join is higher (i.e., lower bulk modulus) in calcite and Mg-calcite [K₀ = 77(3) GPa for Ca₀.(91)Mg₀.06Fe₀.03(CO₃)] than in magnesite, K₀ = 113(1) GPa, and siderite, K₀ = 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., R₃c calcite-type structure vs. R₃ Mg(CO₃), 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 values 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 at high pressures and temperatures.

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

INTRODUCTION

The interest in carbonate mineralogy has grown significantly in the last decades. These minerals in fact can provide clues and information about recent and past Earth’s climate history. Carbonates are involved in fundamental geological processes related to the global carbon cycle. In particular, a shallow carbon cycle (i.e., involving exchanges between atmosphere and hydrosphere reservoirs) is directly related to the dissolution and precipitation of carbonates, mainly calcite, in the oceans. The carbonate-bearing sediments are involved also in subduction processes. The stability of carbonate in these environments is the key issue to understand the transfer of crustal carbon into the inner Earth or its recycling through volcanism. Carbon is also stored in the Earth’s mantle in various forms, as demonstrated by natural occurrence of diamonds. Some of these diamonds also present carbonate, or CO₂, as inclusions (e.g., Berg 1986; Navon 1999). It is now clear that a thermodynamic modeling of carbonate stability in various environments is fundamental for a deeper understanding of global carbon cycle (Oganov et al. 2013). Thermodynamic data on the ternary composition diagram calcite-magnesite-siderite are scarce, especially for iron-bearing carbonates. A direct experimental observation of the stable composition as function of pressure, temperature, and chemical composition is probably the most successful approach for a detailed understanding of carbonate stability. In recent years, the availability

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