Re-examination of the heterotype solid solution between calcite and strontianite and Ca-Sr fluid-carbonate distribution: An experimental study of the CaCO₃-SrCO₃-H₂O system at 0.5–5 kbar and 600 °C

Ferry Schiperski¹,* , Axel Liebscher²† , Matthias Gottschalk², and Gerhard Franz¹

¹Technische Universität Berlin, Department of Applied Geosciences, Applied Geochemistry, 10587 Berlin, Germany
²Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany

ABSTRACT

Carbonates are excellent carriers for divalent cations such as Ca, Mg, and Sr, and knowledge about their stability and solid solutions is important to understanding the global strontium cycle. To shed light on the topology of the two-phase field between calcite-type and aragonite-type (Ca,Sr)CO₃ solid solutions as a function of temperature and pressure, and to learn more about the distribution of Sr and Ca between carbonates and fluid, we studied the system CaCO₃-SrCO₃-H₂O at 600 °C in the pressure range 0.5–5 kbar. Conventional and rapid-quench hydrothermal syntheses were performed using a range of different starting materials. All bulk compositions were within the assumed/postulated two-phase field of calcite-type and aragonite-type (Ca,Sr)CO₃ solid solutions. The run products were analyzed by scanning electron microscopy, electron microprobe analysis, and powder X-ray diffraction with Rietveld refinement. The results show that the heterotype solid solution is more extensive than previously assumed, with calcite incorporating up to 20 mol% SrCO₃, which is twice as much as previously predicted. The compositional range of the aragonite-type solid solution was identical to that found in the literature. Using the data from this study, an updated version of the phase diagram P-X (Sr) at 600 °C for the CaCO₃-SrCO₃ system was calculated. The phase diagram does not support a phase transition within the trigonal (Ca,Sr)CO₃ solid solution associated with rotational disorder of the CO₃-groups. This order-disorder phase transition was previously postulated to explain some observed compositional trends in this system. Our new data are in line with other more recent studies. The distribution of Sr and Ca between the fluid and solid phases D = Xfluid/Xsolid is near to 1.0 for calcite-type and on average around 2.0 for aragonite-type solid solutions. This contrasts with silicate-fluid systems in which Sr typically shows a strong preference for the fluid phase compared with Ca.

Keywords: Strontianite, Sr-calcite, Sr-aragonite, carbonate solid solution, Sr-cycle

INTRODUCTION

As they have the same ionic charge and a comparable ionic radius, Ca and Sr are interchangeable to a certain extent in carbonates with trigonal (Cal-type) and orthorhombic (Arg-type) structure at subsolidus conditions (Chang 1965, 1971; Froese and Winkler 1966; Carlson 1980). A striking feature of the stability relations in the system (Sr,Ca)CO₃ is the occurrence of a two-phase field of coexisting Cal-type and Arg-type (Sr,Ca)CO₃ solid solutions (Figs. 1a and 1b). At atmospheric pressure and a temperature of 600 °C the extent of this field is about 30 mol% and narrows with increasing pressure toward the phase transition Cal/Arg (Fig. 1b). The occurrence of a trigonal disordered phase (rotational disorder of CO₃-groups; Figs. 1a and 1b) was postulated by Carlson (1980) based on his own experiments and data from Goldsmith and Newton (1969) (see Fig. 1c), although the latter data were questioned at the time (e.g., Mirwald 1976). The stability and extent of (Ca,Sr)-solid solutions and the solid fluid-distribution of Ca and Sr are of general importance for the global strontium cycle (e.g., Kump 1989). Besides the carbonates studied here, other minerals relevant to the strontium cycle are anorthite, lawsonite, lawsonite, wakstromite, zoisite, grossularite, and margarite (Dörsam et al. 2007; Liebscher et al. 2009, 2010).

No compositional data from electron microprobe analyses (EMPA) or comparable spatially resolved analytical methods exist for (Ca,Sr)CO₃ solid solutions at elevated pressures and temperatures. Previous studies relied on powder X-ray diffraction (XRD) with calibration curves for X_{Sr} = Sr/(Sr+Ca) (mole fraction with element concentrations in mol%) vs. peak position (e.g., Froese and Winkler 1966; Chang 1965) or the appearance/disappearance method (Carlson 1980), both of which are prone to error when dealing with strongly zoned run products. This is often observed in synthesis experiments involving solvent-mediated phase transformations or kinetically sluggish mineral systems (e.g., Fernández-González et al. 1999; Putnis 2009).

This study experimentally re-examines the subsolidus phase relations of the heterotype solid solutions of Cal-type and Arg-type Ca-Sr carbonates at 600 °C and 0.5–5 kbar using different experimental approaches and starting materials. State-of-the-art analyses (XRD with Rietveld refinement, EMPA, scanning electron microscopy SEM, and inductively-coupled optical emission spectroscopy ICP-OES) provide the chemical and structural resolution necessary to construct a revised two-phase field, which is then verified by thermodynamic modeling. The