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

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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 $D = X_{\text{Str}}^{\text{solid}}/X_{\text{Str}}^{\text{sinid}}$ 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