Order and miscibility in the otavite–magnesite solid solution

F.A. Bromiley, T. Boffa Ballaran, F. Langenhorst, and F. Seifert

1Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany
2Friedrich-Schiller-Universität Jena, Institut für Geowissenschaften, Burgweg 11, D-07749 Jena

ABSTRACT

The effects of cation substitution and ordering in the otavite (CdCO₃)–magnesite (MgCO₃) solid solution have been investigated on samples synthesized at 1 GPa in the temperature range 500–800 °C for run durations up to 120 h. A complete, disordered solid solution, with R₃̅c symmetry, was obtained at 800 °C, whereas Mg and Cd show partial ordering within the cadmium dolomite stability field, with R₃̅ symmetry, at intermediate compositions in the temperature range 500–650 °C. Rietveld refinements for X-ray diffraction data show that variation of the a-axis is linear as a function of composition, independent of the degree of order, whereas the c-axis shows a positive deviation from linearity as a function of composition, decreasing with increasing degree of order. Octahedral bond distances of the 800 °C series vary linearly with composition. Site occupancies were used to determine the long-range order parameter, Q, for samples with R₃̅ symmetry. Q varies linearly as a function of temperature, suggesting a tricritical phase transition with a critical transition temperature Tc of 702(10) °C. EDXTEM compositional microanalyses of samples within two-phase regions are in good agreement with Rietveld refinements, and allow better constraint of phase boundaries.

Keywords: X-ray powder diffraction, otavite–magnesite solid solution, carbonates, phase transition, cation ordering

INTRODUCTION

The magnesite (MgCO₃)–calcite (CaCO₃) join is by far the most studied among the carbonate systems, due to its geological importance. The magnesite and calcite end-members are rhombohedral with R₃̅c symmetry. The hexagonal unit cell consists of layers of M²⁺ atoms alternating with layers of planar CO₃²⁻ groups along the c axis. The M²⁺ atoms are coordinated to 6 oxygen atoms, each belonging to different CO₃²⁻ groups, forming corner-shared octahedra. At intermediate compositions a lower symmetry phase (dolomite [MgCa(CO₃)₂]), space group R̅₃̅) forms due to the ordering of Ca²⁺ and Mg²⁺ onto alternating octahedral layers and slight rotation of the CO₃²⁻ groups. The processes driving the order-disorder phase transition, and the effects of cation substitution, are important for elucidating the behavior of the system. However, unmixing and ordering processes are likely to occur during quenching of samples belonging to the magnesite-calcite join due to the high temperatures required for their syntheses and/or cation disorder, and the high critical temperatures of the two solvi. The study of an analog system can provide easier experimental conditions and thus better constraints on the results obtained. Dolomite-type compounds are also found in other carbonate systems, such as ankerite or ferroan dolomite [Ca(Mg,Fe,Mn)(CO₃)₂], kutnahorite [CaMn(CO₃)₂], minrecio [CaZn(CO₃)₂], and cadmium dolomite [CdMg(CO₃)₂] (see reviews in Reeder 1983 and Goldsmith 1983). From these, however, only Cd-dolomite, although unknown in nature, can be readily synthesized both in the ordered and in the disordered state (Goldsmith 1972; Capobianco et al. 1987). CaFe(CO₃)₂ can be synthesized only as a disordered compound at relatively high CO₂ pressure, and it has been suggested that the ordered phase may be stable at temperatures lower than 450 °C (Davidson et al. 1993). Ordered kutnahorite and minrecio occurs in nature, but to date have not been successfully synthesized (Goldsmith 1983). Goldsmith and Northrop (1965) presented limited data on the solid solubility of ZnCO₃ in calcite, but minrecio, CaZn(CO₃)₂, was not observed in those experiments given that natural minrecio crystallizes at relatively low temperatures (Garavelli et al. 1982). On the other hand, phase relations in the otavite CdCO₃–magnesite MgCO₃ system seem to model those of the CaCO₃–MgCO₃ join at more accessible experimental temperatures (Goldsmith 1972). A complete disordered R₃̅c solid solution exists at temperatures above 850 °C, whereas at intermediate compositions Cd,Mgₓ(CO₃)₂ undergoes a reversible ordering transformation in the temperature range between 675 and 825 °C. The order-disorder phase transformation for a sample of 50:50 composition has been investigated in some detail by Capobianco et al. (1987) who found that the long-range order parameter changes from unity to zero in the temperature range between 600–850 °C. The phase diagram for this system obtained from first principle calculations (Burton and Van de Walle 2003) is in qualitative to semiquantitative agreement with the experiments. Also the two-phase region between CdCO₃ and Cd-dolomite has been calculated to be much smaller than observed experimentally...