High-pressure phase transitions in Ca-Mn carbonates (Ca,Mn)CO₃ studied by Raman spectroscopy

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ABSTRACT

The influence of Mn content on the stability of the high-pressure CaCO₃ phases CaCO₃-I, CaCO₃-II, and CaCO₃-III at 300 K has been investigated up to 40 mol% MnCO₃ using Raman spectroscopy recorded in situ with a diamond-anvil cell at pressures up to 14 GPa. Beyond about 5 mol% MnCO₃, there is a progressive linear upward shift in the pressure of the CaCO₃-I → CaCO₃-II and CaCO₃-II → CaCO₃-III transitions, and expansion of the field of the CaCO₃-II phase, with increase in MnCO₃ content. The shifts in transition pressure are 0.19 GPa/mol% for I → II and 0.26 GPa/mol% for II → III over the 5 to 40 mol% MnCO₃ composition interval, results fully consistent with elevation of transition pressure by the introduction of a smaller cation. However, minor and trace amounts of Mn appear to have a relatively insignificant influence on the pressure of these transitions.

Keywords: Calcite, rhodochrosite, solid solution, high pressure, Raman spectroscopy, diamond-anvil cell

INTRODUCTION

Carbonate minerals of sedimentary origin have long been regarded as a key component of the carbon cycle. Recent reports of inclusions of magnesite, dolomite, and Ba-Sr carbonate in natural diamonds (Wang et al. 1996; Logvinova et al. 2008) show that carbonates are likely stable in the lithospheric mantle and could represent a significant fraction of the CO₂ recycled into the mantle at convergent plate boundaries (Berg 1986; Franzolin et al. 2011). Carbonates also exhibit extensive mutual solid solution, even at moderate temperatures, and have interesting phase relations. However, there have been no laboratory studies on carbonate solid solutions at very high pressure, in particular, on the displacement of high-pressure phase boundaries in solid-solution series. Such studies may also be helpful to gain a better understanding of the effect of minor amounts of Fe and Al on the detailed phase relations of mantle silicates (Ohtani and Sakai 2008).

We studied here the effect of Mn substitution on the stability of the high-pressure CaCO₃ polymorphs CaCO₃-I, CaCO₃-II, and CaCO₃-III at 300 K. All three phases persist in the pressure-temperature stability field of aragonite and are widely regarded as a key component of the carbon cycle. Recent reports of high-pressure phase boundaries in solid-solution series. Such studies may also be helpful to gain a better understanding of the effect of minor amounts of Fe and Al on the detailed phase relations of mantle silicates (Ohtani and Sakai 2008).

EXPERIMENTAL METHODS

Manganese-bearing calcite from Ouray, Colorado, with an EPMA composition of [Ca₉.₂₅Mg₃.₆₅Fe₀.₃₅Mn₀.₉₆]CO₃ was obtained from the University of Western Ontario Dana mineral collection (no. 2651). Binary Ca-Mn carbonate solid solutions [(Ca,Mn)CO₃] were synthesized using a cold-seal hydrothermal pressure vessel, following procedures established in the literature (Goldsmith and Graf 1957; de Capitani and Peters 1981). Carbonates also exhibit extensive mutual solid solution, even at moderate temperatures, and have interesting phase relations. However, there have been no laboratory studies on carbonate solid solutions at very high pressure, in particular, on the displacement of high-pressure phase boundaries in solid-solution series. Such studies may also be helpful to gain a better understanding of the effect of minor amounts of Fe and Al on the detailed phase relations of mantle silicates (Ohtani and Sakai 2008).

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modes and to 538 nm for the symmetric stretch mode ($v_1$), although only the lattice and $v_2$ spectral regions are presently discussed in any detail.

**RESULTS AND DISCUSSION**

The hydrothermal synthesis experiments resulted in homogeneous (Ca, Mn)CO$_3$ solid solutions to the composition limit investigated (40 mol% MnCO$_3$) at 873 K, consistent with literature studies (Goldsmith and Graf 1957; de Capitani and Peters 1981). Calcite-structure Ca-Mn carbonate was the only phase detected. The trace amount of distilled water added to the capsules before sealing served only to promote recrystallization and did not result in a hydrous phase. The addition of MnCO$_3$ resulted in a uniform decrease in $c$ unit-cell parameter but the variations of $a$ and unit-cell volume were very slightly concave toward the composition axis: e.g., quadratic regression of unit-cell volume ($V$; Å$^3$) with MnCO$_3$ content ($X$; mol%) resulted in the equation:

$$V = 368.2(2) - 0.620(14)X + 0.0005(1)X^2$$

(seven observations, including new measurements on CaCO$_3$ and MnCO$_3$). The results of the Raman study at room temperature (300 K) and high pressure in the frequency ranges of interest are summarized in Figures 1 and 2. Raman bands and phase relations for the end-member CaCO$_3$ composition are generally in agreement with earlier research (Fong and Nicol 1971). Raman spectra were collected variously from carbonate grains in both $c$-axis parallel and rhombohedral orientations (Fong and Nicol 1971), although only spectra recorded in the parallel orientation are illustrated in Figure 1. No phase transitions were observed by Raman spectroscopy at the end-member MnCO$_3$ composition: the calcite (CaCO$_3$-I) structure was present over the entire pressure range investigated (0–9.5 GPa; Fig. 1). The band for the symmetric stretch vibration ($v_1$), at about 1082 cm$^{-1}$ for the end-member CaCO$_3$ composition, was a symmetrical singlet for the CaCO$_3$-I phase at 1 bar and an asymmetrical singlet for CaCO$_3$-II.

For CaCO$_3$-III, it was a singlet band with a weak, low-frequency satellite in the $c$-axis parallel orientation and a symmetrical doublet in the rhombohedral orientation.

The Raman spectra for the three high-pressure CaCO$_3$ polymorphs are consistent with: the high symmetry of CaCO$_3$-I; monoclinic symmetry and calcite-like structure of CaCO$_3$-II (Merill and Bassett 1975); and low symmetry and markedly distorted derivative calcite structure of CaCO$_3$-III (Smyth and Ahrens 1997).

Figure 2 documents a progressive upward shift in the pressure of the CaCO$_3$-I $\rightarrow$ CaCO$_3$-II and CaCO$_3$-II $\rightarrow$ CaCO$_3$-III phase transitions with increase in content of MnCO$_3$: rectangles enclose investigated pressure range for CaCO$_3$-I (open symbol), CaCO$_3$-II (black), and CaCO$_3$-III (hatched). Note linear trends of phase boundaries (fitted visually) and change in transition-pressure shifts near 5 mol% MnCO$_3$. Estimated error of transition pressures is ±0.5 GPa.
intervals for the elevation of transition pressure by Mn, marked by a seemingly abrupt change in the upward shifts of transition pressure per unit of composition near 5 mol% MnCO$_3$. From 5 to 40 mol% MnCO$_3$, transition pressure increases linearly with increase in MnCO$_3$ content; the overall shifts in transition pressure being about 0.19 GPa/mol% for CaCO$_3$-I $\rightarrow$ CaCO$_3$-II and 0.26 GPa/mol% for CaCO$_3$-II $\rightarrow$ CaCO$_3$-III. Using these shifts for the 5 to 40 mol% interval, transition pressures extrapolate to about 19 and 26 GPa at the end-member MnCO$_3$ composition for the CaCO$_3$-I $\rightarrow$ CaCO$_3$-II and CaCO$_3$-II $\rightarrow$ CaCO$_3$-III transitions, respectively. However, Santillan and Williams (2004) concluded that rhodochrosite is stable up to about 50 GPa at 300 K, and Ono (2007) reported a phase transition from rhodochrosite to a new (higher pressure) structure at 50 GPa after pre-treatment by laser heating. These observations suggest that the present measurements of transition pressure for these undoubtedly metastable high-pressure CaCO$_3$ phases do not extrapolate across the region of unmixing of Mn-rich binary compositions evident at low pressure (Peters et al. 1978; de Capitano and Peters 1981; Capobianco and Navrotsky 1987).

Preliminary results for the Ca-Mg solid solution [(Ca,Mg)CO$_3$] indicate similar behavior to the Ca-Mn solid solution but without an abrupt change in transition-pressure shifts at low MgCO$_3$ content and with a marked increase in the width of the stability field of the CaCO$_3$-II phase at the expense of CaCO$_3$-III. Of course, the extent of solid solution in this system for starting materials prepared hydrothermally at 973 K is quite limited (e.g., Franzolin et al. 2011), making extrapolation of these results to higher MgCO$_3$ contents uncertain.

The crystal chemistry of the single divalent metal carbonates (MCO$_3$) is well known to be dominated by size of the metal cation (M$^{2+}$). Certainly, in the two carbonate end-member compositions presently considered, the atomic M-O bonding is generally considered to be largely ionic (e.g., Dronskowski 2005) and structure/composition relations correlate qualitatively with simple geometrical parameters like radius ratio. The effective ionic radii for Ca$^{2+}$ and Mn$^{2+}$ in sixfold coordination with oxygen are 1.00 and 0.83 Å, respectively (Shannon 1976). Hence, the present results (Fig. 2) are fully consistent with the progressive elevation of transition pressure by the introduction of a smaller cation. Also, Mn increases the pressure stability of CaCO$_3$-II slightly at the expense of CaCO$_3$-III. This suggests that, at any given bulk composition, CaCO$_3$-II more readily accommodates the smaller sized average (Ca,Mn)$^{2+}$ cation.

The upward shifts in transition pressure are significantly smaller in the 0 to 5 mol% MnCO$_3$ interval (Fig. 2); being only about 0.02 GPa/mol% for the CaCO$_3$-I $\rightarrow$ CaCO$_3$-II transition and 0.03 GPa/mol% for the CaCO$_3$-II $\rightarrow$ CaCO$_3$-III transition. Moreover, these estimates are based on a linear fit from 0 to 5 mol% MnCO$_3$, whereas transition pressure probably increases in a curvilinear manner in this composition interval so that the shifts close to the CaCO$_3$ end-member must be minimal. This suggests that the influence of minor and trace amounts of Mn on transition pressures of calcite and derivative-calcite CaCO$_3$ phases in nature must be relatively insignificant. The small shifts in transition pressure at low MnCO$_3$ content and displacement of the linear phase boundaries to somewhat lower pressure (Fig. 2) remain to be explained, but could be related to difference in the excess molar volume of mixing between the three Ca-Mn carbonate solid solutions. Finally, partitioning of Ca and Mn across phase boundaries was not encountered and not expected due to the low temperature of this investigation inhibiting cation mobility.

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