

LETTER

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

WEIGUANG SHI, MICHAEL E. FLEET,* AND SEAN R. SHIEH

Department of Earth Sciences, University of Western Ontario, London, Ontario N6A 5B7, Canada

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 metastable (e.g., Fong and Nicol 1971; Merrill and Bassett 1975; Carlson 1983; Smyth and Ahrens 1997). CaCO₃-I is high-pressure rhombohedral calcite (space group $R\bar{3}c$). Both CaCO₃-II and CaCO₃-III have monoclinic symmetry and have derivative calcite structures: CaCO₃-II ($P2_1/c$) forms by displacive transition of $R\bar{3}c$ calcite at about 1.5 GPa (300 K) and CaCO₃-III ($C2$) forms by displacive transition of CaCO₃-II at about 2.1 GPa. All phase transitions are non-quenchable in laboratory studies during both compression and decompression. The chemistry and mineralogy of the binary calcite-rhodochrosite solid-solution series [(Ca,Mn)CO₃] have been studied extensively at relatively low pressure by various methods (e.g., Goldsmith and Graf 1957; de Capitani and Peters 1981; Fubini and Stone 1983; Capobianco and Navrotsky

1987; Droomgoole and Walter 1990; Cheng 2001; Lee et al. 2002; Katsikopoulos et al. 2009). Goldsmith and Graf (1957) reported that the solid-solution series was continuous at 823 K but unmixed at lower temperature in the Mn-rich half of the system; the critical point of the solvus was found to be at 813 K and 68 mol% MnCO₃ (de Capitani and Peters 1981). Capobianco and Navrotsky (1987) later predicted from calorimetric measurements a metastable solvus on the Ca-rich side of the system with a critical point of 628 K and about 42 mol% MnCO₃.

EXPERIMENTAL METHODS

Manganese-bearing calcite from Ouray, Colorado, with an EPMA composition of [Ca_{0.922(9)}Mg_{0.006(3)}Fe_{0.001(1)}Mn_{0.070(7)}]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). Starting materials were analytical reagent CaCO₃ (Fisher, 99%) and MnCO₃ (Alfa Aesar, 99%). They were mixed in stoichiometric proportions and contained in sealed pure gold capsules along with a trace amount of distilled water. All synthesis experiments were run at 873 ± 5 K and 1.4 ± 0.1 kbar for 7 days, and quenched at near-isobaric pressure by switching off the furnace. Experiments with before-and-after capsule weight differences >0.001 g were discarded. Products of successful experiments were dried at 378 K for 1 h and stored in a desiccator. All products were characterized by powder X-ray diffraction (Rigaku rotating anode diffractometer CoK α radiation, $\lambda = 1.7902 \text{ \AA}$), and unit-cell parameters were refined using the software PEAKFIT V4.12 and UNITCELL.

High-pressure, room-temperature Raman spectra were obtained using a diamond-anvil cell with low-fluorescence 600 μm culet diamonds (Fig. 1). Samples of fine-grained granular carbonates were loaded into a 200 μm hole drilled into a stainless steel gasket and pre-pressed to a thickness of about 40–80 μm . Ruby chips were placed close to the center and edge of the sample chamber and a 4:1 mixture of methanol and ethanol was used for the pressure medium. Experimental pressure was determined using the ruby R₁ fluorescence method (Mao et al. 1978, 1986), with correction for nonhydrostatic conditions at pressures beyond 12 GPa. An argon ion laser (514.5 nm) served as the excitation source. The micro-Raman system employs holographic optics, with a monochromatic band pass, a spatial filter, a confocal system, and Notch filters, and Raman signals were recorded by a 0.5 m spectrometer, a single ~1800 groove/mm grating, and liquid nitrogen cooled CCD detector (1100 × 330 pixels) in 180° backscattering geometry (Shieh and Duffy 2002). The precision of the measured frequency was better than ±1 cm⁻¹, and scan times were typically 60 s. The laser line position was tuned to 527 nm to collect lattice and in-plane bend (ν_4) vibration

* E-mail: mfleet@uwo.ca

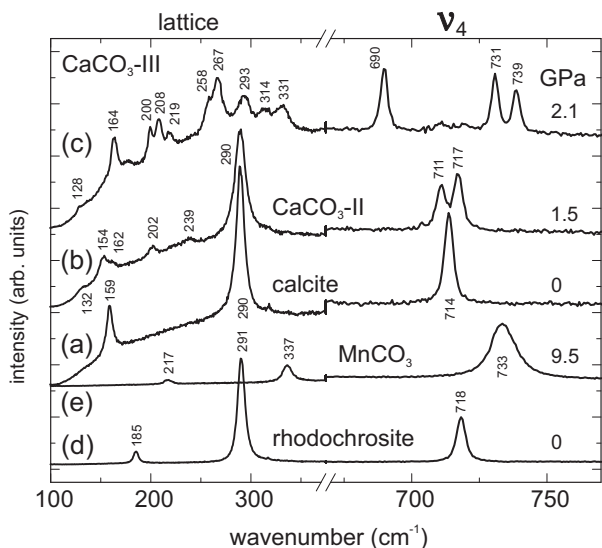


FIGURE 1. Room-temperature Raman spectra of: calcite at 1 bar (a); CaCO₃-II at 1.5 GPa (b); CaCO₃-III at 2.1 GPa (c); rhodochrosite at 1 bar (d); and MnCO₃ at 9.5 GPa (e). All spectra recorded in lattice vibration and in-plane bend (ν_4) regions, with c -axis of calcite in parallel orientation. Estimated error for band positions is ± 1 cm⁻¹.

modes and to 538 nm for the symmetric stretch mode (ν_1), although only the lattice and ν_4 spectral regions are presently discussed in any detail.

RESULTS AND DISCUSSION

The hydrothermal synthesis experiments resulted in homogeneous (Ca,Mn)CO₃ solid solutions to the composition limit investigated (40 mol% MnCO₃) 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 MnCO₃ 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 ; Å³) with MnCO₃ 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 CaCO₃ and MnCO₃). 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 CaCO₃ 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 MnCO₃ composition: the calcite (CaCO₃-I) structure was present over the entire pressure range investigated (0–9.5 GPa; Fig. 1). The band for the symmetric stretch vibration (ν_1), at about 1082 cm⁻¹ for the end-

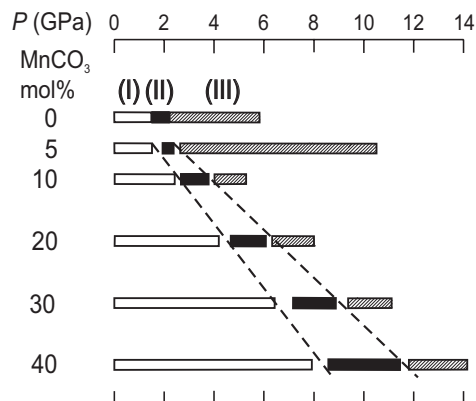


FIGURE 2. Progressive increase in pressure of the CaCO₃-I → CaCO₃-II and CaCO₃-II → CaCO₃-III phase transitions with increase in content of MnCO₃; rectangles enclose investigated pressure range for CaCO₃-I (open symbol), CaCO₃-II (black), and CaCO₃-III (hatched). Note linear trends of phase boundaries (fitted visually) and change in transition-pressure shifts near 5 mol% MnCO₃. Estimated error of transition pressures is ± 0.5 GPa.

member CaCO₃ composition, was a symmetrical singlet for the CaCO₃-I phase at 1 bar and an asymmetrical singlet for CaCO₃-II. For CaCO₃-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 CaCO₃ polymorphs are consistent with: the high symmetry of CaCO₃-I; monoclinic symmetry and calcite-like structure of CaCO₃-II (Merrill and Bassett 1975); and low symmetry and markedly distorted derivative calcite structure of CaCO₃-III (Smyth and Ahrens 1997).

Figure 2 documents a progressive upward shift in the pressure of the CaCO₃-I → CaCO₃-II and CaCO₃-II → CaCO₃-III transitions, along with expansion of the field for CaCO₃-II, with increase in MnCO₃ content. The present measurements on synthetic (Ca,Mn)CO₃ solid solutions are supported by the pressure stability fields obtained for the Mn-bearing calcite from Ouray with about 7 mol% MnCO₃, which were 0 to 2.1 GPa for CaCO₃-I, 2.3 to 3.0 GPa for CaCO₃-II, and 3.3 to 6.5 GPa for CaCO₃-III. All Raman spectra presently discussed were collected in sequence of increasing pressure because the decompression sequence required prohibitively long relaxation times to avoid hysteresis: the CaCO₃-III → CaCO₃-II transition was skipped in several experiments with CaCO₃-III converting directly to CaCO₃-I at lower pressure. However, transition pressures recorded in sequence of increasing compression were quite reproducible within the accepted pressure uncertainty (± 0.5 GPa). All band half-widths increased progressively with increase in MnCO₃ content and pressure, to the extent that the lattice and ν_4 bands for the CaCO₃-III phase at 40 mol% MnCO₃ and 14 GPa were quite diffuse. For these limiting conditions, the symmetric stretch (ν_1) band was helpful in following change in pressure of the CaCO₃-II → CaCO₃-III transition. Broadening of Raman bands could indicate a tendency of the solid solution to cluster at extreme pressure, but a tendency for the more Mn-rich compositions to amorphize at high pressure seems more likely.

It is evident from Figure 2 that there are two composition

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% MnCO₃. From 5 to 40 mol% MnCO₃, transition pressure increases linearly with increase in MnCO₃ content; the overall shifts in transition pressure being about 0.19 GPa/mol% for CaCO₃-I → CaCO₃-II and 0.26 GPa/mol% for CaCO₃-II → CaCO₃-III. Using these shifts for the 5 to 40 mol% interval, transition pressures extrapolate to about 19 and 26 GPa at the end-member MnCO₃ composition for the CaCO₃-I → CaCO₃-II and CaCO₃-II → CaCO₃-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 CaCO₃ 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)CO₃] indicate similar behavior to the Ca-Mn solid solution but without an abrupt change in transition-pressure shifts at low MgCO₃ content and with a marked increase in the width of the stability field of the CaCO₃-II phase at the expense of CaCO₃-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 MgCO₃ contents uncertain.

The crystal chemistry of the single divalent metal carbonates (MCO₃) is well known to be dominated by size of the metal cation (M²⁺). 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 Ca²⁺ and Mn²⁺ 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 CaCO₃-II slightly at the expense of CaCO₃-III. This suggests that, at any given bulk composition, CaCO₃-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% MnCO₃ interval (Fig. 2); being only about 0.02 GPa/mol% for the CaCO₃-I → CaCO₃-II transition and 0.03 GPa/mol% for the CaCO₃-II → CaCO₃-III transition. Moreover, these estimates are based on a linear fit from 0 to 5 mol% MnCO₃, whereas transition pressure probably increases in a curvilinear manner in this composition interval so that the shifts close to the CaCO₃ 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 CaCO₃ phases in nature must be relatively insignificant. The small shifts in transition pressure at low MnCO₃ 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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