LETTER

A high pressure X-ray diffraction study of aragonite and the post-aragonite phase transition in CaCO$_3$

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ABSTRACT

CaCO$_3$-aragonite has been examined to pressures of 50 GPa using angle-dispersive synchrotron X-ray diffraction at 300 K. A progressive pressure-induced change takes place in the diffraction patterns, with the (021) and (111) diffraction lines of aragonite converging toward one another with compression. The ultimate convergence of these lines and shifts in intensity in the diffraction pattern imply that CaCO$_3$-aragonite undergoes a transition to a trigonal structure near 50 GPa. This transition is similar to that occurring in BaCO$_3$ at 7 GPa and SrCO$_3$ at 35 GPa. Indeed the $b/a$ ratio of aragonite at 50 GPa is $\sqrt{3}$: the critical value for producing a transition to a trigonal structure, and similar to that of BaCO$_3$ at low pressure. The occurrence of this phase transition is in general accord with systematics in aragonite-structured divalent cation carbonates. If free CaCO$_3$ exists in the deep mantle, either as a consequence of subduction or carbonate melt fractionation, we anticipate that it is likely to occur as a trigonal phase.

INTRODUCTION

The idea that isostructural compounds containing different cations will undergo similar phase transitions at progressively higher pressures as cation radii decrease is well known (Ringwood 1975). This trend has been shown to occur in high-pressure, high-temperature static compression studies of carbonate minerals (Lin and Liu 1997a; Santillán and Williams 2004). Among calcite-structured carbonates, for example, MgCO$_3$-magnesite has been shown to be stable to pressures in excess of 31 GPa at 1200(200) K (Gillet et al. 1993), and is stable at 300 K to pressures of 70 GPa (Fiquet et al. 2002; Fiquet and Reynard 1999). In comparison, CaCO$_3$-calcite becomes unstable relative to aragonite at pressures below 3 GPa, but has two metastable phase transitions at 1.5 and 2.2 GPa (Merrill and Bassett 1975). CaMg(CO$_3$)$_2$-dolomite (essentially a doubled calcite structure) has been observed to undergo a phase transition to a structure compatible with metastable calcite-III at pressures greater than 20 GPa at 300 K (Santillán et al. 2003).

Among aragonite-structured carbonates, SrCO$_3$-strontianite and PbCO$_3$-cerrusite have been studied under static compression using in situ Raman spectroscopy and have been shown to undergo phase transitions at 35 and 17 GPa, respectively (Lin and Liu 1997b). The structure of this post-witherite phase was refined via single-crystal X-ray diffraction in a diamond anvil cell (DAC) and was indexed as having a trigonal structure, with a volume change of less than 1% relative to the witherite phase (Holl et al. 2000).

CaCO$_3$-aragonite, the prototypical orthorhombic carbonate, has been observed to be notably stable under static compression. Kraft et al. (1991) studied aragonite to pressures of 23 GPa using Raman spectroscopy and to 40 GPa using infrared spectroscopy. Similarly, Gillet et al. (1993) studied aragonite to 30 GPa using Raman spectroscopy. No phase transitions were observed in either the infrared or Raman studies. Vizgirda and Ahrens (1982), however, proposed that aragonite may undergo a shock-induced phase transition between 5.5 and 7.6 GPa. Based on the ionic radii-based systematics, CaCO$_3$-aragonite is anticipated to require the highest pressures of any of the orthorhombic carbonates to undergo a phase transition comparable to those observed in BaCO$_3$, SrCO$_3$, and PbCO$_3$ (Lin and Liu 1997a; Santillán and Williams 2004). Here, we statically compress aragonite to 50 GPa, and characterize this material with in situ X-ray diffraction to determine whether such a phase transition occurs in CaCO$_3$. Notably, the order of this transition remains uncertain even for BaCO$_3$, with Holl et al. (2000) reporting that it is marked by a progressive change in lattice parameters, a $b/a$ ratio that ultimately approaches $\sqrt{3}$ at the pressure of transition, and a volume change lower than 1%.

EXPERIMENTAL TECHNIQUE AND RESULTS

Natural samples of aragonite were obtained from Wards Natural Science. The starting material was from the optically clear samples used by Kraft et al. (1991), who confirmed the lack of contaminating phases via Raman and infrared spectroscopy. X-ray analysis of the starting material yielded lattice parameters of $a = 4.96(1)$, $b = 7.97(1)$, and $c = 5.74(1)$ Å and a volume of 226.7(3) Å³. These values are in excellent agreement with those of the JCPDS standard (card no. 5-0453) (Swanson and Fuyat 1953). Electron microprobe analysis revealed trace amounts of Na$_2$O (∼0.1 wt%) and BaO (∼0.35 wt%). Samples were prepared by grinding the starting material into 1–3 μm particles. The samples were then mixed with gold in a ratio of 98% aragonite, 2% gold by weight, with the gold serving as an internal standard for the determining sample to detector distance. This sample mixture was placed in a gasket made from initially 300 μm thick rhenium with a sample chamber predrilled to a diameter of 120 μm. A methanol:ethanol:water mixture in a 16:3:1 ratio was placed in the sample chamber to serve as a pressure