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A calcite → aragonite-type phase transition in $CdCO_3$

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ABSTRACT

Otavite ($CdCO_3$) recovered from experiments at $P > 170$ kbar and $T \approx 1000$ °C contained material with the aragonite structure, indicating that a phase transition occurred. The lattice parameters of the aragonite-type $CdCO_3$ are $a = 4.989 \pm 0.003$, $b = 7.822 \pm 0.003$, and $c = 5.713 \pm 0.004$ Å at ambient conditions. The ambient molar volume is 33.57 ± 0.06 cm^3, which is 2.1% smaller than that of otavite. The same kind of transition was not observed in rhodochrosite ($MnCO_3$), which is stable at least up to 280 kbar at ~1000 °C. Lack of any observations of another phase transition type suggests that the aragonite-type structure is the only likely high-pressure modification of the smaller-cation carbonates such as $MgCO_3$ at high pressures.

INTRODUCTION

Like the pair graphite and diamond, calcite and aragonite are among the best known polymorphous minerals in nature. For these minerals, it is well known that diamond is the high-pressure polymorph of C and aragonite is the high-pressure polymorph of $CaCO_3$ (e.g., Jamieson 1953; Liu and Bassett 1986). Except for $CaCO_3$, which occurs as the polymorphs calcite and aragonite, no other carbonates are so far known to occur in both structures at ambient conditions, although there are more than ten carbonates that exist either with the calcite or aragonite structure. We report here, for the first time, the formation of a carbonate that, like $CaCO_3$, can exist in both the calcite and aragonite structures at ambient conditions.

The volume of isostructural compounds is commonly found to relate to the cation size of these compounds. In Figure 1, the ambient molar volumes of all the carbonates that exist with the calcite- and aragonite-type structures, compiled by Robie et al. (1966), were plotted against the cation radii of these carbonates. $SrCO_3$ and $BaCO_3$ with the calcite structure (shown by open triangles) are stable only at high temperatures, and their ambient molar volumes were estimated from the lattice parameters of these phases published by Chang (1965). It is obvious from Figure 1 that the correlation among the carbonates having the calcite-type structure is well defined. A similar correlation also exists for carbonates having the aragonite-type structure. The volume of the aragonite-type carbonates is generally 7–8% smaller than that of the calcite-type carbonates (except for $CdCO_3$, which is addressed later).

Since aragonite is the high-pressure polymorph of $CaCO_3$, it would be expected that other carbonates having the calcite structure at low pressure may transform to an aragonite-type structure at high pressures or high temperatures or both, if there is no interference from other types of modification. Empirically, $CdCO_3$ should follow this type of transition at the lowest pressure, followed by $MnCO_3$; the smallest, $MgCO_3$ and $NiCO_3$, would be expected to follow the same transition at the highest pressures (Liu and Bassett 1986).

If the calcite → aragonite phase transition cannot be found in otavite ($CdCO_3$) or rhodochrosite ($MnCO_3$) in a few hundred kilobars pressure, one may conclude that the same phase transition should not occur in magnesite ($MgCO_3$) within the pressure range of the Earth's mantle. If otavite or rhodochrosite were found to transform to yet another structure, then the new structure should also be a model structure for magnesite at high pressures. So, the experimental data for otavite and rhodochrosite should provide us with fundamental information concerning the high-pressure behavior of magnesite, the most likely stable carbonate in the Earth's deep mantle (e.g., Kushiro et al. 1975; Brey et al. 1983; Redfern et al. 1993).

SAMPLES AND EXPERIMENTAL PROCEDURES

$CdCO_3$ with a purity greater than 97% purchased from Fluka Ltd. and a natural sample of rhodochrosite were used in the present study. Pink rhodochrosite from Mexico was supplied by T. Munson. Chemical composition of the rhodochrosite was confirmed using an electron probe (0.98 $MnCO_3$, 0.01 $MgCO_3$, and 0.01 $CaCO_3$). A standard X-ray diffraction pattern of the powdered samples showed no detectable impurities, and their X-ray diffraction data are in good agreement with those published in the JCPDS card catalog.

The finely powdered samples were intimately mixed with a trace amount of graphite (< 1% by weight), which served to absorb the laser radiation and thus heat the sample under compression. Samples thus prepared were compressed in a diamond-anvil press fitted with a lever-and-spring assembly and irradiated by a continuous YAG laser while the samples were maintained at high pressures. The loading pressures of the sample at the central

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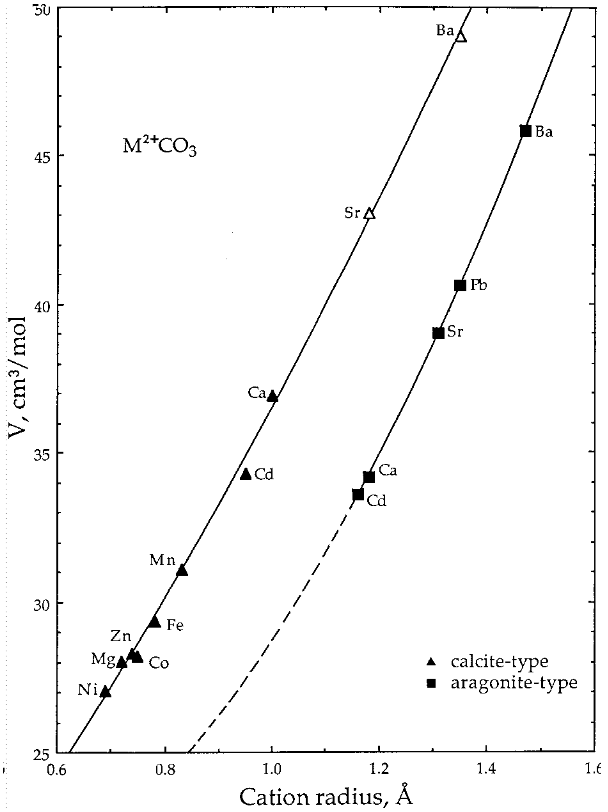

FIGURE 1. The correlation between the ambient molar volume and the cation size of carbonates possessing either the calcite or the aragonite structure. The values for calcite-type $SrCO_3$ and $BaCO_3$, shown by open triangles, were estimated from high-temperature data of Chang (1965) by linear extrapolation. The molar volume for the aragonite-type $CdCO_3$ was obtained in the present study.

TABLE 1. Room temperature and 1 bar pressure X-ray diffraction data for $CdCo_3$ quenched from ~250 kbar and ~1000 °C

Observed		Otavite*			Aragonite-type $CdCO_3$†		
I/I_{100}‡	*d* (Å)	*d* (Å)	*hkl*	I/I_{100}	*d* (Å)	*hkl*	I/I_{100}
40	4.20				4.21	110	10
90	3.78	3.78	012	80			
60	3.39				3.39	111	100
5	3.23				3.23	021	43
100	2.945	2.95	104	100			
10	2.716	2.72	006	4	2.71	121	1
40b	2.46	2.46	110	35	2.49	200	14
15	2.363				2.363	112	17
30	2.241	2.245	113	8			
5	2.105				2.103	220	6
40	2.061	2.066	202	25			
30	1.973				1.974	221	27
25	1.888	1.890	024	14	1.879	202	11
40b	1.838	1.838	018	25	1.850	041	10
		1.825	116	35	1.800	132	18
15	1.735				1.735	141	13
<5	1.694				1.694	222	3
30b	1.580	1.582	122	16	1.565	311	6
20b	1.522	1.522	1.0.10	4	1.524	232	2
25	1.498	1.500	214	12			
10	1.473	1.473	208	6			
20	1.420	1.423	300	8	1.428	004	1
10	1.358	1.357	0.0.12	2	1.355	242	1
<5	1.295	1.293	0.2.10	4	1.304	060	1
15	1.263	1.263	128	6			
10b	1.218				1.215	134	3

Note: X-ray data collected using Co$K\alpha$ radiation.

* From JCPDS 8-456.

† Calculated from cell dimensions of $a = 4.989$, $b = 7.822$, and $c = 5.713$ Å. The relative intensities were calculated by assuming Cd^{2+} replacing Ca^{2+} in aragonite.

‡ Estimated visually. The letter b denotes broad line.

portion of the anvil were estimated from the length of the spring, which was calibrated according to the room temperature NaCl pressure scale (Weaver et al. 1971). Pressures thus estimated are probably accurate within ± 10%. Except for the sample itself, no pressure medium was used in the present experiment so as to avoid possible reactions between sample and pressure medium at high pressure and high temperature. Thus, deviatoric stresses must exist in the pressure chamber. Fortunately, however, the pressure gradient is the smallest in the central portion of the anvil where the high-pressure phase transition was observed. The transition pressure estimated in this type of experiment does not appear to be grossly different from those determined in other high-pressure apparatus such as in a multi-anvil press (see, e.g., Liu and Bassett 1986).

Temperatures were estimated on the basis of the intensity of incandescent light emitted from sample and were subject to large uncertainty. In the present study, temperatures of about 800–1200 °C were estimated. At lower pressures, rhodochrosite sometimes absorbs the laser radiation by itself. In this case, rhodochrosite was probably heated in excess of 2000 °C in the present experiment. After quenching and release of pressure, samples were transferred to a modified 57.3 mm diameter Debye-Scherrer camera for X-ray diffraction study using Fe-filtered Co radiation. Because of fluorescence, some samples of rhodochrosite were studied using Ni-filtered Cu radiation. Details of the experimental procedure have been described elsewhere (Liu and Bassett 1986).

RESULTS

$CdCO_3$ was found to have the calcite structure (or otavite) at pressures below about 160 kbar. New X-ray diffraction lines were observed in the samples recovered from the experiments between 180 and 250 kbar (inclusive). The number and intensity of the new lines increase at higher pressures. The X-ray diffraction data for the sample, which was laser heated at 250 kbar, are given in Table 1, and a photograph of the diffraction pattern is shown in Figure 2. The products were approximately 65% otavite and 35% the new phase, on the basis of their relative intensities. The appearance of otavite is probably due to a pressure gradient across the diamond anvil and the chill zones of the sample in direct contact with the diamond anvils. As shown in Table 1, there are nine new

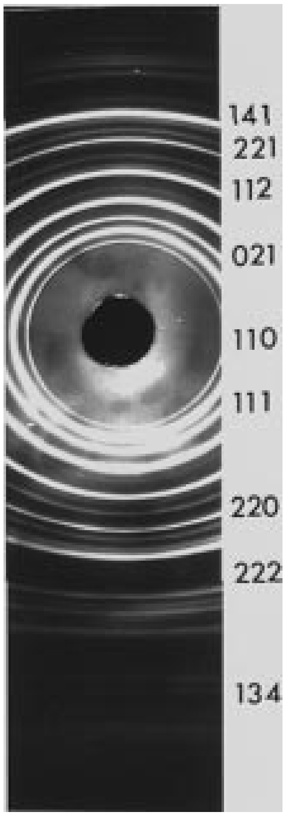

FIGURE 2. Photograph of the X-ray diffraction pattern of $CdCO_3$ quenched from about 250 kbar and 1000 °C. The diffraction lines corresponding to the aragonite structure, but not superimposed on those of otavite, are marked by Miller indices at the edge of the photograph.

diffraction lines that do not correspond to otavite but can be indexed for the orthorhombic aragonite structure. By using the Novak-Colville least-squares cell parameter refinement program, the lattice parameters of the aragonite-type $CdCO_3$ calculated from these lines are $a = 4.989 \pm 0.003$, $b = 7.822 \pm 0.003$, and $c = 5.713 \pm 0.004$ Å at ambient conditions. These values are compared with those of other carbonates possessing the aragonite structure in Figure 3. If the lattice parameters of these carbonates vary linearly with the cation size, the values of the lattice parameters of the aragonite-type $CdCO_3$ obtained in this study are in good agreement with those of the others shown in Figure 3. The ambient molar volume is calculated to be 33.57 ± 0.06 cm^3 (Fig. 1), which is 2.1% smaller than otavite. Compared with those of otavite, the spacings measured in the present experiment should be accurate within ± 0.003 Å. The relative intensities of aragonite-type $CdCO_3$ were also calculated and are listed in Table 1 for comparison. The relative intensities of the 110 and 021 reflections of the aragonite-type $CdCO_3$ are in the reverse order of those for aragonite. This is probably due to preferred orientation.

When rhodochrosite was heated at 40 kbar, at some spots the sample temperature was estimated to be as high as ~2000 °C because the sample itself absorbed the laser radiation. At these spots, gas bubbles were observed during heating and void spaces were found after quenching and release of pressure. The X-ray diffraction pattern of the recovered sample revealed that the sample was composed of rhodochrosite and manganosite (MnO). Thus, we conclude that some of the rhodochrosite sample was heated at 40 kbar to the temperature at which the sample decomposed into the mixture MnO + CO_2. The gas bubbles observed during heating should be CO_2 gas, and it was lost when pressure was released. The same phenomenon was not observed in experiments between 60 and 280 kbar (inclusive), in which only rhodochrosite was observed. Thus, it is reasonable to concluded that rhodochrosite is stable at least up to 280 kbar at ~1000 °C.

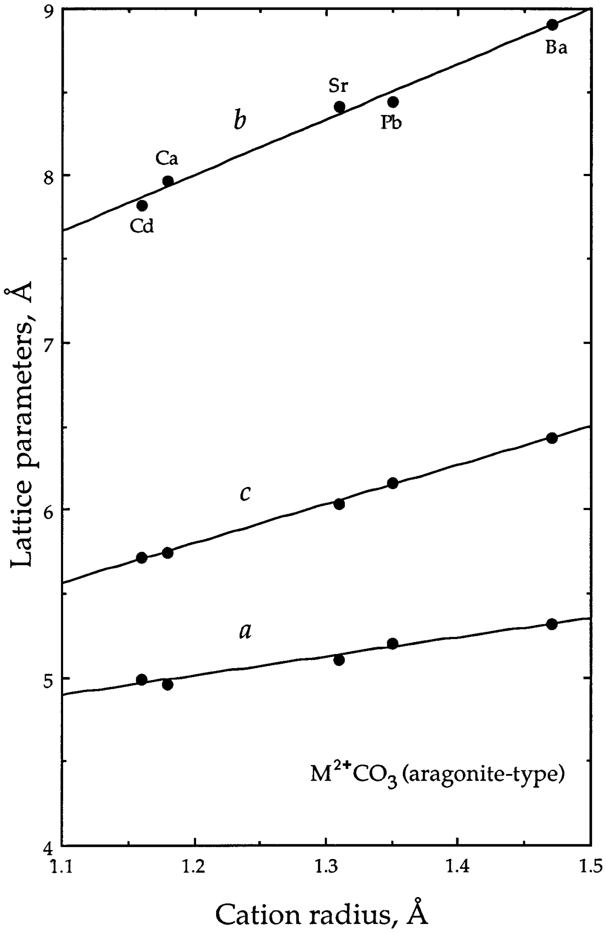

FIGURE 3. The variation of the lattice parameters of the aragonite-type carbonates with the cation size.

DISCUSSION

The size of Cd^{2+} is only about 5% smaller than that of Ca^{2+} in the calcite-type structure (Fig. 1), and it entails about 180 kbar at ~1000 °C to form the aragonite-type $CdCO_3$. The same transition was not found in $MnCO_3$ in the experiments up to 280 kbar at ~1000 °C, and Mn^{2+}

is about 17% smaller than Ca^{2+}. Thus, it should be expected that $MgCO_3$ would not adopt the aragonite structure until some extremely high pressure was reached, because Mg^{2+} is about 28% smaller than Ca^{2+}. Except for the aragonite structure, no other new types of structure were revealed in the present study of $CdCO_3$ and $MnCO_3$ at high pressures and high temperatures. Thus, this may also suggest that no other high-pressure modification of $MgCO_3$ is likely, except the aragonite structure. However, the calcite → aragonite-type transition may not occur in $MgCO_3$ at the pressures prevailing in the Earth's lower mantle (no phase transition was found in magnesite up to 550 kbar at ~1300 °C by Katsura et al. 1991). On the other hand, if the transition pressure for the calcite → aragonite-type transition in $CaCO_3$ and $CdCO_3$ were linearly related to the cation size of these carbonates, the linear extrapolation of this relationship would yield a transition pressure of about 820 kbar at ~1000 °C for magnesite. In this case, the calcite → aragonite-type transition may occur in $MgCO_3$ at the *P-T* conditions of the lower mantle.

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