American Mineralogist, Volume 90, pages 667–671, 2005

Post-aragonite phase transformation in CaCO3 at 40 GPa

SHIGEAKI ONO,[1],* TAKUMI KIKEGAWA,[2] YASUO OHISHI,[3] AND JUN TSUCHIYA[4]

[1]Institute for Research on Earth Evolution, Japan Agency for Marine-Earth Science and Technology, 2-15 Natsushima-cho, Yokosuka-shi, Kanagawa 237-0061, Japan
[2]High Energy Acceleration Research Organization, 1-1 Oho, Tsukuba 305-0801, Japan
[3]Japan Synchrotron Radiation Research Institute, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan
[4]Department of Chemical Engineering and Material Science, Minnesota Supercomputing Institute for Digital Technology and Advanced Computations, University of Minnesota, 421 Washington Avenue SE, Minneapolis, Minnesota 55455, U.S.A.

ABSTRACT

Phase transformations of calcium carbonates ($CaCO_3$) were investigated using a laser-heated diamond anvil cell combined with a synchrotron X-ray diffraction method. Calcite, which is the stable phase at ambient conditions, transforms to aragonite at high P-T conditions that correspond to the uppermost part of the upper mantle. The phase transformation from aragonite to a new form of calcium carbonate was observed at pressures higher than about 40 GPa, corresponding to the lower mantle. The new carbonate has orthorhombic symmetry ($P2_12_12$) and was confirmed to remain stable at least up to 86 GPa (2000 kilometer depth). This indicates that carbon might be stored in the new calcium carbonate phase in the deep mantle.

INTRODUCTION

Calcite is the dominant carbon-bearing phase in the Earth's crust, and acts as a buffer for the long-term cycling of CO_2 between the atmosphere, oceans, and solid Earth. It is unsurprising, therefore, that the high-pressure stability and behavior of $CaCO_3$ and related phases has attracted considerable interest. It is generally known that CO_2 and H_2O are the dominant volatile components in the Earth's mantle. Magmas originating from the mantle, such as MORB, hot-spot, and kimberlite, contain CO_2 gas. This carbon is supplied by subducted slabs, which include carbonate minerals (Marty and Jambon 1987). Recently, Keppler et al. (2003) reported that the carbon solubility in olivine is exceedingly low. This indicates that most carbon must be present as a separate phase in the upper mantle. To understand carbon recycling in the mantle, there have been several investigations into the pressure response of the structure of $CaCO_3$ polymorphs, ranging from the pioneering work of Bridgman (1939) to recent static and dynamic high-pressure studies (e.g., Tyburczy and Ahrens 1986; Biellmann et al. 1993; Fiquet et al. 1994; Martinez et al. 1995, 1996; Suito et al. 2001; Luth 2001; Ivanov and Deutsch 2002). It is generally known that calcite transforms to aragonite, which often occurs in high-pressure metamorphic rocks, at high P-T that correspond to the lower crust and the uppermost upper mantle. It is unknown whether aragonite transforms to a new high-pressure phase in the deep mantle. In this study, therefore, the high-pressure stability limit of aragonite was investigated using a laser-heated diamond anvil cell combined with a synchrotron X-ray diffraction method.

EXPERIMENTAL METHOD

High-pressure X-ray diffraction experiments were performed using a laser-heated diamond anvil cell (LHDAC) high-pressure apparatus. Synthetic powdered $CaCO_3$ (purity 99.9%) was loaded into a 50–100 μm diameter hole that was drilled into a rhenium gasket using an excimer laser. The $CaCO_3$ powder was mixed with 8 wt% platinum to absorb the laser radiation to provide a heat source, and the Pt was also used as an internal pressure calibrant. These were mechanically ground in an agate mortar for several hours to ensure homogeneity and a sufficiently fine grain size. In some experiments, NaCl was used as a pressure transmitting medium to reduce deviatoric stress and temperature gradients in the sample. The sample thickness was 10–30 μm. The samples were heated with a TEM_{01}-mode YLF laser or multi-mode YAG laser to overcome potential kinetic effects on possible phase transitions. The size of the heating spot was about 30–100 μm. The laser beam was not scanned to heat the sample, because scanning causes huge temperature gradients and thus promotes chemical disequilibrium in the sample. The reaction between the sample and the rhenium gasket was negligible, as the temperatures of the rhenium gasket were much lower than those of the samples during the laser heating. The sample temperature in some experiments was measured using the spectroradiometric method. The spectroradiometric system consists of a thermoelectrically cooled CCD detector (Princeton Instruments, HAM 256 × 1024) and a spectrograph (Acton Research, SpectraPro-150). The spectrometer allows us to measure a temperature profile across a laser-heated spot. Temperatures were determined by fitting the thermal radiation spectrum between 600 and 800 nm to the Planck radiation function:

$$I = 2\pi hc^2\varepsilon(\lambda)\lambda^{-5}/[\exp(hc / k\lambda T) - 1],$$

where I is the spectral intensity, ε emissivity, λ wavelength, and T temperature. The system response was calibrated with a tungsten ribbon lamp (OL550, Optronic Laboratories) of known radiance. The accuracy of temperature measurement using spectral radiometry in the diamond anvil cell is affected by the wavelength dependence of emissivity and the system's optical aberration. However, no data for high P-T emissivity are available. Therefore, the emissivity of tungsten (De Vos 1954) was used to model the radiation spectrum from the heated sample. In the several experiments made without the spectroradiometric method, the temperature was estimated from the emission of the heated sample. The pressure was determined from the observed unit cell volume of platinum from the Pt equation of state (EOS) of Holmes et al. (1989), with the electronic thermal pressure correction (Tsuchiya and Kawamura 2002). The samples were probed using an angle-dispersive X-ray diffraction technique at the synchrotron beam lines BL10XU, SPring-8 (Ono et al. 2002a) and BL13A, Photon Factory (Ono et al. 2002b) in Japan. A monochromatic incident X-ray beam with a wavelength of λ ~ 0.42 Å was used. The X-ray beams were collimated to a diameter of 15–30 μm, and the angle-dispersive X-ray diffraction patterns were obtained with an imaging plate. The observed intensities on the imaging plates were integrated as a function of 2θ using the ESRF Fit2d

---

* E-mail: sono@jamstec.go.jp

0003-004X/05/0004–667$05.00/DOI: 10.2138/am.2005.1610

code (Hammersley et al. 1996) to obtain conventional, one-dimensional diffraction profiles. Experimental details are described in Ono et al. (2002a, 2002b).

RESULTS

In the first set of experiments using the pressure transmitting medium, the pressure was increased directly to about 40 GPa at room temperature, and an X-ray diffraction pattern of the sample was recorded (Fig. 1). It was difficult to identify $CaCO_3$ phases at room temperature before the sample was heated. A strain-broadening of the diffraction peaks occurred, because a large differential stress was induced in the diamond anvil cell experiments as the pressure increased. After the desired pressure was achieved, the sample was heated to about 1500–2000 K to relax the differential stress and to overcome potential kinetic effects on possible phase transitions. After heating some new peaks appeared in the diffraction pattern (Fig. 1). This implies that the starting material transformed to a new high-pressure (post-aragonite) phase. The post-aragonite phase was unquenchable because it transformed to calcite, which is stable at room pressure and temperature, after the pressure was reduced to ambient conditions. After decompression, the diffraction patterns showed that no extra phase was present, other than calcite, Pt, and NaCl (Fig. 2). In the second set of experiments using the pressure-transmitting medium, the pressure was increased directly to about 25 GPa, and the sample was then heated. The diffraction patterns indicate that the starting materials transformed to aragonite (Fig. 2). After the pressure was decreased to ambient conditions, aragonite remained stable, which is consistent with previous multianvil and diamond anvil cell experiments (e.g., Fiquet et al. 1994; Suito et al. 2001; Kraft et al. 1991; Shirasaka et al. 2002). In the next set of experiments, the spectroradiometric method was used to determine the precise heating temperatures. Although experimental conditions were up to 86 GPa and 2450 K, no phase transition and no dissociation of the post-aragonite phase was observed.

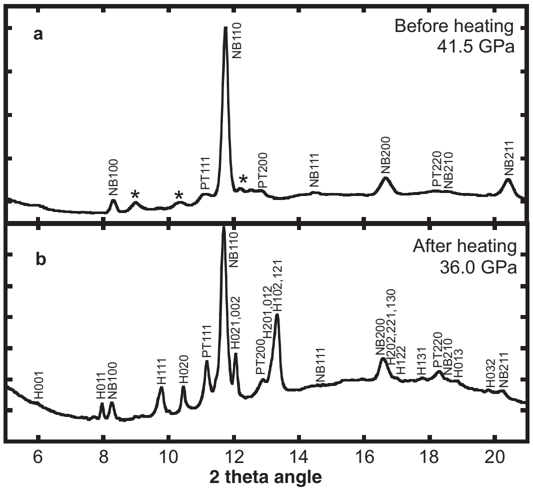

FIGURE 1. Examples of observed X-ray diffraction patterns of the sample. (**a**) Before heating at 41.5 GPa; (**b**) after heating at 36.0 GPa. Abbreviations are as follows: H = post-aragonite; Pt = platinum; NB = B2-type sodium chloride. Asterisks indicate broad peaks of the starting material.

Three additional experiments, both with and without the pressure transmitting medium, were performed. The experimental pressures of this study were from 11 to 86 GPa. The typical diffraction patterns of calcium carbonates are shown in Figure 2. No significant difference was observed between patterns collected with or without the pressure-transmitting medium. This indicates that the reaction between the sample and the NaCl pressure medium was negligible during heating. The transition pressure from aragonite to the post-aragonite phase was located at about 35 GPa and room temperature after heating (Fig. 3). Kraft et al. (1991) reported that aragonite was observed up to 40 GPa. A likely explanation for this inconsistency is that the uncertainty of estimated experimental pressures at high temperatures may affect the potential transformation pressure. In the vicinity of the phase-transition pressure, both this and the previous study estimated the pressures before and/or after heating. However, pressures during heating were different from those measured before and after heating (e.g., Kavner and Duffy 2001; Ono et al. 2002c). A pressure calibration experiment showed that pressures decreased about 5–10 GPa during the temperature quench in this experimental assembly because of the thermal pressure effect. Consequently, the phase transition from aragonite to the post-aragonite phase was likely to occur at around 40 GPa at high temperatures. The uncertainties in the pressure were not small in either of the studies, and therefore the result of this study is generally consistent with the previous study (Kraft et al. 1991).

The post-aragonite phase is likely to be orthorhombic. The number of molecules of this phase in a unit cell (*Z*) is 2. The

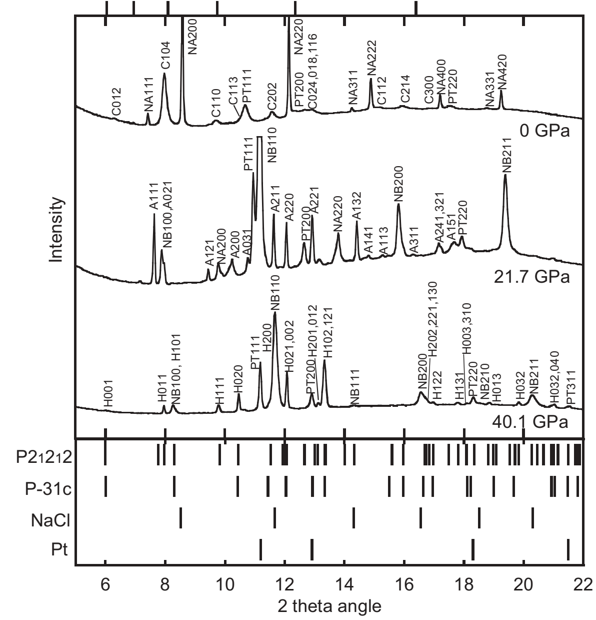

FIGURE 2. Examples of observed X-ray diffraction patterns of the samples at 300 K. Top, calcite at 0 GPa after decompression; middle, aragonite at 21.7 GPa after heating; bottom, post-aragonite at 40.1 GPa after heating. Abbreviations are as follows: C = calcite; A = aragonite; H = post-aragonite; Pt = platinum; NA = B1-type sodium chloride; NB = B2-type sodium chloride. Vertical bars indicate the calculated positions of the diffraction lines of each phase.

lattice parameters at 66.4 GPa and 300 K, for example, are $a = 4.101(12)$, $b = 4.561(4)$, and $c = 3.964(3)$ Å, with a unit cell volume of 74.1(2) $Å^3$. The X-ray diffraction peaks of the post-aragonite phase can be reasonably indexed on the basis of orthorhombic symmetry (Table 1). The space group of this phase is $P2_12_12$. Holl et al. (2000) reported on the phase transformation of $BaCO_3$, which has the aragonite-type structure under ambient conditions. At approximately 7 GPa, a first-order transformation to space group $P\overline{3}1c$ was observed. The diffraction pattern of the post-aragonite phase observed in this study was similar to that of the high-pressure $BaCO_3$ phase (Holl et al. 2000). However, some diffraction peaks, such as 011, 111, 201, and 012, cannot be indexed using this trigonal symmetry (Fig. 2). Therefore, the post-aragonite phase of $CaCO_3$ is likely to have orthorhombic symmetry ($P2_12_12$). Recently, the phase transition of $SrCO_3$, which seems to be an analog material of $CaCO_3$, from aragonite-type to orthorhombic structure ($P2_12_12$) was reported at 10 GPa (Ono et al. 2005). The phase transition sequence of $CaCO_3$ observed in this study agrees with that of $SrCO_3$.

As seen in Figure 3, a discontinuity in volume between aragonite and the post-aragonite phase indicates that this is a first-order phase transformation. At 35 GPa, the relative volume change is about 5%. A refinement of the post-aragonite volume data yields third-order Birch-Murnaghan equations of state parameters: the bulk modulus $K_0 = 127$ (± 14) GPa and the volume $V_0 = 98.3$ (± 1.9) $Å^3$ when the first pressure derivative of the bulk modulus, K_0', is fixed at 4. The density of the post-aragonite phase at 66 GPa is 3.77 g/cm^3. This is lighter than $MgSiO_3$ perovskite, which is generally expected to be the dominant phase in the Earth's lower mantle. Therefore, the post-aragonite phase may be buoyant in the lower mantle.

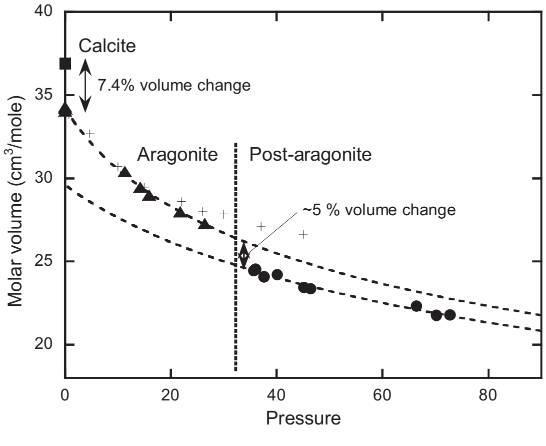

FIGURE 3. Relative volume of $CaCO_3$ phases as a function of pressure at 300 K. The symbols are as follows: squares, calcite; triangles, aragonite; circles, post-aragonite. The crosses are volumes of aragonite from Santillán and Williams (2004). Dashed lines are Birch-Murnaghan equations of state for the aragonite and post-aragonite phases. Aragonite: $K_0 = 67.1$ (±6.3) GPa, $K_0' = 4.7$ (±0.8), and $V_0 = 227.2$ (±1.0) $Å^3$; post-aragonite: $K_0 = 127$ (±14) GPa and $V_0 = 98.3$ (±1.9) $Å^3$ when K_0' is fixed at 4.

DISCUSSION

Recently, Santillán and Williams (2004) reported on the post-aragonite phase transition in $CaCO_3$. They observed a trigonal phase ($P\overline{3}1c$) at 50 GPa with the same structure as the high-pressure $BaCO_3$ phase reported by Holl et al. (2000). However, their result is inconsistent with our study. The most important difference between two studies is the experimental temperature condition. In our study, the sample was heated to overcome potential kinetic effects on possible phase transitions and to minimize any pressure inhomogeneity in the sample chamber. In contrast, Santillán, and Williams (2004) acquired X-ray data only at room temperatures without heating. Therefore, their X-ray diffraction data showed that significant strain-broadening of the diffraction peaks occurred. This indicated that a large differential stress was induced in the sample chamber as the pressure increased. In Figure 3, the aragonite volumes reported by Santillán, and Williams (2004) are plotted. The discrepancy of compression curves between their and our data is observed at pressure above 15 GPa. Table 2 shows a comparison of compressive behavior of aragonite reported in our and previous studies. Santillán and Williams (2004) reported a significantly high value of the bulk modulus of aragonite compared with other studies. These evidences indicate that a large deviatoric stress was induced in their study. Therefore, the trigonal $CaCO_3$ phase reported by Santillán and Williams (2004) is likely to be metastable and due to a large deviatoric stress.

TABLE 1. Observed and calculated X-ray diffraction pattern of the post-aragonite phase at 40 GPa and room temperature

hkl	d_{obs}, Å	d_{calc}, Å	d_{obs}-d_{calc}	I_{obs}	I_{calc}
001	4.065	4.063	0.002	< 3	3
110		3.138			5
011	3.063	3.065	–0.002	15	19
101	2.925	2.933	–0.008	19	47
111	2.489	2.484	0.005	15	55
020	2.333	2.335	–0.002	40	17
200*		2.119			80
021	2.023	2.024	–0.001	75	36
012	1.861	1.863	–0.002	5	< 1
102	1.832	1.832	0.000	100	9
121	1.832	1.827	0.005	100	100
211		1.743			13
112		1.705			5
220		1.569			13
022	1.535	1.533	0.002	< 3	3
221	1.460	1.464	–0.004	10	19
130	1.460	1.461	–0.001	10	5
031	1.460	1.454	0.006	10	1
122	1.443	1.441	0.002	3	6
131	1.376	1.375	0.001	5	3
003	1.352	1.354	–0.002	< 3	6
310	1.352	1.352	0.000	< 3	1
301		1.334			6
013	1.300	1.301	–0.001	5	1
311		1.283			7
113	1.235	1.243	0.008	5	3
222	1.235	1.242	0.007	5	2
032	1.235	1.236	–0.001	5	5
231		1.197			2
132		1.186			1
023	1.170	1.171	–0.001	3	12
040	1.166	1.168	–0.002	5	9

Notes: Calculated *d*-spacings are based on orthorhombic unit cell dimensions of $a = 4.238(3)$, $b = 4.670(3)$, and $c = 4.062(2)$ Å, and $V = 80.40(9)$ $Å^3$. Wyckoff symbols and the positions of each atom are: Ca, 2a, (0, 0, 0.15); C, 2b, (0, 0.5, 0.47); O1, 2b, (0, 0.5, 0.17); O2, 4c, (0.55, 0.23, 0.40).
*The 200 peak is overlapped by the 100 peak of NaCl.

TABLE 2. Comparison of elastic parameters of aragonite and post-aragonite phases for our results and previous studies

K_0 (GPa)	K_0'	References
	Aragonite	
64.5	4	Martens et al. (1982)
64.8	4	Martinez et al. (1996)
65.4	2.7	Martinez et al. (1996)
88	4	Santillán and Williams (2004)
73.1 (±2.2)	4 (fixed)	This study
67.1 (±6.3)	4.7 (±0.8)	This study
	Post-aragonite	
127 (±14)	4 (fixed)	This study

Note: Numbers in parentheses represent the error. K_0 and K_0' are the isothermal bulk modulus and the first derivative of the isothermal bulk modulus at 300 K.

Selverstone and Gutzler (1993) hypothesized that cooling during the Cenozoic was produced by removal of CO_2 from the ocean-atmosphere system into subduction zones. Although their specific arguments regarding paleoclimate are controversial (Kerrick and Calderia 1998), Selverstone and Gutzler (1993) emphasized that carbonate is present in deeply subducted slabs. From geological observations, the most dominant carbonates are calcite, $CaCO_3$, and dolomite, $(Mg,Ca)CO_3$. Marine sediments and hydrothermally altered oceanic crust containing these carbonates are likely to subduct into the mantle. Kushiro et al. (1975) suggested that calcite (or aragonite) is unstable in Ca-poor rock compositions such as peridotite. Calcite (or aragonite) changes to dolomite and magnesite at pressures higher than 4 GPa. However, it is likely that calcite (or aragonite) remains stable in Ca-rich rock compositions, such as the subducted oceanic crust and the marine sediment. Previous studies support the idea that deep subduction of Ca-carbonate in the altered oceanic crust provides a potentially significant CO_2 source (Yaxley and Green 1994; Kerrick and Connolly 1998). It is important to clarify whether these carbonates break down to oxides or remain stable in the Earth's mantle, because decomposed carbon dioxide changes the physical properties of mantle rock. It is generally accepted that volatile components, such as carbon dioxide and water, become a super-critical fluid and are mobile at high pressures and high temperatures. Figure 4 shows a phase diagram for carbonates as determined by this and previous studies. By considering the mantle geotherm, calcite, which has five different modifications, transforms to aragonite at about 1 GPa (Suito et al. 2001). In contrast to calcite, dolomite breaks down into magnesite, $MgCO_3$, and aragonite at about 5–7 GPa (e.g., Shirasaka et al. 2002; Sato and Katsura 2001). A previous study reported that magnesite is stable in the lower mantle (Fiquet et al. 2002). Moreover, a recent study showed that there is a possibility that magnesite transforms to a denser phase at the base of the lower mantle (Isshiki et al. 2004). The stability of aragonite was previously unknown at lower mantle conditions. This study shows that aragonite transforms to a post-aragonite phase at about 40 GPa, corresponding to 1000 km depth. This and previous experimental studies indicate no observation of decomposition of calcium and magnesium carbonates in the lower mantle. A new and significant finding of this study is that Ca-carbonate-bearing rock could exist in the deep mantle and that the post-aragonite phase seems to be an important host phase for carbon. The understanding of carbon recycling in the deep mantle is likely to shed light on the genesis of natural diamond and carbon-rich volcanism, such as carbonatite and kimberlite.

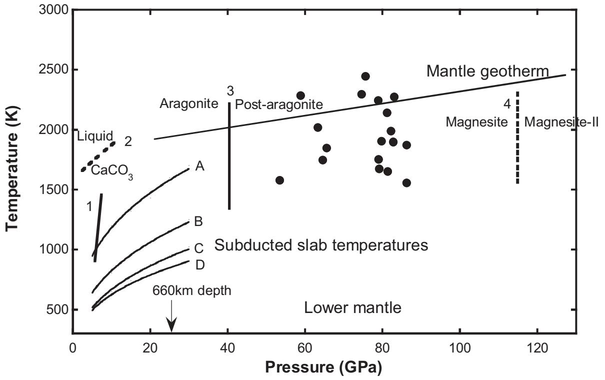

FIGURE 4. Pressure-temperature conditions of in situ observations of the post-aragonite phase. The solid circles show the *P-T* conditions where the post-aragonite phase was observed. The thick solid and dashed lines are phase boundaries: 1 = dolomite dissociation into aragonite + magnesite (e.g., Shirasaka et al. 2002; Sato and Katsura 2001); 2 = melting curve of $CaCO_3$ (Suito et al. 2001); 3 = phase transition from aragonite to post-aragonite phase (this study); 4 = phase transition from magnesite to magnesite-II (Isshiki et al. 2004). Solid thin lines are the minimum temperatures inside subducted slabs calculated from subduction zone thermal models. A, B, C, and D are the slab classes of Kirby et al. (1996).

ACKNOWLEDGMENTS

The authors thank Y. Tatsumi, N. Sata, Y. Nishio, and M. Handler for their help in carrying out the present work. The synchrotron radiation experiments were performed at the PF, KEK (proposal no. 2001G222) and at SPring-8, JASRI (proposal no. 2002A0106-ND2-np and 2002B0162-ND2-np). This work was partially supported by the Ministry of Education, Culture, Sport, Science, and Technology, Japan.

REFERENCES CITED

Biellmann, C., Guyot, F., Gillet, P., and Reynard, B. (1993) High-pressure stability of carbonates: quenching of calcite-II, high-pressure polymorph of $CaCO_3$. European Journal of Mineralogy, 5, 503–510.

Bridgman, P.W. (1939) The high pressure behavior of miscellaneous minerals. American Journal of Science, 239, 7–18.

De Vos, J.C. (1954) A new determination of the emissivity of tungsten ribbon. Physica 20, 690–714.

Fiquet, G., Guyot, F., and Itie, L.P. (1994) High-pressure X-ray diffraction study of carbonates: $MgCO_3$, $CaMg(CO_3)_2$, and $CaCO_3$. American Mineralogist, 79, 15–23.

Fiquet, G., Guyot, F., Kunz, M., Matas, J., Andrault, D., and Hanfland, M. (2002) Structural refinements of magnesite at very high pressure. American Mineralogist, 87, 1261–1265.

Hammersley, A.P., Svensson, S.O., Hanfland, M., Fitch, A.N., and Häusermann, D. (1996) Two-dimensional detector software: From real detector to idealized image or two-theta scan. High Pressure Research, 14, 235–245.

Holl, C.M., Smyth, J.R., Laustsen, H.M.S., Jacobsen, S.D., and Downs, R.T. (2000) Compression of witherite to 8 GPa and the crystal structure of $BaCO_3$II. Physics and Chemistry of Minerals, 27, 467–473.

Holmes, N.C., Moriarty, J.A., Gathers, G.R., and Nellis, W.J. (1989) The equation of state of platinum to 660 GPa (6.6 Mbar). Journal of Applied Physics, 66, 2962–2967.

Isshiki, M., Irifune, T., Hirose, K., Ono, S., Ohishi, Y., Watanuki, T., Nishibori, E., Takadda, M., and Sakata, M. (2004) Stability of magnesite and its high-pressure form in the lowermost mantle. Nature, 427, 60–63.

Ivanov, B.A. and Deutsch, A. (2002) The phase diagram of $CaCO_3$ in relation to shock compression and decomposition. Physics of the Earth and Planetary Interiors, 129, 131–143.

Kavner, A. and Duffy, T.S. (2001) Pressure-volume-temperature paths in the laser-heated diamond anvil cell. Journal of Applied Physics, 89, 1907–1914.

Keppler, H., Wiedenbeck, M., and Schcheka, S.S. (2003) Carbon solubility in olivine and the mode of carbon storage in the Earth's mantle. Nature, 424, 414–416.

Kerrick, D.M. and Calderia, K. (1998) Metamorphic CO_2 degassing from orogenic belts. Chemical Geology, 145, 213–232.

Kerrick, D.M. and Connolly, J.A.D. (1998) Subduction of ophicarbonates and recycling of CO_2 and H_2O. Geology, 26, 375–378.

Kirby, S.H., Stein, S., Okal, E.A., and Rubie, D.C. (1996) Metastable mantle phase transformations and deep earthquakes in subducting oceanic lithosphere. Reviews of Geophysics, 34, 261–306.

Kraft, S., Knittle, E., and Williams, Q. (1991) Carbon stability in the Earth's mantle: a vibrational spectroscopic study of aragonite and dolomite at high pressures and temperature. Journal of Geophysical Research, 96, 17997–18009.

Kushiro, I., Satake, H., and Akimoto, S. (1975) Carbonate-silicate reactions at high pressures and possible presence of dolomite and magnesite in the upper mantle. Earth and Planetary Science Letters, 28, 116–120.

Luth, R.W. (2001) Experimental determination of the reaction aragonite + magnesite = dolomite at 5 to 9 GPa. Contributions to Mineralogy and Petrology, 141, 222–232.

Martens, R., Rosenbauer, M., and Von Gehlen, K. (1982) Compressibilities of carbonates. In W. Schreyer, Ed., High pressure researches in geoscience, p. 235–238. Schweizerbartsche Verlagsbuchhandlung, Stuttgart, Germany.

Martinez, I., Deutsch, A., Schärer, U., Ildefonse, P., Guyot, F., and Agrinier, P. (1995) Shock recovery experiments on delomite and thermodynamical calculations of impact induced decarbonation. Journal of Geophysical Research, 100, 15465–15476.

Martinez, I., Zhang, J., and Reeder, R.J. (1996) In situ X-ray diffraction of aragonite and dolomite at high pressure and high temperature: Evidence for dolomite breakdown to aragonite and magnesite. American Mineralogist, 81, 611–624.

Marty, B. and Jambon, A. (1987) $C/^3He$ in volatile fluxes from the solid Earth: implications for carbon geodynamics. Earth and Planetary Science Letters, 83, 16–26.

Ono, S., Hirose, K., Isshiki, M., Mibe, K., and Saito, Y. (2002a) Equation of state of hexagonal aluminous phase of natural composition to 63 GPa at 300 K. Physics and Chemistry of Minerals, 29, 527–531.

Ono, S., Hirose, K., Kikegawa, T., and Saito, Y. (2002b) The compressibility of a natural composition calcium ferrite-type aluminous phase to 70 GPa. Physics of the Earth and Planetary Interiors, 131, 311–318.

Ono, S., Hirose, K., Murakami, M., and Isshiki, M. (2002c) Post-stishovite phase boundary in SiO_2 determined by in situ X-ray observations. Earth and Planetary Science Letters, 197, 187–192.

Ono, S., Shirasaka, M., Kikegawa, T., and Ohishi, Y. (2005) A new high-pressure phase of strontium carbonate. Physics and Chemistry of Minerals, in press.

Santillán, J. and Williams, Q. (2004) A high pressure X-ray diffraction study of aragonite and the post-aragonite phase transition in $CaCO_3$. American Mineralogist, 89, 1348–1352.

Sato, K. and Katsura, T. (2001) Experimental investigation on dolomite dissociation into aragonite-magnesite up to 8.5 GPa. Earth and Planetary Science Letters, 184, 529–534.

Selverstone, J. and Gutzler, D.S. (1993) Post-125-Ma carbon storage associated with continent-continent collision. Geology, 21, 885–888.

Shirasaka, M., Takahashi, E., Nishihara, Y., Matsukage, K., and Kikegawa, T. (2002) In situ X-ray observation of the reaction dolomite = aragonite + magnesite at 900–1300 K. American Mineralogist, 87, 922–930, 2002.

Suito, K., Namba, J., Horikawa, T., Taniguchi, Y., Sakurai, N., Kobayashi, M., Onodera, A., Shimomura, O., and Kikegawa, T. (2001) Phase relations of $CaCO_3$ at high pressure and high temperature. American Mineralogist, 86, 997–1002.

Tsuchiya, T. and Kawamura, K. (2002) First-principles electronic thermal pressure of metal Au and Pt. Physical Review B, 66, 094115.

Tyburczy, J.A. and Ahrens, T.J. (1986) Dynamic compression and volatile release of carbonates. Journal of Geophysical Research, 91, 4730–4744.

Yaxley, G.M. and Green, D.H. (1994) Experimental demonstration of refractory carbonate-bearing eclogites and siliceous melt in the subduction regime. Earth and Planetary Science Letters, 128, 313–325.

Manuscript received January 26, 2004
Manuscript accepted October 19, 2004
Manuscript handled by Sang-Heon Dan Shim