DETERMINATION OF THE DECOMPOSITION BOUNDARY OF $CaCO_3$ AT HIGH TEMPERATURE: IMPLICATIONS FOR IMPACT-INDUCED DEGASSING OF $CaCO_3$.
K. Ishibashi[1], T. Yagi[2], and T. Matsui[3], [1]Dept. of Earth Planet. Sci., Univ. of Tokyo (7-3-1, Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan; ishibashi@eps.s.u-tokyo.ac.jp), [2] Institute for Solid State Physics, Univ. of Tokyo (5-1-5, Kashiwanoha, Kashiwa, Chiba, 277-8581, Japan), [3]Dept. of Complexity Sci. and Eng., Univ. of Tokyo (5-1-5, Kashiwanoha, Kashiwa, Chiba, 277-8561, Japan).

Introduction: Hypervelocity impact is one of the most common and important physical and chemical processes affecting the evolution of terrestrial planets. When impactors such as asteroids or comets impact on the surface of planets, volatile components are released from surface and/or impactor due to high-pressure and -temperature states caused by the passage of intense shock waves. This has been called the “impact-induced degassing”. Degassed components (e.g., CO_2 from carbonate) may have played an important role in evolution of the surface environment of terrestrial planets (e.g., mass extinction, evolution of planetary atmosphere, and so on) [e.g., 1-3].

The typical shock pressures treated in the previous studies on impact-induced degassing so far were relatively low (< ~70 GPa). Thus, impact-induced degassing at high-shock pressure region has not been understood well. The degassing mechanism may change at adequately high-shock pressure from the conventional view on impact-induced degassing. In the conventional theoretical models the shock-loaded material is not assumed to decompose just after the passage of shock wave. The material will decompose and will be degassed when the temperature and pressure satisfy the decomposition condition after the pressure release [e.g., 4]. The change in degassing mechanism may occur when the thermodynamic state on Hugoniot becomes to satisfy the decomposition condition of minerals. This type of decomposition might lead intensive degassing, because it does not require appropriate pressure release that the conventional mechanism assumes [5]. Complete decomposition may not occur until this condition is satisfied.

Thus, it is essential for understanding the impact-induced degassing to study this new mechanism. However, for this purpose, we need to know the information on decomposition boundary of minerals at high pressure and temperature to determine the critical shock pressure where the decomposition occurs on Hugoniot. However, this is difficult because, in general, the temperature region of the phase diagrams of minerals reported so far was limited under ~2000 K. Therefore, we need to determine the decomposition boundaries at high-temperature (and high-pressure) region.

In this study, we experimentally determined the decomposition boundaries of $CaCO_3$. $CaCO_3$ is one of the most important minerals for impact-induced degassing and evolution of the terrestrial environment. It has been known that $CaCO_3$ decomposes into CaO and CO_2 at high temperature region.

Experiments: In this study, we used a technique of laser-heated diamond-anvil cell (LHDAC) to determine the decomposition boundary of $CaCO_3$ at high-pressure and -temperature regions.

LHDAC is the static compression device which can produce high-pressure and high-temperature conditions up to several gigapascal and several thousand degrees kelvin. LHDAC has been usually used to study the structures of Earth and planetary interiors. However, in this study, we apply this technique to investigate impact phenomenon characterized by dynamic compression. It may seem to be inadequate that we use the static compression method to investigate dynamic phenomenon. However, it has been known that the duration of pressure loading in planetary-scale impact is second-order, which is much longer than the typical reaction time of chemical reactions. Thus, we consider that the static compression method can be applied to study planetary-scale impact phenomena.

First, we pressurized $CaCO_3$ up to some pressure with diamond-anvil cell (DAC). Then, the sample within DAC was heated by CO_2 laser irradiation through the diamond anvil. Temperature under laser irradiation was measured by spectroradiometry. After heating, we analyzed the recovered sample by Raman spectroscopy to identify CO_2, which is one of the decomposition products of $CaCO_3$. If CO_2 exists, it means that decomposition of $CaCO_3$ occurs.

Results and discussion: The results of LHDAC experiments and the decomposition boundary of $CaCO_3$ determined from those data are shown in Figure 1. We determined the decomposition boundary of $CaCO_3$ up to ~10 GPa and ~5000 K, which is the upper-limit temperature of the LHDAC experimental system used in this study.

Figure 2 compares the decomposition boundary of $CaCO_3$ determined in this study with that estimated in the previous studies. The decomposition boundaries at high-pressure and -temperature regions have been estimated only theoretically so far [6, 7]. However, these estimations may not give any reliable decomposition boundary because thermodynamic properties of treated species (i.e., $CaCO_3$, CaO, and CO_2) at such pressure and temperature regions were not known well. These estimated decomposition boundaries suggest that the decomposition temperature never exceed 4000 K even at 80 GPa. However, our data suggests that the decomposition boundary locates at lower-pressure and higher-temperature regions than that estimated in the previous studies: The decomposition does not occur even at ~5000 K at ~10 GPa. This means that $CaCO_3$ is more stable against decomposition at high-pressure region than previously thought.

The result of this study indicates that the pressure at the intersection between the Hugoniot and the decomposition boundary of $CaCO_3$ is at least ~115 GPa, which is much higher than both that determined by using theoretically estimated decomposition boundary [6, 7] (i.e., ~85-90 GPa) and the complete decomposition pressure assumed in the previous numerical simulations of impact [2, 8] (i.e., 20 GPa and 70 GPa) (Figure 2). This means that much higher pressures are required for the intensive degassing. Thus, the amount of degassed CO_2 may be much smaller than that previously estimated.

Degassed CO_2 is thought to have affected the surface environment of terrestrial planets. For example, the global warming due to the greenhouse effect of CO_2 is one of the advocated hypotheses that explain the mass extinction at the Cretaceous-Palaeogene (K-P) boundary ~65 Ma [e.g., 1, 2]. However, the result of this study suggests that the global warming caused by impact-induced degassing of CO_2 may have little effect on the mass extinction at K-P boundary.

The results of LHDAC experiments also show that the liquid field of the phase diagram of $CaCO_3$ extends up to at least ~5000 K since the lower-pressure side of the decomposition boundary is the liquid field. This suggests that a large amount of $CaCO_3$ melt is potentially produced when impact on $CaCO_3$-rich target occurs. This is consistent with the results of recent geological analysis of crater deposits [e.g., 9, 10].

References: [1] O'Keefe J. D. and Ahrens T. J. (1989) *Nature 388*, 247-249. [2] Pierazzo E. et al. (1998) *JGR 103*, 28607-28625. [3] Matsui T. and Abe Y. (1986) *Nature 319*, 303-305. [4] Tyburczy J. A. and Ahrens T. J. (1986) *JGR 91*, 4730-4744. [5] Ivanov B. A. and Deutsch A. (2002) *Phys. Earth Planet. Inter. 129*, 131-143. [6] Bobrovskii S. V. et al. (1976) *Journal of Mining Science 12*, 273-279. [7] Martinez I. et al. (1995) *JGR 100*, 15465-15476. [8] Pope K. O. et al. (1997) *JGR 102*, 21645-21664. [9] Graup G. (1999) *Meteor. Planet. Sci. 34*, 425-438. [10] Osinski G. R. and Spray J. G. (2001) *Earth Planet. Sci. Lett. 194*, 17-29.

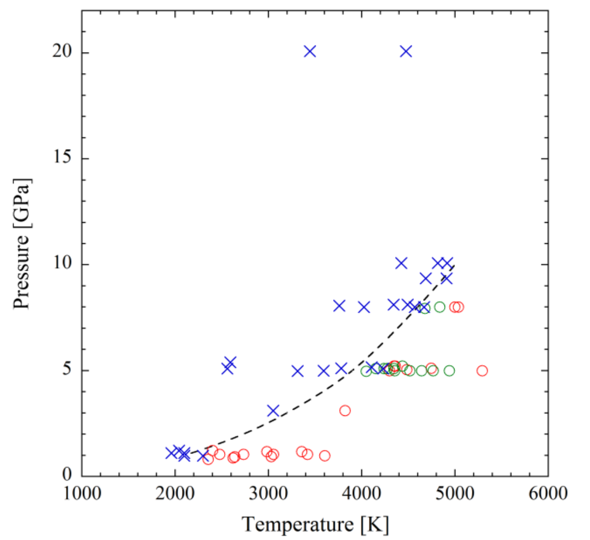

Figure 1: The results of LHDAC experiments on decomposition of $CaCO_3$. ○ (red circle): $CaCO_3$ decomposes (CO_2 is detected by the Raman spectroscopic measurement). ○ (green circle): $CaCO_3$ decomposes (judging only by texture). × (blue cross): $CaCO_3$ does not decompose. The broken line represents decomposition boundary of $CaCO_3$.

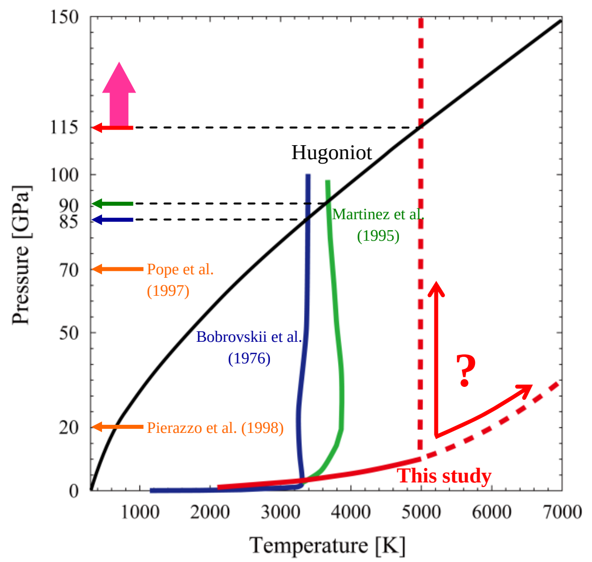

Figure 2: The decomposition boundary and the Hugoniot of $CaCO_3$. The blue line and the green line are theoretically estimated decomposition boundaries. The red line is the experimentally determined decomposition boundary by this study. The decomposition boundary was determined up to ~5000 K, which is the upper-limit temperature of the LHDAC experimental system used in this study. Even though the decomposition boundary goes upward sharply from the highest-pressure and temperature point (i.e., ~10 GPa and ~5000 K), the pressure at the intersection between the Hugoniot and the decomposition boundary might be ~115 GPa. If the pressure of the decomposition boundary rises more moderately against temperature, the Hugoniot decomposition pressure becomes higher. These pressures are much higher than those determined using the theoretically estimated decomposition boundaries (~85 GPa and ~90 GPa) and the complete degassing pressure assumed in the numerical simulations of Chicxulub impact (20 GPa and 70 GPa).