

## 論文内容の要旨

論文題目:

An experimental study on decomposition of  $\text{CaCO}_3$  at high pressure and high temperature using laser-heated diamond-anvil cell: Implication to impact-induced degassing of  $\text{CO}_2$  from carbonate

〔レーザー加熱式ダイヤモンドアンビル装置を用いた高圧・高温下における  $\text{CaCO}_3$  の分解  
の実験的研究: 炭酸塩からの  $\text{CO}_2$  の衝突脱ガスへの応用〕

氏名 石橋 高

Hypervelocity impact is one of the most common and important in 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 from surface and/or impactor are released due to high pressure and temperature states caused by passage of intense shock waves. This has been called the “impact-induced degassing”. Degassed components (e.g.,  $\text{CO}_2$  from carbonate, S-bearing gases from sulfate, and so on) 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). The goal of this thesis is to understand the degassing mechanism at high shock pressure regions where the previous studies were not able to discuss intensively.

There have been many studies on impact-induced degassing. The degassing mechanism has been theoretically discussed and experimentally assessed. However, the shock pressures treated in these studies so far were relatively low ( $< \sim 70$  GPa). This is because breaking-up of sample container makes the experiments at higher-shock pressure regions difficult. In addition, the theoretical studies were not able to treat high-shock pressure regions because the assumption of conventional model may not be applicable to those regions. Thus, there has been discussed so far almost only the shock pressure required for “incipient decomposition” (i.e., beginning of degassing). Thus, impact-induced degassing at high-shock pressure region is not understood

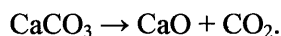
well.

The degassing mechanism may change from the conventional view on impact-induced degassing at adequately high-shock pressure. In the conventional model, it has been assumed that the minerals do not decompose at the moment when the shock wave passes but decompose after the pressure release. However, if the shock pressure is high enough, minerals might decompose even on Hugoniot (i.e., decompose at the compressed state before pressure release). This type of decomposition might lead intensive degassing because it does not require appropriate pressure release that the conventional mechanism requires. Thus, it is essential for the impact-induced degassing to study this new mechanism.

The change in degassing mechanism might occur when the thermodynamic state on Hugoniot becomes to satisfy the decomposition condition of minerals. That is, the shock pressure and temperature exceed the decomposition boundary of minerals on their  $P$ - $T$  phase diagrams. Thus, 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, in general, this is difficult because the temperature region of the phase diagrams of minerals reported so far was limited under  $\sim 2500$  K. This is much less than the temperature achieved in planetary impacts, which is more than several thousand degrees kelvin. The phase diagrams were mainly used for the studies in the Earth's interior. The temperature at core-mantle boundary is estimated to be  $\sim 3000$  K. Then, the phase diagrams over 3000 K are not necessary as long as we discuss the Earth's mantle. Therefore, we need to determine the decomposition boundaries at high-temperature (and pressure) region to study the impact-induced degassing mechanism.

In this study, therefore, first, we developed a new method to estimate the temperature and determined the decomposition boundaries of  $\text{CaCO}_3$  by using laser-heated diamond-anvil cell (LHDAC). Then, we discussed the mechanism of impact-induced degassing of  $\text{CO}_2$  from  $\text{CaCO}_3$ .  $\text{CaCO}_3$  is one of the most important minerals for impact-induced degassing and evolution of the terrestrial environment. It has been known that  $\text{CaCO}_3$  decomposes at high temperature region:



The decomposition boundary was experimentally determined for the regions on its  $P$ - $T$  phase diagram lower than  $\sim 100$  bar and  $\sim 1700$  K. The decomposition boundaries theoretically estimated suggest that the decomposition temperature never exceed 4000 K even at 80 GPa. However, such estimates are based on unreasonable assumptions.

This thesis consists of three parts. In Part I, first we briefly explain the temperature

measurement system and point out the problems of the method of temperature measurement in LHDAC experiments. Then, we propose more reliable temperature determination than before from the data with errors due to chromatic aberration. In Part II, we show the results of determination of the decomposition boundary of  $\text{CaCO}_3$  at high-pressure and high-temperature region. Finally, in Part III, we discuss the impact-induced degassing of  $\text{CO}_2$  from  $\text{CaCO}_3$  by using the decomposition boundary newly determined in this study.

The main results are summarized as follows In Part I, we proposed a new method of temperature measurement in LHDAC experiments in which the chromatic aberration is effective. One of the most important issues in LHDAC experiments is to estimate a reliable temperature. However, it has been known that use of refractive optics results in the problem of chromatic aberration if we measure the temperature by spectroradiometry, which is a typical temperature measurement method in LHDAC system. Therefore, we presented a new method to determine more reasonable temperature from the data obtained in the experimental system using refractive optics. We determined temperatures by the combination of spectroradiometric method and the method that uses spectral intensity.

The advantage of this method is to use the spectral intensity at the focusing wavelength (630 nm for our experimental system) where the spectral intensity is a close to real one even though the chromatic aberration is effective. We found that the temperatures measured by spectroradiometry in high-radiance region are reliable because the chromatic aberration is not effective in this region. Thus, the high-radiance-region temperatures are fitted to the theoretical intensity-temperature relation for the 630-nm-wavelength light. Then, that relation is extrapolated to the low-radiance region. The temperatures in the low-radiance region were estimated by substituting the intensity at 630 nm to the extrapolated intensity-temperature relation.

In Part II, we developed the experimental method to determine the decomposition boundary of  $\text{CaCO}_3$  at high temperature and high pressure region.  $\text{CaCO}_3$  samples were pressurized and heated with LHDAC and were quenched. Temperatures were estimated by the method proposed in Part I. Then, the recovered quenched samples were analyzed with Raman spectroscopy and energy-dispersive X-ray spectroscopy (EDS) to identify  $\text{CO}_2$  and/or  $\text{CaO}$  that are the products of decomposition of  $\text{CaCO}_3$ . We determined the decomposition boundary of  $\text{CaCO}_3$  up to  $\sim 10$  GPa and  $\sim 5000$  K. In the previous studies the decomposition boundary was experimentally determined for the region lower than  $\sim 100$  bar and  $\sim 1700$  K. The theoretical estimations of the decomposition boundary suggested that it never exceed 4000 K even at  $\sim 80$  GPa. However, our experimental data suggest that the decomposition boundary locates lower-pressure and higher-temperature regions and that the decomposition does not occur even

at ~5000 K and ~10 GPa. This means that  $\text{CaCO}_3$  is more stable against decomposition than previously thought.

In Part III, we discussed (i) the impact-induced degassing of  $\text{CO}_2$  from  $\text{CaCO}_3$  target at high-shock pressure region and (ii) impact induced  $\text{CaCO}_3$  melt generation using the results described in Part II.

We estimated the “Hugoniot decomposition pressure”, which we define as the pressure on the intersecting point of Hugoniot with the decomposition boundary. Intensive degassing may occur above this pressure. The results indicate that the Hugoniot decomposition pressure is over ~115 GPa, which is much higher than the assumed pressure for complete decomposition in the previous studies (20-30 GPa). This indicates that much higher shock pressure is required for intensive degassing to occur than previously thought. Thus, the amount of degassed  $\text{CO}_2$  may be much smaller than that previously estimated. In the case of Chicxulub impact, the amount of degassed  $\text{CO}_2$  may be almost one order smaller than that previously estimated. Thus, the global warming caused by impact-induced degassing of  $\text{CO}_2$  may have little effect on the mass extinction at the Cretaceous-Paleogene (K-P) boundary.

The results of LHDAC experiments also show that the liquid field of the phase diagram of  $\text{CaCO}_3$  extends up to at least ~5000 K. This suggests that a large amount of  $\text{CaCO}_3$  melt is potentially produced when impacts on  $\text{CaCO}_3$ -rich target occurs. This is consistent with the results of recent geological analysis of crater deposits.

The decomposition boundary of  $\text{CaCO}_3$  at high-temperature and pressure regions was experimentally determined for the first time. This makes it possible to discuss the impact-induced degassing of  $\text{CO}_2$  from  $\text{CaCO}_3$  at high-shock pressure. The experimental method developed in this study may be applicable to other important minerals for impact-induced degassing, such as sulfate, which is thought to play an important role in the mass extinction at Cretaceous-Paleogene boundary.