

AN EXPERIMENTAL STUDY OF SHOCK-INDUCED DEVOLATILIZATION OF CALCITE: DEPENDENCE ON THE AMBIENT PRESSURE. S. Ohno¹, K. Ishibashi¹, T. Sekine², K. Kurosawa¹, T. Kobayashi³, S. Sugita⁴ and T. Matsui¹, ¹Planetary Exploration Research Center, Chiba Institute of Technology (2-17-1 Tsudanuma, Narashino, 275-0016 Chiba, Japan, ohno@perc.it-chiba.ac.jp). ²Hiroshima University, 1-3-1 Kagamiyama, Higashihiroshima, Hiroshima, Japan. ³National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki, Japan. ⁴University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba, Japan.

Introduction: Shock-induced devolatilization of minerals caused by hypervelocity impacts has played important roles in the formation of the atmosphere of terrestrial planets and the evolution of Earth's surface environment [e.g., 1]. In particular, the shock-induced devolatilization of carbonates is a key to understanding the killing mechanism of the mass extinction at the end of Cretaceous [e.g., 2].

Many experimental studies have focused on shock-induced devolatilization. Shock recovery of solid remnants using tightly enclosed sample containers [e.g., 3] and Hugoniot measurements [e.g., 4] are the typical experimental methods used to study shock-induced devolatilization. These studies have shown from Hugoniot measurements the degree of shock-induced devolatilization as a function of peak shock pressures. Recently, experimental methods for direct analysis of shock-induced gas release in open systems have been developed [5-7]. The results of these studies have shown that devolatilization during pressure release is significant and has important geological implications.

One of the most important parameters to consider in relation to devolatilization during pressure release is specific volume. Ivanov and Deutch [8] calculated the specific volume of CaCO₃, CaO + CO₂, and their mixtures on a CaCO₃ decomposition curve. They showed that the degree of decomposition is strongly dependent on the specific volume. Therefore, if shock-induced devolatilization occurs during pressure release, the degree of devolatilization largely depends on the volume of free space available for released gas. A systematic study of the relationship between the volume of free space for released gas and the degree of devolatilization is required to better understand the devolatilization process. In this study, we constrain the dependence of the degree of shock devolatilization on the volume of free space, in order to confirm that devolatilization occurs during pressure release.

Experimental Methods: We conducted shock recovery experiments of gas released from CaCO₃ using newly designed sample containers and a propellant gun at the National Institute for Materials Science (NIMS), Japan. Figure 1 shows the structure of the sample container, which has an internal gas chamber of variable volume. We sealed the target sample material and ambient N₂ gas in the sample container before the experi-

mental shot. A cylindrical stainless steel impactor plate was accelerated using the propellant gun to create a plane shock wave to compress the target sample material. After the shot, the mixture of ambient N₂ gas and shock-induced vapor released from the target material were introduced through a variable leak valve into a quadrupole mass spectrometer (QMS) and analyzed. During the QMS measurements, the QMS was differentially evacuated using a turbomolecular vacuum pump. We used pure Ca¹³CO₃ powder as the target sample material. Isotopically doped calcite was used to distinguish between ambient N₂ and shock-induced carbon monoxide gas during QMS analysis. We conducted a total of seven shots, as well as additional blank shots for QMS analysis. The impact velocity was set to 1.6 km/s and we varied the mass of Ca¹³CO₃ and volume of free space in the sample container. The peak shock pressure and temperature were respectively estimated to be 14 GPa and 980 K based on a one-dimensional impedance match solution including the effects of sample porosity and the Mie-Grüneisen thermal relation [9,10].

Results: Figure 1 shows an example of the mass spectrum of the mixture of ambient N₂ and shock-induced vapor released from the target material obtained by the QMS. The signal of mass number 28 is derived from the ambient N₂ gas sealed in the sample container before the experimental shot. The signals of an air component, such as O₂⁺ (mass number 32) and Ar⁺ (mass number 40), are much smaller than those of shock-induced gases released from Ca¹³CO₃, such as ¹³CO⁺ (mass number 29) and ¹³CO₂⁺ (mass number 45). This implies that air leak into the container during the experiments was negligible.

We calculated the (¹³CO + ¹³CO₂)/N₂ molar ratio from the QMS current of each experimental shot and from sensitivity data for the QMS. We introduced standard gas and air into the QMS to determine the sensitivity of the QMS. Details of the sensitivity determination methods are described in Ohno et al. [11]. The moles of devolatilized Ca¹³CO₃ (i.e., moles of released (¹³CO + ¹³CO₂) gas) were calculated from the (¹³CO + ¹³CO₂)/N₂ molar ratio of each experimental shot.

Figure 2 shows the mass of devolatilized Ca¹³CO₃ in each experimental shot as a function of the volume

of free space in the sample containers. The experimental results clearly indicate that the mass of devolatilized $\text{Ca}^{13}\text{CO}_3$ and the degree of devolatilization monotonically increase as the volume of free space increases. This strongly suggests that the mass of devolatilized $\text{Ca}^{13}\text{CO}_3$ is primarily determined by the volume of free space at a given peak shock pressure and not by the initial sample mass.

Discussion: The mass of dissolved $\text{Ca}^{13}\text{CO}_3$ may not only be dependent on the volume of free space in the sample containers, as phase diagram considerations also support the occurrence of devolatilization during pressure release. CaCO_3 is more stable than ($\text{CaO} + \text{CO}_2$) under the estimated pressure and temperature conditions of shock compression (14 GPa and 980 K, respectively), assuming chemical equilibrium [e.g., 8]. Therefore, devolatilization reactions during the shock compression stage are not plausible under the experimental conditions of this study. However, the pressure and temperature conditions during pressure release would have passed through the CaCO_3 decomposition curve and permitted effective devolatilization reactions. We conclude that our experimental results indicate that devolatilization occurs during pressure release.

Our results suggest that the degree of shock-induced devolatilization is controlled by the efficiency with which released gas can escape, and further imply that the degree of devolatilization depends on the location in the impact cratering process. Devolatilization would occur relatively easily in the impactor and ejecta regions because of the large free space present. In contrast, the degree of devolatilization in the compressive region would be relatively low because shock-induced gas does not have sufficient free space to expand and escape. The escape efficiency of the released gas is important for understanding large-scale impact events, such as the Cretaceous–Paleogene impact event, because shock-induced gas will not easily escape from great depths.

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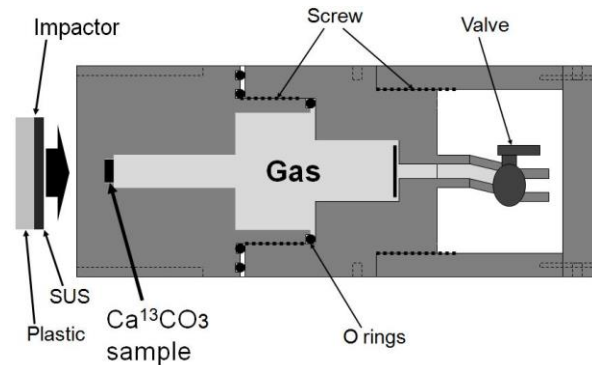


Figure 1. Schematic of the newly designed sample container for the shock-induced gas recovery experiments in this study.

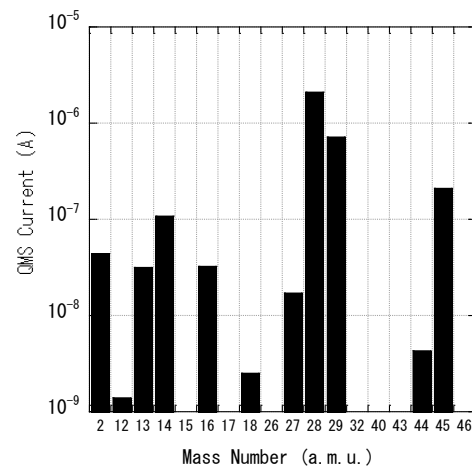


Figure 2. An example of the mass spectrum of a sample gas measured by quadrupole mass spectrometer (QMS).

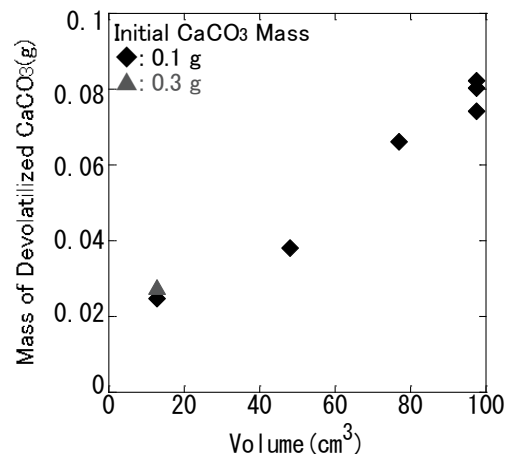


Figure 3. Mass of devolatilized $\text{Ca}^{13}\text{CO}_3$ in each experiment as a function of the volume of free space in the sample containers. Black circles indicate the results of experimental shots with 0.1 g of initial $\text{Ca}^{13}\text{CO}_3$. The gray triangle indicates the result of the experimental shot with 0.3 g of initial $\text{Ca}^{13}\text{CO}_3$.