Gas recovery experiments to determine the degree of shock-induced devolatilization of calcite

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Abstract. Shock-induced devolatilization of volatile-bearing minerals has played an important role in the formation of the atmosphere and evolution of surface environments of terrestrial planets. The dependence of the degree of devolatilization on ambient pressure has not been investigated in detail before, even though ambient pressure dramatically affects the degree of devolatilization. In this study, we conducted shock recovery experiments on calcite (CaCO₃) using newly designed sample containers for released gas analysis, and assessed the dependence of the degree of devolatilization on the partial pressure of CO₂. Our results clearly show that the degree of devolatilization increases as the sample container volume increases and the initial mass of calcite decreases.

1. Introduction

Earth and other planets in the solar system have experienced many hypervelocity impact events. During such an impact, the temperature of materials in the impactor and target rocks is raised and volatiles in minerals are released from the rock as gas. This shock-induced devolatilization of minerals caused by hypervelocity impacts has played an important role in the formation of the atmosphere of terrestrial planets and the evolution of Earth’s surface environment e.g., [1]. In particular, the devolatilization of carbonates is a key to understanding what drove the mass extinction at the end of the 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 and showed that the degree of decomposition is strongly dependent on the specific volume. For example, at normal pressure (1 bar = 0.0001 GPa), 1% decomposition requires a specific volume 25 times larger than solid CaCO₃ and complete decomposition requires a specific volume 2,500 times larger than solid CaCO₃. 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.

2. 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 is made from Type 304 stainless steel and has an internal gas chamber of variable volume. We sealed the target sample material and ambient N₂ gas in the sample container before the experimental shot. A cylindrical Type 304 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 turbo molecular vacuum pump.

We used pure Ca¹³CO₃ powder as the target sample material (porosity ~0.2). 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. We determine the shock pressure using the planar impact approximation (AKA impedance matching) and Hugoniot data of calcite (initial density = 2.670 g/cm³) [9] and SS-304 (initial density = 7.90 g/cm³) [10]. We also determine determined the shock temperature using Mie-Gruneisen parameter [10]. The peak shock pressure and temperature were respectively estimated to be 14 GPa and 980 K. The parameters of the different experimental shots are summarized in table 1.

![Figure 1](image-url)
Table 1. Experimental shots conducted in this study.

| Shot  | Mass of initial Ca$^{13}$CO$_3$ (g) | Volume of free space (cm$^3$) | Mass of devolatilized Ca$^{13}$CO$_3$ (g) | Impact velocity (km/s) |
|-------|---------------------------------|-------------------------------|------------------------------------------|-----------------------|
| Shot 1 | 0.10                            | 13                            | 0.025                                    | 1.638 ± 0.009         |
| Shot 2 | 0.30                            | 13                            | 0.028                                    | 1.648 ± 0.006         |
| Shot 3 | 0.10                            | 48                            | 0.038                                    | 1.617 ± 0.007         |
| Shot 4 | 0.10                            | 76                            | 0.066                                    | 1.591 ± 0.006         |
| Shot 5 | 0.10                            | 96                            | 0.082                                    | 1.697 ± 0.009         |
| Shot 6 | 0.10                            | 96                            | 0.074                                    | 1.606 ± 0.006         |
| Shot 7 | 0.10                            | 96                            | 0.080                                    | 1.627 ± 0.006         |

3. Experimental results

Figure 2 shows an example of the mass spectrum of the mixture of ambient N$_2$ and shock-induced vapor released from the target material obtained by the QMS. The signal of mass number 28 is derived from the ambient N$_2$ gas sealed in the sample container before the experimental shot. The signals of an air component, such as O$_2$ (mass number 32) and Ar$^+$ (mass number 40), are much smaller than those of shock-induced gases released from Ca$^{13}$CO$_3$, such as $^{13}$CO$^+$ (mass number 29) and $^{13}$CO$_2$ (mass number 45). This implies that air leak into the container during the experiments was negligible.

We calculated the ($^{13}$CO + $^{13}$CO$_2$)/N$_2$ 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 determinations are described in Ohno et al. [11].

The moles of devolatilized Ca$^{13}$CO$_3$ (i.e., moles of released ($^{13}$CO + $^{13}$CO$_2$) gas) were calculated from the ($^{13}$CO + $^{13}$CO$_2$)/N$_2$ molar ratio of each experimental shot.

Figure 3 shows the mass of devolatilized Ca$^{13}$CO$_3$ 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 Ca$^{13}$CO$_3$ and the degree of devolatilization monotonically increase as the volume of free space increases. In addition, the difference in the mass of devolatilized Ca$^{13}$CO$_3$ between experimental shots 1 and 2 is much smaller than the dependence of the mass of devolatilized Ca$^{13}$CO$_3$ on the volume of free space. This strongly suggests that the mass of devolatilized Ca$^{13}$CO$_3$ is primarily determined by the volume of free space and not by the initial sample mass.

Figure 2. Mass spectrum of a sample gas measured by quadrupole mass spectrometer (QMS).
Figure 3. Mass of devolatilized Ca\textsuperscript{13}CO\textsubscript{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 Ca\textsuperscript{13}CO\textsubscript{3}. The gray triangle indicates the result of the experimental shot with 0.3 g of initial Ca\textsuperscript{13}CO\textsubscript{3}. The peak shock pressure and temperature estimated assuming 1D impedance matching method [e.g., 9] and using Mie-Gruneisen parameter [e.g., 11] are 14 GPa and 980 K.

4. Discussion
The mass of dissolved Ca\textsuperscript{13}CO\textsubscript{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\textsubscript{3} is more stable than CaO + CO\textsubscript{2} at 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\textsubscript{3} decomposition curve and permitted effective devolatilization reactions. Devolatilization during pressure release would be required to explain the high degree of devolatilization in experimental shots 5, 6, and 7 (~80%). 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.

5. Summary
We have conducted shock recovery experiments of gas released from Ca\textsuperscript{13}CO\textsubscript{3} using a newly designed sample container and a propellant gun. The mass of dissolved Ca\textsuperscript{13}CO\textsubscript{3} monotonically increases as the volume of free space increases. Our study strongly suggests that devolatilization takes place during pressure release. The escape efficiency of the released gas is important in understanding large-scale impact events and their effect on the environmental.

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