IMPACT DEVOLATILIZATION OF CALCITE: DIRECT MEASUREMENTS USING A LASER GUN.
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Introduction: Devolatilization of minerals caused by hypervelocity impacts has played an important role in atmosphere formation [e.g., 1] and the evolution of surface environments, such as the K/T event [e.g., 2]. Many experimental studies have focused on impact-devolatilization. However, the physical and chemical mechanisms of the devolatilization process have not been studied extensively and no scaling laws regarding impact-devolatilization have yet been established. This is mainly due to experimental difficulties.

Direct observation of the released gas by impact-induced devolatilization solves the experimental problems such as the reflection of shock waves and high ambient partial pressures after the shock compression. Here we report a new experimental method to observe impact-induced devolatilization of rock directly by gas analysis using a laser gun and a quadrupole mass spectrometer (QMS). Observation using a QMS is suitable for impact-induced devolatilization experiments, similar to the study by Sugi et al. [3] of impact-vaporization of ice. We used a laser gun for this study to avoid contamination by soot and gun debris. In this study, we used crystalline calcite ($CaCO_3$) as targets, observed devolatilization of calcite, and determined the shock pressure required for devolatilization.

Methods: The configuration of our experimental system is shown in Fig 1. We set a thin metal foil as a flyer and a rock sample in the vacuum chamber. Then, we irradiate a laser pulse on the metal foil in the chamber. The laser pulse vaporizes the surface of the metal foil and generates a vapor plume. The flyer is then accelerated by the reaction of the expanding vapor plume. The gas released by the impact is measured using a QMS. No reflectance shock wave is generated in this study because the flyer is much smaller and thinner than the rock sample. For devolatilization experiments, we use copper sheet flyers with thickness of 5 μm and 10 μm and gold sheet flyers with thickness of 2.5 μm and 10 μm. Target samples are single crystal calcite. Laser beam diameter is ~800 μm and laser shot energy is ~35 - 44 J. Shock pressures are calculated using a one-dimensional impedance match solution [4]. The shock pressures range from 24.4 GPa to 68.6 GPa.

Results: We estimate the degree of devolatilization of calcite from the amount of CO_2 released in each shot. The degree of devolatilization is determined as the molar ratio of the amount of released CO_2 to amount of shock compressed calcite. Figure 2 shows that the degree of devolatilization is approximately unity in all the shots with shock pressures higher than ~30 GPa, although the error is somewhat large. On the other hand, the degree of devolatilization is as small as ~0.1 in the shot with ~25 GPa in shock pressure. These results also indicate that the degree of devolatilization increases steeply at pressures between ~25 GPa and ~30 GPa.

The results show that the degree of devolatilization is approximately unity at shock pressures higher than ~34 GPa, independent of the flyer metal composition. This suggests that devolatilization of calcite occurs completely in the isobaric region at very near from the impact surface on these shots. In this study, complete devolatilization of calcite requires shock pressure higher than 33.9 ± 4.6 GPa. The shot using a 10 μm thickness gold flyer results in the degree of devolatilization of ~0.1. Partial devolatilization is likely to have occurred in this shot. This indicates that 24.9 ± 2.6 GPa is the upper limit of the incipient shock pressure and the lower limit of the complete shock pressure for devolatilization.

We also carried out "background shots" using gold sheet flyers and copper sheet flyers. We used Pyrex glass substitute for calcite sample for the background shots and other conditions were the same as the calcite shots. The background components were subtracted from the each result of the calcite shots.

Degassed CO_2 (mass number 44) from calcite was analyzed in each of the experimental runs of this study. The net reaction during the devolatilization of calcite in this study is

$CaCO_3 \rightarrow CaO$ (solid) + CO_2 (gas).

Discussions: The shock pressures for devolatilization estimated in this study are lower than the incipient and complete devolatilization shock pressures estimated by many recent experimental studies such as shock recovery experiments and observations of shock compression. The incipient and complete devolatilization shock pressures estimated by shock recovery experiments are ~10 GPa and ~70 GPa [5] and 30-35 GPa and ~45 GPa [6]. Boslough et al. [7] suggests devolatilization of calcite may occur at less than ~30

GPa. A more recent study [8] shows that the incipient and complete shock pressure for Devolatilization of dolomite is ~60 and ~70 GPa. Most of these estimates are higher than that of this study except for the incipient shock pressure by Lange and Ahrens [5]. This difference may be derived from the influence of sample containers used in the previous shock recovery experiments which experience reflectance shock waves and high ambient pressures.

The low shock pressures obtained in this study strongly suggests devolatilization during the pressure release process. Shock pressures required for the complete devolatilization of calcite along Hugoniot have been estimated by real time observations [e.g., Gupta et al. [9] (~110 ±10 GPa) and Yang et al. [10] (103 ±12 GPa)]. These values are also significantly higher than the estimate in this study. This is because the devolatilization occurs during pressure release, although Gupta et al. [9] and Yang et al. [10] observed decomposition along the Hugoniot. Gupta et al. [9] also discussed the possibility that devolatilization during pressure release generates the difference between their estimate and that of Gupta et al. [11], i.e., 17.8 ±2.9 GPa for incipient and 54.1 ±5.3 GPa for complete. A recent study [12] also suggests that pressure release process is important to devolatilization, based on their re-evaluation of the shock experiments data and the phase diagram of calcite.

The low shock pressure required for devolatilization of calcite obtained in this study strongly suggests that a large amount of CO_2 gas was released by impacts on carbonate-bearing sites. Estimates of released CO_2 mass by the K/T impact strongly depend on the shock pressure required for devolatilization. For ~10 km diameter impactor, an estimate assuming 10 GPa for devolatilization shock pressure results in 10^4 to 10^5 Gt of CO_2 [13], an estimate assuming 20 GPa results in 880 to 2960 Gt [14], and an estimate assuming 30 GPa results in ~220 Gt [15]. Note that these studies take into consider the effect of porosity and use lower devolatilization shock pressure than that of crystal calcite. More CO_2 release results in a more severe green house effect.

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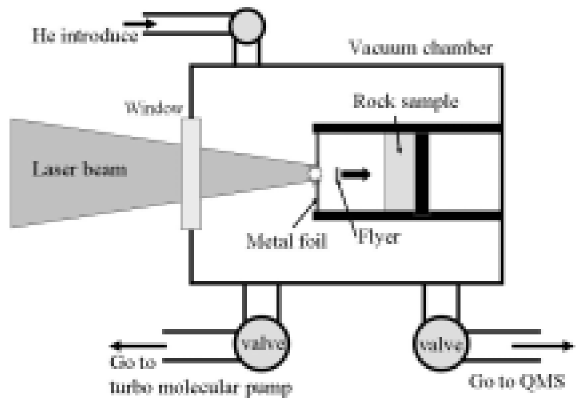

Figure 1. Configuration of experimental equipments. A laser pulse is irradiated into a vacuum chamber and vaporizes the surface of a metal sheet. The metal sheet is accelerated by the metal vapor and impacts on the target sample. Gas released by the impact is analyzed by a QMS.

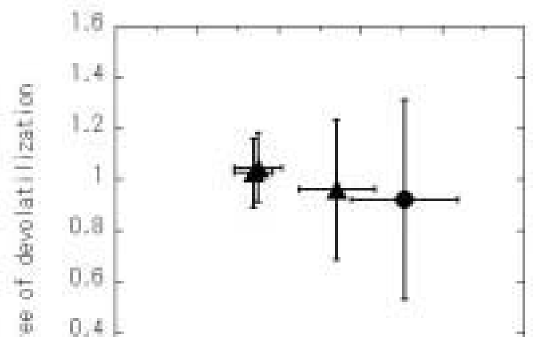

Figure 2. The degree of devolatilization of calcite as a function of shock pressure. Triangles are the results using copper sheets and spots are the results using gold flyers. The error in the degree of devolatilization derives from the error in the amount of released CO_2 and the error in shock pressure derives from the error in the impact velocity.