EXPERIMENTAL STUDY OF SO_3/SO_2 RATIO IN IMPACT VAPOR CLOUDS USING A HIGH-SPEED LASER GUN. S. Ohno[1], T. Kadono[2], K. Kurosawa[3], T. Hamura[3], T. Sakaiya[4], S. Sugita[3], K. Shigemori[2], Y. Hironaka[2], T. Watari[2], and T. Matsui[1], [1]Planetary Exploration Research Center, Chiba Institute of technology (PERC/Chitech) (ohno@perc.it-chiba.ac.jp, 2-17-1 Tsudanuma, Narashino, 275-0016 Chiba, Japan), [2]Institute of Laser Engineering, Osaka University, [3]The Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, University of Tokyo, [4]Department of Earth and Space Science, Graduate School of Science, Osaka University.

Introduction: A large impact is widely accepted as the cause of the mass extinction at the K-Pg boundary [e.g., 1, 2]. However, the mechanism of the environmental perturbation caused by the impact and the killing mechanism of the mass extinction are still controversy. Some previous studies have shown the importance of sulfuric oxide gasses which were released from the S-rich sediments of the Chicxulub impact site [e.g., 3].

SO_3/SO_2 ratio of the impact vapor cloud is a key parameter to assess the mechanism and influence of the environmental perturbation caused by the impact-induced sulfur oxides: The residence time of sulfuric acid aerosol in the stratosphere changes dramatically depending on the SO_3/SO_2 ratio [4]. If the released sulfur oxides were dominated by SO_3, the estimated residence time of the released sulfur in the atmosphere is very short and intense acid rain would have acidified oceanic surface layer significantly [5]. On the other hand, if the released sulfur oxides were dominated by SO_2, the residence time was longer than that of SO_3 and sunlight blockage and cooling caused by sulfuric acid aerosol could have worked [6].

Despite its geologic importance, no previous experimental studies observed chemical composition of actual impact vapor clouds of anhydrite, because of experimental difficulty. Some previous studies have tried to estimate the SO_3/SO_2 ratio in impact vapor clouds using their experimental results of laser-simulated impact vapor clouds [4, 7]. They suggest that the sulfur oxides in the K-Pg impact vapor cloud have been dominated by SO_3, not SO_2. However, direct application of their experimental results to impact vapor clouds are difficult because of the poor understandings of equation of state and chemical reaction rates in high temperature and pressure vapor clouds. Some recent studies show that a combinational method of laser gun experiments and direct gas analysis is applicable for the impact-induced vaporization experiments [e.g., 8]. In this study, we experimentally created impact-induced vapor plume of sulfate and analyzed the chemical composition.

Experimental Methods: Figure 1 is a schematic diagram of the experimental setup. We accelerate metal flyer foil using a large powered and high speed laser gun (GEKKO XII-HIPER facility of Institute of Laser Engineering of Osaka University. Detail of the facility is described by Kadono et al. [9].). The flyer and target sample are set in a large vacuum chamber and low pressure condition ($<10^{-3}$ mbar). We irradiated a laser pulse (1054nm, 10-20ns, ~1 kJ) on a 50 μm-thick plastic ablator, which is set in front of a 30 μm-thick tantalum flyer. The ablator is vaporized by the laser pulse and the generated high temperature vapor accelerates the flyer to ~14 to 25 km/s. The flyer impacts on the anhydrite ($CaSO_4$) target rock. The anhydrite target is vaporized by the impact, because the peak pressure is much higher than the vaporization threshold of anhydrite [e.g., 10]. A 200 μm-thick gold spacer is set between the flyer and the anhydrite target.

The chemical compositions of the impact-induced vapor plumes were measured directly using a quadrupole mass spectrometer (QMS). We introduce the released S-bearing gas to the QMS through a SUS inhalation tube. We use an aluminum hollow sphere in order to avoid dispersion of the released gas to the vacuum chamber and to improve the S/N ratio of the QMS analysis.

Experimental Results: Figure 2a shows an example of time series data of the QMS measurements. We observed significant amount of sulfur oxides released by the foil impact. The blank level, the QMS currents before the impact, is much lower than the QMS current values of the impact-induced sulfur oxide gasses. Figure 2b shows an example of integrated QMS Currents of one experimental run. The ratio of mass number 49/48, 50/48, 65/64, 66/64, 81/80, and 82/80 are consistent with the terrestrial isotopic ratios of sulfuric oxides. This consistency indicates that these signals are derived from the released sulfur oxides. Figure 3 shows the SO_3/SO_2 ratio in impact vapor clouds observed in this study as a function of peak shock pressure. The SO_3/SO_2 ratio was larger than 10 on all the experimental conditions of this study. This indicates that the sulfur oxides generated by the anhydrite impact experiments are dominated by SO_3.

Implication to the K-Pg event: The SO_3 rich chemical composition observed in this study implies that the sulfur oxides generated by natural planetary scale impacts are dominated by SO_3, not SO_2. It is because the SO_3/SO_2 ratio of natural planetary scale

impact vapor clouds would have been larger than that of the experimental result of this study. There are two reasons. The first reason is the chemical composition in the vapor clouds. The experiments in this study generates not only pure $CaSO_4$-composition impact vapor but also potential reducing agent such as the vapor of plastic ablator and metal flyer. These vapors can reduce the sulfur oxide derived from the $CaSO_4$ vapor. Thus, the SO_3/SO_2 ratio observed in this study can be lower than that of impact vapor cloud of pure anhydrite composition. The second reason is the difference in the sizes of vapor clouds. The sizes of natural planetary scale impact vapor clouds such as the Chicxulub impact vapor cloud are much larger than that of this study. Larger impact vapor clouds have smaller cooling rate and lower quenching temperature of chemical reactions in them. Thus, more SO_3 is formed in larger impact vapor clouds, because SO_3 is more stable at low temperatures [4].

The high SO_3/SO_2 ratio in the K-Pg impact vapor cloud would have resulted in global dense sulfuric acid rain after the Chicxulub impact. Such global acid rain would have caused severe oceanic acidification and resulting strong environmental perturbation [5].

References:

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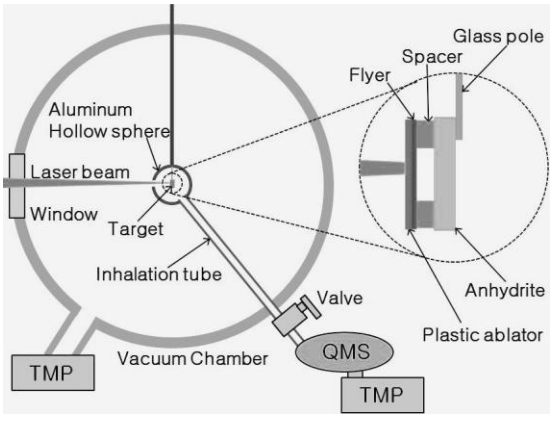

Figure 1: A schematic diagram of the experimental setup.

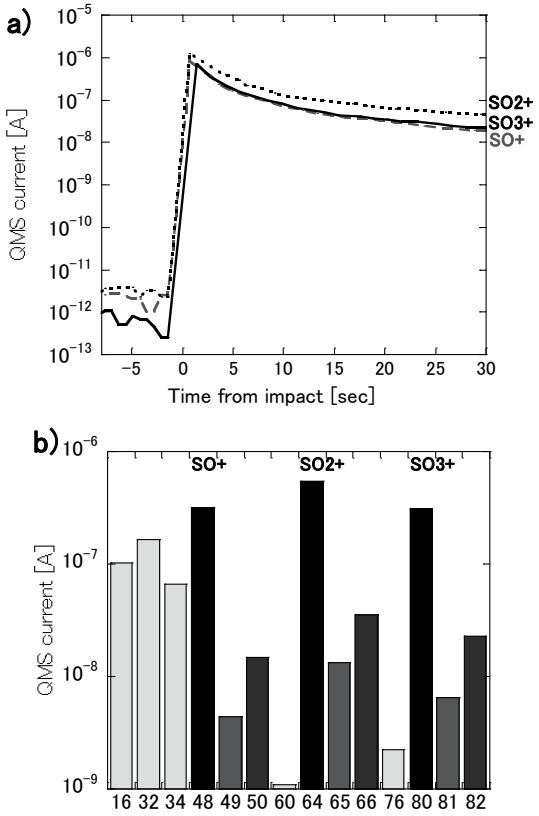

Figure 2: a) An example of the time-series data of the QMS measurements. The QMS currents of SO^+, SO_2^+, SO_3^+ are the signals of sulfuric oxides. The QMS currents increased significantly at the timing of the impact. The time-lag of SO^+, SO_2^+, and SO_3^+ is caused by a time delay of the QMS. **b)** A mass spectrum of the released gas observed in this study.

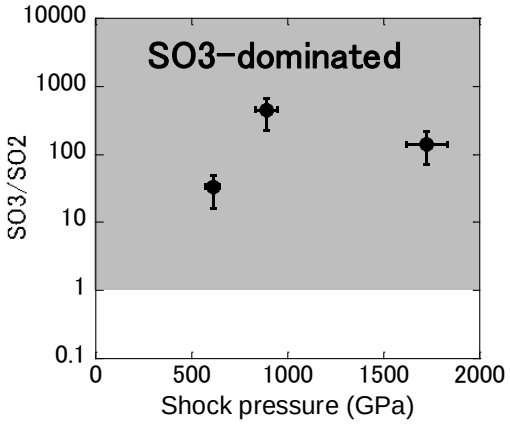

Figure 3: The SO_3/SO_2 ratio against the peak shock pressures calculated using the impedance matching method..