Sulfur Chemistry in K/T-Sized Impact Vapor Clouds. S. Ohno, S. Sugita, T. Kadono, S. Hasegawa, G. Igarashi, Dept. of Earth and Planetary Science, University of Tokyo (email: ono@space.eps.s.u-tokyo.ac.jp), Institute for Frontier Research on Earth Evolution, Japan Marine Science and Technology Center, The Institute of Space and Astronomical Science, Laboratory for Earthquake Chemistry, University of Tokyo

Introduction: The geologic record indicates that the mass extinction at K/T boundary, 65 Myrs ago, was caused by a hypervelocity impact of an asteroid or a comet [1]. During the K/T impact event, a large amount of sulfur was degassed from the impact site [e.g., 2, 3, 4]. The degassed sulfur converts to sulfuric acid aerosol and stays in the stratosphere for a long time [3, 4]. This reduces the sunlight significantly and leads to a mass extinction. However, if the degassed sulfur is dominated by SO$_3$ not SO$_2$, then the conversion to sulfuric acid aerosol occurs very rapidly and the blockage of sunlight does not last for a long time [3, 4, 5]. The chemical reaction of sulfur-oxides in an impact vapor cloud, nevertheless, has not been studied in detail previously, and the SO$_2$/SO$_3$ ratio in a vapor cloud is yet highly uncertain. The purpose of this study is to estimate the SO$_2$/SO$_3$ ratio in the K/T impact vapor cloud. Here we discuss the results of calculation of chemical equilibrium and kinetics of sulfur-containing species in an impact vapor cloud as well as mass spectroscopic analysis of vapor plumes created by laser irradiation on anhydrite.

Chemical Equilibrium Calculation: We calculated equilibrium chemical composition in vapor clouds generated from calcium sulfate (CaSO$_4$). We assumed several different impact velocities and different types of projectiles for the K/T impact.

The result of the calculation indicates that SO$_2$+1/2O$_2$ is more stable at high temperatures and high pressures and that SO$_3$ is more stable at low temperatures and low pressures. Over the entire range of the impact conditions we assumed, the SO$_2$/SO$_3$ ratio dramatically changes in the range between 600K and 1000K. If the reaction SO$_2$+O to SO$_3$ quenches at a temperature higher than 1000K, most of impact-degassed sulfur is released to the environment as SO$_2$. However, if the reaction SO$_2$+O to SO$_3$ quenches at a temperature lower than 600K, SO$_3$ is dominant.

Kinetics of Redox Reaction of Sulfur Oxides: We estimate the SO$_2$/SO$_3$ ratio in vapor clouds at the quenching temperature using a theoretical evaluation of chemical reaction rate of the reaction SO$_2$+O+M to SO$_3$+M [6]. The result of the calculation indicates that the SO$_2$/SO$_3$ ratio is smaller for a vapor cloud with a larger mass and that the SO$_2$/SO$_3$ ratio in a K/T-size vapor cloud is approximately unity. Because the result of this kinetic model estimation is an upper limit of the SO$_2$/SO$_3$, the SO$_2$/SO$_3$ ratio in K/T-size impact vapor cloud may have been much smaller than unity.

Laser Irradiation Experiment: A YAG laser beam (1.06µm of wave length, 25-400 mJ of pulse energy, 0.5-2 mm of irradiation spot diameter) was irradiated to a sample of anhydrite in a vacuum chamber. Vapor degassed by laser irradiation was analyzed with a quadrupole mass spectrometer (QMS). The gas sample obtained in every laser irradiation experiment was dominated by SO$_3$, but SO$_2$ was also detected. The SO$_2$/SO$_3$ ratios measured in experiments were between 80 and 300, and decrease with the laser beam diameter. The dependence of the SO$_2$/SO$_3$ ratio on laser beam diameter is SO$_2$/SO$_3$ = 120$^{-0.61}$.

The SO$_2$/SO$_3$ ratio in the experiment is about 10$^3$ time that in the kinetic model estimation for the size of vapor clouds produced in the laboratory. Our experimental results also show that the rate of decrease in the SO$_2$/SO$_3$ ratio obtained in the laser experiment as a function of vapor mass is higher than that predicted by the kinetic calculation. The power-low relation obtained in the laser experiments predicts that it will be 10$^6$ for a K/T-size impact vapor cloud. This strongly suggests the possibility that SO$_3$ was dominant in the degassed sulfur by the K/T impact.

Conclusion: Chemical equilibrium calculation indicates that SO$_3$ is more stable than SO$_2$+1/2O$_2$ at low temperatures and low pressures. Kinetic model calculation shows that the SO$_2$/SO$_3$ ratio in a K/T-size vapor cloud is less than unity. The SO$_2$/SO$_3$ ratio estimated based on the laser-irradiation experiments is about 10$^6$ for a K/T-size vapor cloud. Three lines of evidence strongly suggest that the SO$_2$/SO$_3$ ratio in K/T impact vapor cloud may have been much smaller than 1. Then sulfuric acid aerosol may not have blocked the sunlight for a long time. Instead, there may have been an extremely intense global acid rain immediately after (<100 days) the K/T impact.