SULFUR CHEMISTRY IN K/T-SIZED IMPACT VAPOR CLOUDS. S. Ohno[1], S. Sugita[1], T. Kadono[2], S. Hasegawa[3], G. Igarashi[4], [1]Dept. of Earth and Planetary Science, University of Tokyo (email: oono@space.eps.s.u-tokyo.ac.jp), [2] Institute for Frontier Research on Earth Evolution, Japan Marine Science and Technology Center, [3]The Institute of Space and Astronomical Science, [4]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_2, but SO_3 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 $SO_2/SO_3 = 120D^{-0.61}$.

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 lass 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 suggests 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.

References: [1] Alvarez, L.W. et al. (1990) *Science, 208,* 1095-1108. [2] Sigurdsson, H. et al. (1992) *EPSL, 109,* 543-559. [3] Pope, K.O. et al. (1994) *EPSL., 128,* 719-725. [4] Pope, K.O. et al. (1997) *JGR, 102,* 21645-1664. [5] Ohno et al, (2002) *Earth Planet. Sci. Lett.,* Submitted. [6] Troe, J., (1978) *Ann. Rev. Phys. Chem., 29,* 223.