# Sulfur chemistry in laser-simulated impact vapor clouds: Implications for the K/T impact event

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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. During the K/T impact event, a large amount of sulfur was degassed from the impact site. The degassed sulfur converts to sulfuric acid aerosol and stays in the stratosphere for a long time. This reduces the sunlight significantly and leads to a mass extinction. The duration time of the blockage of the sunlight by the sulfuric acid aerosol in the stratosphere depends strongly on the ratio of SO2/SO3. Thus, the purpose of this study is to estimate the ratio of SO2/SO3 of the K/T impact vapor cloud. In this study, we calculated SO2/SO3 chemical equilibrium in vapor clouds. We also report the result of mass spectroscopic analysis of vapor plumes created by laser irradiation on anhydrite.

Chemical Equilibrium Calculation: We calculated chemical equilibrium in vapor clouds. The assumption in our chemical equilibrium calculation is following. (1) Temperature and pressure of expanding vapor clouds are determined assuming ideal gas and adiabatic expansion. Both mean molecular weight and the ratio of heat capacities (gamma) are determined by the chemical equilibrium calculation. (2) The molar ratio of S to O in the system is fixed to 1:3. (3) SO2, SO3, SO, S, O2, and O are dominant, and other species are negligible.

To estimate the SO2/SO3 ratio in the K/T impact vapor cloud, we assumed several different impact velocities and different types of projectiles for the K/T impact. The result of the calculation indicates that SO2+1/2O2 is more stable at high temperatures and high pressures and that SO3 is more stable at low temperatures and low pressures. Over the entire range of the impact conditions we assumed, the SO2/SO3 ratio dramatically changes in the range between 600K and 1000K.

Laser Irradiation Experiment: YAG laser was irradiated to a sample of anhydrite in a vacuum chamber. Vapor degassed by laser irradiation was analyzed with a quadrupole mass spectrometer (QMS). We determined the sensitivity of QMS for SO2 and SO3 using standard gasses in order to calibrate the SO2/SO3 ratio obtained in the laser experiments. The conditions of the experiments are as follows. (1) YAG laser is kept irradiating until output current of QMS became stable. (2) The range of laser beam diameter on the surface of target is varied from 0.4 to 1.6 [mm]. (3) Laser beam intensity on the surface of target is 4x10^8[W/cm2]

The gas sample obtained in every laser irradiation experiment was dominated by SO2, but SO3 was also detected. The SO2/SO3 ratio was between 80 and 300. It indicates that the reaction to convert SO2 to SO3 experiences a quench near the upper limit of the range of SO2-SO3 transition. The SO2/SO3 ratios measured in experiments decrease with the laser beam diameter. It indicates that SO2/SO3 ratio in a lager vapor plume quenched at a lower temperature. This is because the cooling rate of larger vapor plume is smaller. The dependence of the SO2/SO3 ratio on laser beam diameter is SO2/SO3 = 120 D^-0.64.