AN EXPERIMENTAL METHOD TO ESTIMATE THE CHEMICAL REACTION RATE IN VAPOR CLOUDS: AN APPLICATION TO THE K/T IMPACT.

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Introduction: The final products of impact vapor clouds plays an important role in the evolution of surface environment of planets such as the K/T event [e.g., 1, 2]. Some previous studies employed laser irradiation in order to create hot and dense vapor clouds substituting for hypervelocity impact experiments [e.g., 2, 3, 4]. Although both laser irradiation experiments and model calculation have been carried out [e.g., 2], the quenching temperature of chemical reactions in large vapor clouds is lower than that in a laboratory scale. Thus we need to know the reaction rate in order to establish the size scaling law of the final chemical composition in vapor clouds. Prediction based on such chemical reaction rate is much more reliable than a simple extrapolation. However, experimental data at the temperatures between normal temperatures and several thousand kelvin is relatively poor. Nevertheless, no method to estimate the chemical reaction rate in vapor clouds has been established yet. In this study, we propose an experimental method to estimate the chemical reaction rate in vapor clouds. We also apply it to the redox reactions of sulfur oxides.

Principle of the method: Impact vapor clouds have extremely high temperature and pressure during early stages of its expansion. Consequently, the chemical reaction rates controlled by kinetics are larger than the rate of change in the chemical equilibrium composition in expanding vapor clouds: $(d[X]/dt)_{re} \geq (d[X]/dt)_{eq}$, where $(d[X]/dt)_{eq}$ is the rate of change in the chemical equilibrium composition in an adiabatically expanding vapor cloud, and $(d[X]/dt)_{re}$ is the chemical reaction rate controlled by kinetics. Thus, the impact vapor clouds are generally in a local chemical equilibrium.

After temperature and pressure of the vapor clouds become low enough, however, chemical reaction ceases to catch up with expansion; quenching occurs. At the quenching temperature, the chemical reaction rates controlled by kinetics are equal to the rate of change in the chemical equilibrium composition in expanding vapor clouds: $(d[X]/dt)_{re} = (d[X]/dt)_{eq}$. Thus, we can estimate the chemical reaction rates controlled by kinetics using the rate of change in the chemical equilibrium composition.

Spectroscopic measurements: We choose $CaSO_4$ as the first target sample material for an actual application of the method to estimate the chemical reaction

rate of redox reactions in vapor clouds. We use laser irradiation in order to generate vapor clouds, instead of hypervelocity impacts. Then we observe the spectrum of the emission lines from vapor clouds and determine the temperature and pressure conditions of the expanding vapor clouds [e.g., 5, 6].

First, we estimated the temperature of the vapor clouds using the intensities of atomic Ca lines. Figure 1 shows an observed spectrum of emission lines from laser-induced vapor clouds 80ns-180ns after the irradiation of a laser pulse. We obtain that the temperature in the vapor cloud after 80ns-180ns from laser irradiation is 6500±600K.

Then we estimate the pressure in the vapor clouds using the full width half maximum (FWHM) of 393.37nm line of Ca^+ ion emission. Figure 2 shows the profile of the Ca^+ 393.37nm emission line 80ns-180ns after laser pulse irradiation. The observed Ca^+ line is significantly broadened by Stark broadening. The estimated pressure in the vapor cloud is ~3.0×10^4bar.

Using these results, we carried out chemical equilibrium calculations in order to determine the p-T curve and chemical equilibrium composition in the expanding vapor clouds. The detail of the chemical equilibrium calculation is discussed in [2].

Mass spectroscopic observation of chemical composition at the quenching point: We carried out laser irradiation experiments and mass spectroscopic measurements of vapor clouds with a quadrupole mass spectrometer (QMS). QMS measurements determine the chemical composition in vapor clouds after the vapor clouds have expanded and cooled down sufficiently and the chemical reactions in them have quenched. Figure 3 shows the SO_2/SO_3 ratio measured in the experiments as a function of laser beam diameter. We can estimate the temperature and pressure at the quenching point by comparing the chemical composition at the quenching point and the calculated chemical equilibrium composition.

Estimation of the net reaction rate: Using the estimated quenching temperature, we estimated the net reaction rate from SO_2 to SO_3. Figure 4 shows the net reaction rate of the conversion reactions from SO_2 to SO_3 at the quenching point as a function of temperature. It can be seen that the net reaction rates at temperatures lower than 1200K are very large. The timescale of the conversion from SO_2 to SO_3 at tempera-

tures lower than 1200K is smaller than 10seconds. This is far shorter than the cooling timescale of large vapor clouds such as the K/T impact vapor cloud.

Implication to the K/T event: The result of the theoretical model calculation by Ohno et al. [2], which uses the rate coefficient data of a gas-phase reaction path $SO_2+O+M \rightarrow SO_3+M$ [7], is that the final SO_2/SO_3 ratio in K/T sized impact vapor clouds is approximately unity. However, the net reaction rate at 1150K is 3000times as large as the reaction rate by Troe [7]. The larger reaction rates suggest a lower final SO_2/SO_3 ratio in the K/T-sized impact vapor cloud. Thus, the final SO_2/SO_3 ratio in the K/T impact vapor cloud may have been much smaller than unity.

If the sulfur bearing gasses generated by the K/T impact was dominated by SO_3, they may have formed sulfuric acid aerosol quickly [1]. The residence time of the sulfuric acid aerosol during the K/T event have been estimated [e.g., 1, 8, 9]. However, their model ignores the coagulation between particles with different kind of particles. In addition to coagulation between sulfuric acid aerosol particles, numerous large-sized silicate aerosol particles are expected to have existed in the stratosphere immediately after the K/T impact and should have significantly promoted particle growth. This accelerated the descent.

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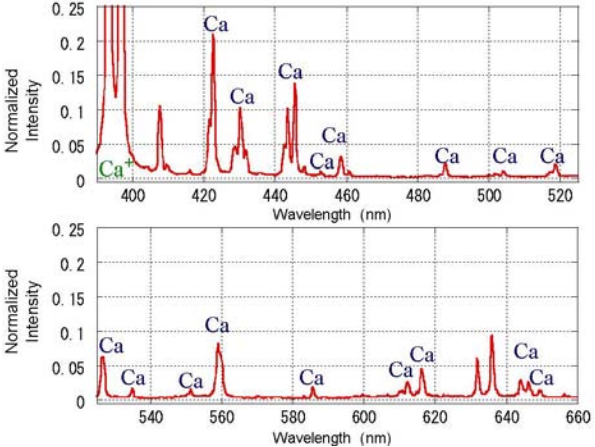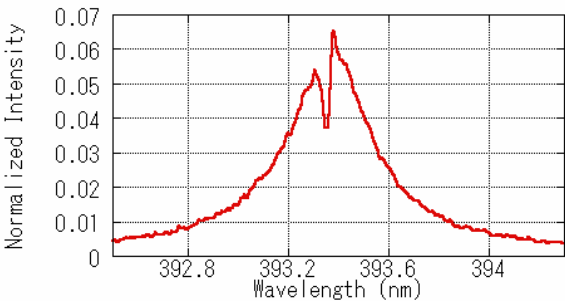

Fig. 2. The profile of the Ca+ 393.37nm emission line after 80ns-180ns from laser pulse irradiation. The observed Ca+ line is significantly broadened.
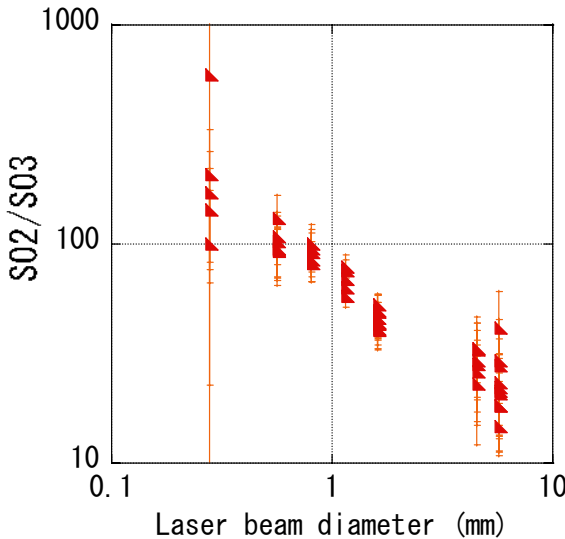

Fig. 3. The SO_2/SO_3 ratio measured in the experiments as a function of laser beam diameter. Error bars in the figure are the standard deviation (1σ) of the time series data.

Fig. 1. An observed spectrum of emission lines from laser-induced vapor clouds 80ns-180ns after the start of a laser pulse. The labels "Ca"and "Ca+" indicate the emission lines of Ca atoms and Ca+ ions, respectively.
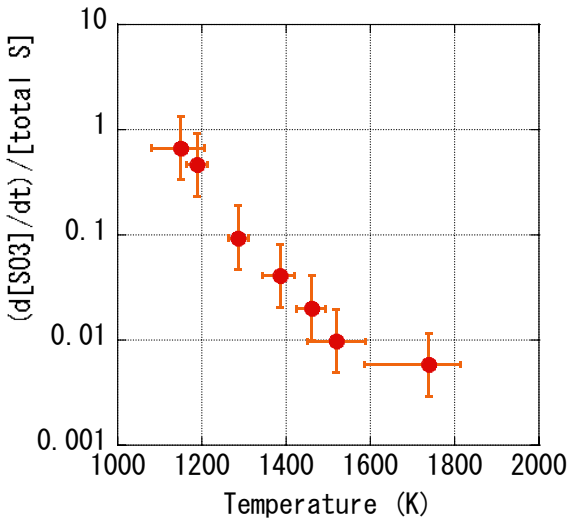

Fig. 4. The net reaction rate of the conversion reactions from SO_2 to SO_3 at the quenching point as a function of temperature.