OXIDATION OF CARBON COMPOUNDS BY SiO_2-DERIVED OXYGEN WITHIN LASER-INDUCED VAPOR CLOUDS. K. Ishibashi[1], S. Ohno[2], S. Sugita[2], T. Kadono[3], and T. Matsui[2], [1]Univ. of Tokyo, Dept. of Earth Planet. Sci. (Hongo, Bunkyo-ku, Tokyo 113-0033, JAPAN, ishibashi@eps.s.u-tokyo.ac.jp), [2]Univ. of Tokyo, Dept. of of Complexity Sci. and Eng. (Kashiwanoha, Kashiwa, Chiba 277-8561, JAPAN), [3]IFREE, JAMSTEC (Yokosuka, Kanagawa 273-0061, JAPAN).

Introduction: Hypervelocity impacts on the surface of growing planets may generate impact-induced vapor clouds and many chemical species are produced within such vapor clouds. These species may control the surface environments of the planets, such as temperature and redox state of the atmosphere. It is, thus, important to understand the composition of gases produced within an impact-induced vapor cloud. However, chemical reactions in a vapor cloud are so complicated that the composition of produced gases is poorly known. In particular, chemical reactions between silicates and carbon compounds are not understood well.

In the previous theoretical studies on gases generated within a impact-induced vapor cloud, only the volatile components are considered; effects of silicates are ignored [e.g., 1-3]. This is because silicates are assumed to condense and not to participate in the reactions among carbon compounds. However, Mukhin *et al*. [4] suggested that oxygen released from silicates reacts with carbon compounds within a vapor cloud. They irradiated pulsed laser on terrestrial rocks and chondrites to simulate impact vaporization and showed that the gas products within vapor clouds are composed mainly of oxidized species, such as CO and CO_2. They proposed that oxygen derived from thermal decomposition of silicates oxidizes carbon. However, the oxidation process has not been investigated in detail. No clear evidence that indicates oxidation of carbon by silicate-derived oxygen has been presented. Also, we do not know which molecular species in silicates supply oxygen to oxidize carbon. Thus, it is still uncertain whether silicate-derived oxygen really plays a key role in chemical reactions within a vapor cloud.

A large amount of silicates are contained in asteroids (or even in comets) and in surfaces of terrestrial planets. Thus, if silicate-derived oxygen affects the reactions among carbon compounds in a vapor cloud, the composition and oxidation state of produced gases should be influenced very much and differ greatly from the composition predicted by the theoretical studies that neglect effects of silicates.

In this study, in order to examine whether oxygen derived from thermally decomposed SiO_2, which is a main component of silicates, reacts with carbon compounds within a vapor cloud, we conducted laser-pulse heating experiments using mixtures of SiO_2 and carbon compounds. The mixing ratio of SiO_2 was systematically changed. If SiO_2-derived oxygen reacts with carbon, the composition of produced gas will change with the target composition.

Experiments: We irradiated the target sample with Nd:YAG laser pulses, and degassed gas product was measured with a quadrupole mass spectrometer (QMS). Laser heating is a very efficient method to simulate impact-induced vapor cloud [e.g., 4-8]. The experimental system is shown in Figure 1. The laser wavelength is 1.064 μm, and the pulse width is ~13 nsec. The energy of laser beam is fixed at ~100 mJ/pulse. The diameter of laser beam at the surface of targets is ~1 mm. The intensity of laser is $\sim 1 \times 10^9$ W/cm^2. This intensity is high enough to evaporate SiO_2. The frequency of beam pulses is set to ~0.5 Hz.

Polyethylene-SiO_2 mixture (PE-SiO_2) and coal-SiO_2 mixture (coal-SiO_2) were used as targets. Polyethylene was used because it is a pure sample of carbon compound. Polyethylene consists only of carbon and hydrogen, and the elemental composition is C/H=1/2. Since polyethylene contains no oxygen, production of oxygen-bearing gas, such as CO or CO_2 within vapor plumes indicates occurrence of reactions between SiO_2-derived oxygen and carbon. Coal was used to simulate insoluble carbon components in carbonaceous chondrites (i.e., kerogen). Coal that we used consists mainly of C, H, O, N and S, and the elemental composition is C/H/O/N/S=100/58.8/18.3/ 1.5/0.1. Polyethylene (PE) powder and coal powder were prepared and each was mixed with SiO_2 powder in several different ratios. Targets were made by compressing these mixed powders. The mixing ratio and elemental composition of PE-SiO_2 target and coal-SiO_2 target are listed in Table 1 and 2, respectively.

A target was placed on the X-Y stage that can be moved in both x and y directions in the vacuum chamber. A rotary pump and a turbomolecular pump are connected to the vacuum chamber, and pressure of $\sim 1 \times 10^{-8}$ mbar can be achieved.

Before each set of experiment, we baked both the vacuum chamber and QMS to remove materials adsorbed on the walls. After the vacuum chamber and the QMS reached room temperature, we conducted laser irradiation experiments. The pressure of the vacuum chamber was kept at $\sim 1 \times 10^{-3}$ mbar during

QMS measurement. If the chamber pressure is lower than this level, pressure fluctuation due to each laser-induced degassing causes significant noise in QMS measurement.

Results and discussion: Results of laser-pulse heating on PE-SiO_2 targets are shown in Figure 2. Figures 2 (a) and (b) show CO/CH_4 and CO_2/CH_4 ratios of produced gas as functions of the C/O ratio of target, respectively. Increase in SiO_2 ratio (decrease in C/O ratio) of targets leads to increase in CO/CH_4 and CO_2/CH_4 ratios of produced gas. Though polyethylene contains no oxygen, oxygen-bearing species, such as CO and CO_2, were produced from PE-SiO_2 targets within vapor plumes. In addition, the ratios of the oxygen-bearing species in produced gas increased with the SiO_2 ratio of targets. These unambiguously show that SiO_2-derived oxygen reacts with carbon. Chemical reactions between carbon and SiO_2-derived oxygen were, thus, confirmed.

Results of laser-pulse heating on coal-SiO_2 targets are shown in Figure 3. Figures 3 (a) and (b) show CO/CH_4 and CO_2/CH_4 ratios in produced gas as functions of the C/O ratio of target respectively. The general trends are the same as the case of PE-SiO_2 targets. Both CO/CH_4 ratio and CO_2/CH_4 ratio increase as C/O ratio of target decreases, strongly suggesting that SiO_2-derived oxygen reacts with carbon within coal as well. This means that SiO_2-derived oxygen reacts with carbon even when carbon compounds contain O, N, and S. Here, it is noted that the change in the CO/CH_4 and CO_2/CH_4 ratios as functions of C/O ratio is weaker for coal-SiO_2 samples than that of PE-SiO_2 samples. This might be because coal contains oxygen while polyethylene does not contain oxygen, and the effect of SiO_2-derived oxygen might be reduced in the case of coal-SiO_2 targets.

We may not be able to conclude only from these experimental results that the oxidation of carbon compounds by SiO_2-derived oxygen occurs within a large-scale vapor cloud. It is shown clearly, however, that such oxidation occurs within a small scale vapor cloud.

Conclusion: We confirmed that SiO_2-derived oxygen reacts with carbon compounds within a laboratory-scale vapor cloud. Thus, we cannot neglect effects of the oxygen released from silicates in chemical reactions in an impact-induced vapor cloud. The oxidation process by thermally decomposed silicates needs to be considered.

References: [1] Mckay, C. P. et al. (1989) *LPS XX*, 671-672. [2] Borunov, S. et al. (1997) *Icarus*, 125, 121-134. [3] Kress, M. E. and McKay, C. P. (2004) *Icarus*, 168, 475-483. [4] Mukhin L. M. et al. (1989) *Nature*, 340, 46-48. [5] Kadono, T. et al. (2002) *GRL*, 29, 20, 1979. [6] Managadze, G. G. et al. (2003) *GRL*, 30, 5, 1247 [7] Sugita, S. et al. (2003) *LPS XXXIV,* Abstract #1573. [8] Ohno, S. et al. (2004) *EPSL*, 218, 347-361.

Table 1. Mixing ratio and C/O ratio of polyethylene(PE)-SiO_2 targets.

Polyethylene:SiO_2 (mass ratio)	C/O (mole ratio)
4.46 : 95.54	0.1
10.45 : 89.55	0.25
18.92 : 81.08	0.5
31.82 : 68.18	1
48.28 : 51.72	2
82.35 : 17.65	10

Table 2. Mixing ratio and C/O ratio of coal-SiO_2 targets.

coal:SiO_2 (mass ratio)	coal/(SiO_2+coal)	C/O (mole ratio)
12.5 : 87.5	0.125	0.237
25 : 75	0.25	0.522
50 : 50	0.5	1.315
100 : 0	1	5.466

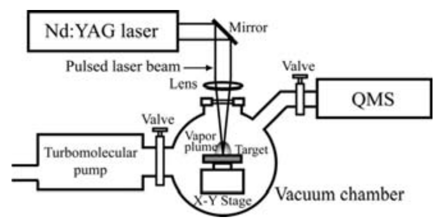

Figure 1. Experimental system.

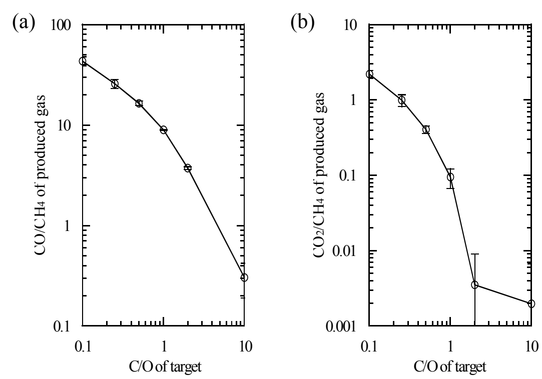

Figure 2. Results of laser-pulse heating on PE-SiO_2 targets. CO/CH_4 ratio of produced gas (a) and CO_2/CH_4 ratio of produced gas (b) as functions of C/O ratio of targets.

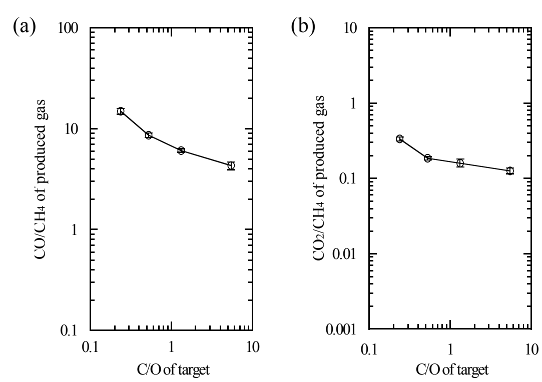

Figure 3. Results of laser-pulse heating on coal-SiO_2 targets. CO/CH_4 ratio of produced gas (a) and CO_2/CH_4 ratio of produced gas (b) as functions of C/O ratio of targets.