AN EXPERIMENTAL STUDY ON HCN PRODUCTION IN REDOX-NEUTRAL ATMOSPHERES BY OBLIQUE IMPACTS: SIZE AND VELOCITY SCALING. K. Kurosawa[1], K. Ishibashi[2], S. Sugita[1], T. Kadono[3], S. Ohno[4], and T. Matsui[1],[1]Dept. of Complexity Sci. & Eng., Univ. of Tokyo (Kashiwanoha, Kashiwa, Chiba 277-8561, JAPAN, kurosawa@impact.k.u-tokyo.ac.jp), [2]Dept. of Earth and Planet. Sci., Univ. of Tokyo (Hongo, Bunkyo-ku, Tokyo, JAPAN), [3]Inst. of Laser Eng., Osaka Univ., (Yamadaoka, Suita, Osaka, JAPAN), [4]Inst. for Study of the Earth's Interior, Okayama Univ. (Yamada, Misasa, Tottori, JAPAN)

Introduction: HCN may have played an important role in the origin of life, because it can help forming amino acids and nucleic acid bases [e.g., 1]. However, the production rate of HCN in the early Earth is highly uncertain. Furthermore, it is estimated to be extremely low if the early Earth atmosphere is redox neutral (i.e., N_2-CO_2 dominant) [e.g., 2].

Hypervelocity impact experiments show that nitrogen from the ambient atmosphere and carbon from fine-grained fragments from obliquely impacted C-rich projectiles react to form CN radicals even when the atmosphere is very oxidizing (N_2-O_2 dominant) [3, 4]. A CN forming region is much more reducing than an ambient atmosphere because this process can supply organic carbon atoms included in impact fragments into the ambient atmosphere. We call such a reducing gas around fine-grained fragments "ablation vapor".

In our previous study, we showed experimentally that vaporized carbon converted to HCN very efficiently in ambient atmospheres containing as much as a few hundred mbar of CO_2. The conversion ratio from C to HCN is 2 – 0.1 % for 0 – 400 mbar of CO_2. [5]

However, the ablation vapor size and initial gas temperature for the laboratory experiments and those for the planetary-scale impacts are very different. These are the key parameters for the yield of final products from rapidly cooling high-temperature gas-phase chemical reactions because these parameters control the pressure-temperature path of hot vapor. Initial gas temperature is controlled by impact velocity. Thus, the empirical scaling rules of conversion ratio from C to HCN are necessary for estimating HCN yield for actual meteoritic impacts within the early Earth atmosphere.

In this study, we investigate the effects of ablation vapor size and impact velocity on the conversion ratio ϕ from vaporized carbon to HCN molecules. Here, the total amount of HCN is given by $N_{HCN} = \phi N_C$, where N_C is the total amount of vaporized carbon.

Experiments: We conducted laser ablation experiments with the same methods as our previous study under a much wider range of laser conditions (i.e., beam diameter and intensity). The partial pressures of N_2, CO_2, and H_2O were fixed at 105, 27, and 27 mbar, respectively in this study.

Two series of experiments were conducted in this study. First, the laser intensity was fixed at 5 x 10^8 W/cm^2, while the laser beam diameter was varied from 1.25 to 2.65 mm. Second, the laser beam diameter fixed at 2 mm, while the laser beam intensity was varied from 3.0 x 10^8 to 9.0 x 10^8 W/cm^2.

During the laser irradiation, optical spectroscopic observations of laser-induced high-temperature gas were conducted. After laser irradiations, one milliliter of the final product gas was sampled using a syringe and was analyzed with the gas cchromatograph-mass spectrometer, GCMS (Shimadzu Corp. QP2010).

Analysis: To estimate the total amount of vaporized carbon, we measured the geometory of laser-ablation craters of graphite target with scanning electron micropobe, SEM (Keyence, VE-9800).

Then we carried out spectral-form inversion analysis of observed spectra to investigate a temperature of laser-induced hot CN with basically the same method as described in [6]. The computer software package SPRADIAN (Structured Package for Radiation Analysis) [7] was used to calculate theoretical spectrum.

The GCMS was calibrated using standard HCN gas. The detection limit of HCN is about 0.4 nmol/pulse under out experimental conditions.

Experimental results: The main result in this study is the conversion ratio ϕ from C to HCN as a function of laser beam diameter, corresponding to impactor size, and laser intensity, corresponding to impact velocity.

The results of SEM analysis of laser-ablation craters of target show that the floors are very flat and that their depths per a laser shot is approximately a laser wavelength (~ 1 μm) regardless of laser intensity. Thus, we assume that depth of crater is 1 μm under all the experimental conditions in this study. This allows us to estimate the molar amount N_c of vaporized carbon.

Fig. 1 shows that temperature of hot CN as a function of beam cross section and intensity. The dependence of ablation vapor size on gas temperature is small. This is because available laser energy for unit mass of vaporized carbon is the same when laser intensity is fixed. In contrast, gas temperature increases as beam intensity increases.

The procedure to obtain the relation between impact velocity and gas temperature is as follows. The chemical interaction between impact fragments and an ambient atmosphere occurs around very small fragments in mostly free-molecular collision regime [8]. Gas tem-

perature is estimated by energy balance equation on the fragment surface using the ablation model in free-molecular collision regime [8]. Note that initial fragment velocity is nearly equal to impact velocity [9]. Gas temperatures estimated for our laser vapor plumes correspond to 3 - 7 km/s of impact velocity under the laboratory impact experiment conditions (~30 mbar of air) by [3].

Fig. 2 shows that the total amount of vaporized carbon and of generated HCN per a laser pulse as a function of beam cross section and beam intensity. Fig. 3 shows that ϕ as a function of beam cross section and corresponding impact velocity. The conversion ratio ϕ is proportional to -1.8th power of plume radius and -0.79th power of corresponding impact velocity when beam cross section and corresponding impact velocity are greater than 2.4 mm^2 and 5.6 km/s, respectively.

Discussions & Conclusions: The reason for the observed decrease in ϕ for increasing plume size is probably that the reaction process among C, H, and N involve diffusion within the hot vapor plumes. Diffucsion processes work more slowly as the size of the system increases. The cause of decrease in ϕ for higher impact velocity (i.e., laser intensity) is consistent with the thermodynamic stability of HCN at lower temperatures. Chemical reactions within a vapor plume due to a higher velocity impact would quench at higher temperatures because of its higher initial temperature.

These decreaseing trends would lead to lower HCN yield at planetary scales. Nevertheless, the effect of the decreases is not very large. This is because the observed rate of decrease in ϕ as a function of impact velocity is small. Furthermore, the effects of ablation vapor scale on ϕ may be also small because ablation vapor is generated around sub-micron size impactor fragments. An impact-comminuted projectile is broken up further by aerodynamic pressure from the colliding ambient atmosphere.

For expample, a simple model for fragment dispersal dynamics of an obliquely impacted (30° from the horizontal) carbonaceous body 300 m in diameter (i.e., carbon content is ~8 x 10^{11} mol [10]) within 1 bar of redox-neutral atmosphere show that the resulting column density of HCN is ~10 mol/m^2 over ~10^2 km^2 of surface area, where 0.1% of ϕ is used. Since this is a preliminary estimate, its use needs caution. However, this column density is equivalent to HCN production accumulated for ~1 x 10^4 years by lightening within a strongly reducing (i.e., "highly fertile") atmosphere [11]. This is a significant concentration of HCN, although such high HCN concentration is limited in both time and space. Such a temporally and spatially-concentrated supply of HCN may have played an important role in the origin of life.

References: [1] J. P. Ferris & W. J. Hagan, *Tetrahedron*, **40**, 1093-1120, 1984. [2] B. Fegley Jr, et al., *Nature*, **319**, 305-308, 1986. [3] S. Sugita & P. H. Schultz, *LPSC, XXXI*, #2029, 2000. [4] S. Sugita & P. H. Schultz, *JGR*, **108** (E6), 5051, doi:10.1029/2002JE001959, 2003a. [5] K. Kurosawa et al., *LPSC, **XXXVIII***, #1629, 2007. [6] K. Fujita et al., *JTHT*, **16**, 77-82, 2002. [7] K. Fujita & T. Abe, *ISAS Rep.*, **669**, 1997. [8] S. Sugita & P. H. Schultz, *JGR*, **108** (E6), 5052, doi:10.1029/2002JE001960, 2003b. [9] P. H. Schultz & D. E. Gault, *GSA Sp. Pap.*, **247**, 239-261, 1990. [10] J. T. Wasson & G. W. Kallemeyn, *Phil. Trans. R. Soc. Lond.*, A, **325**, 535-544, 1988. [11] R. Stribling & S. L. Miller, *Origins of life*, **17**, 261-273, 1986.

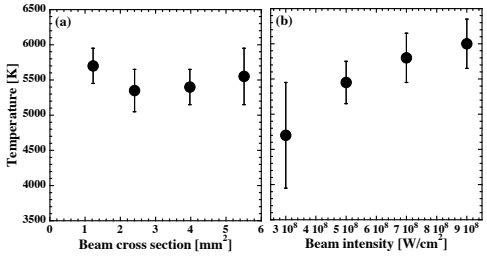

Figure 1. Temperature of laser-induced CN as a function of (a) beam cross section and (b) beam intensity.

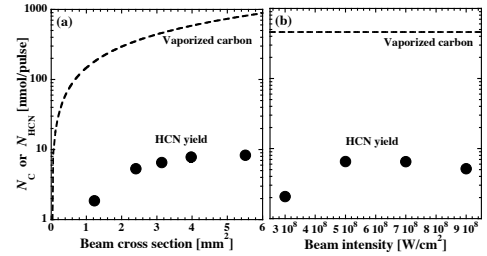

Figure 2. The total mol N_C of vaporized carbon and that N_{HCN} of generated HCN per a laser pluse as a function of (a) beam cross section and (b) beam intensity.

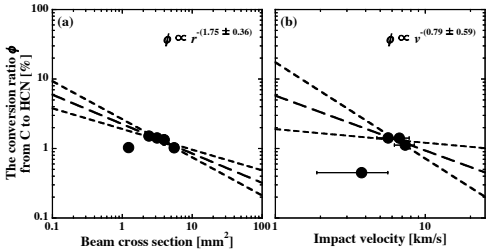

Figure 3. The conversion ratio ϕ from C to HCN as a function of (a) beam cross section and (b) corresponding impact velocity. The variable r is plume radius, which is proporational to the 2/3rd power of laser beam radius.