CYANIDE PRODUCTION BY CHEMICAL REACTIONS BETWEEN IMPACTOR MATERIAL AND AN AMBIENT ATMOSPHERE AFTER AN OBLIEQUE IMPACT. K. Kurosawa[1], K. Ishibashi[2], Y. Sekine[1], S. Sugita[1], T. Kadono[3], S. Ohno[4], N. Ohkouchi[5], N. O. Ogawa[5], and T. Matsui[1], [1]Dept. of Complexity Sci. & Eng., Univ. of Tokyo (5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8561, JAPAN; kurosawa@impact.k.u-tokyo.ac.jp), [2]Dept. of Earth and Planet. Sci., Univ. of Tokyo (7-3-1, Hongo, Bunkyo-ku, Tokyo, JAPAN), [3]Inst. of Laser Eng., Osaka Univ. (2-6, Yamadaoka, Suita, Osaka, JAPAN), [4]Inst. for Study of the Earth's Interior, Okayama Univ. (827, Yamada, Misasa, Tottori, JAPAN), [5]IFREE, JAMSTEC (2-15, Natsushima, Yokosuka, Kanagawa, JAPAN)

Introduction: Cyanide are considered as one of the most important compounds in the chemical evolution phase of the origin of life [e.g., 1]. However, the production rate of cyanide is estimated to be extremely low if the early Earth atmosphere is redox-neutral (i.e., N_2-CO_2 dominant) [e.g., 2].

Recent studies for the Late Heavy Bombardment suggests that the projectiles during this period contain a large amount of carbons [3, 4]. Such carbon-rich impactor may have played an important role in the origin of life. Hypervelocity impact experiments show that nitrogen from an 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) [5, 6]. A CN forming region is much more reducing than the ambient atmosphere because this process can supply carbon atoms included in impact fragments into the ambient atmosphere. We call such a reducing gas around fine-grained fragments "ablation vapor". The ablation vapor is likely to subsequently react with the ambient redox-neutral atmosphere. This process may be a much more efficient cyanide production mechanism than that proposed in previous studies because of two reasons. First, CN bond is more stable because the ablation vapor is much more reducing than the ambient atmosphere. Second, this process can use nitrogen from the ambient atmosphere. However, this process has not been investigate experimentally.

In this study, we conduct laser ablation experiments within redox-neutral atmospheres to simulate chemical reactions between impactor material and an ambient atmosphere. We analyze final products from laser-induced ablation vapors using a gas chromatograph-mass spectrometer (GC-MS; Shimadzu Corp. QP2010) and a fourier transform-infrared spectrometer (FT-IR; ParkinElmer, Spectrum 2000) for gas and solid, respectively.

Experiments: We experimentally investigated the effects of the partial pressure of CO_2 on the conversion ratio ϕ from vaporized carbon to HCN molecules and the dependence of atmospheric composition on the relative amount of CN bond in condensates from laser-induced ablation vapors. Here, the total amount of HCN is given by $N_{HCN} = \phi N_C$, where N_C is the total

amount of vaporized carbon. Basically, we use the same experimental systems in our previous study [7].

In this study, we used graphite and cast iron (Fe: 94 wt%; C: 3.5 wt%; Si: 2.2 wt%; S: 0.068 wt%) targets were used for gas and solid analysis as analogs of chondrite material, respectively.

Gas-phase analysis: We investigated the total molar amount of vaporized carbon, N_C, the temperature of laser-induced CN, T_{CN}, and the total molar amount of laser-induced HCN, N_{HCN}.

Water vapor, CO_2, N_2, and Ar were introduced into the vacuum chamber after evacuating air. The partial pressures of N_2 and H_2O were fixed at 5.0×10^2 and 30 mbar, respectively. The partial pressure of CO_2, P_{CO2}, was varied from 0.0 to 5.3×10^2 mbar. We use Ar to adjust the total pressure in the chamber to be 1.1×10^3 mbar. The number of laser pulse irradiations was $\sim 3.0 \times 10^2$. The GC-MS was calibrated using standard HCN gas. The detection limit of HCN is about 0.4 nmol/pulse under our experimental conditions.

During the laser irradiation, optical spectroscopic observations of laser-induced ablation vapor were conducted. After laser irradiations, one milliliter of the final product gas was sampled using a syringe and was analyzed with the GC-MS.

Solid-phase analysis: We investigated the conposition of condensates from laser-induced ablation vapors qualitatively.

Gas mixtures of N_2, CO_2, and Ar were used. The total pressure in the chamber was fixed at 13 mbar. We set a CaF_2 disk as a deposition plate on the stage in the chamber. The distance between the laser irradiation spot and the disk is ~5 mm. The number of laser pulse irradiations was $\sim 1.9 \times 10^3$. After laser irradiations, we analyzed condensates on CaF_2 disks by IR absorption spectroscopy with the FT-IR.

The mass and temperature of vapor: To estimate the total amount of vaporized carbon, we assumed that the shape of laser-ablation craters are cylinder and the depth of that are equal to the wavelength of the laser pulse (~1 μm) that is a characteristic scale of energy deposition of laser irradiations. Thus, we estimated that N_C is ~5×10^2 nmol/pulse.

We carried out band-tail fitting analysis of observed spectra to investigate a temperature of laser-induced

hot CN [8]. The computer software package SPRADIAN (Structured Package for Radiation Analysis) [9] was used to calculate theoretical spectrum.

Experimental results of gas phase: The main result in this study is the conversion ratio ϕ from C to HCN as a function of P_{CO2}.

An observed emission spectrum from laser-induced ablation vapor is shown in Fig. 1. Swan band system of C_2 and Violet band system of CN are mainly observed. Thus, CN radical was formed under our experimental condition. We estimated T_{CN} using Band-tail fitting method. It is nearly constant, ~6500 K, regardless of P_{CO2}. This temperature corresponds to ~8 km/s of impact experiments. This temperature-velocity relation was obtained using a heat balance equation on the fragment surface between energy transfer from the colliding atmosphere and the latent heat of fragments [10].

The HCN yield investigated with the GC-MS decreaces as the P_{CO2} increases. Figure 2 shows ϕ as a function of P_{CO2}. However, it is important that 0.1 – 1 % of HCN was formed in ambient atmospheres contained as much as a few hundred mbar of CO_2.

Experimental results of solid phase: We focused on absorption band around 2200 cm^{-1} in IR spectra. This band corresponds to $C\equiv N$, $-N=C=N$, and $C\equiv C$ bands [e.g., 11]. Figure 3 shows IR spectra of condensates under three different gas mixtures. These results indicate that the composition of condensates strongly depends on the composition of gas mixtures. Althogh the abundance of CN bond decreases if gas mixture contains CO_2, CN bond is fixed into a condensed phase under redox-neutral atmospheres.

Discussions & Conclusions: An impact-comminuted projectile is broken up further by aerodynamic pressure from the colliding ambient atmosphere. Thus, the size of each ablation vapor around impact fragments may approach to that of laser-induced ablation vapors. Our results are likely to apply to actual oblique impacts if impact fragments are dispersed very efficiently. 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 [12]) 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 atmosphere [13]. This is a significant concentration of HCN, although such high HCN concentration is limited in both time and space. Further-

more, this process may supply condensates which contain cyanide compounds into proto ocean and/or lakes. Such a temporally and spatiallyconcentrated supply of cyanide compound may have played an important role in the origin of life.

References: [1] J. P. Ferris & W. J. Hagan (1984), *Tetrahedron*, **40**, 1093-1120. [2] B. Fegley Jr, et al. (1986), *Nature*, **319**, 305-308. [3] R. Gomes et al. (2005), *Nature*, **435**, 166-169. [4] R. G. Strom et al. (2005), *Science*, **309**, 1847-1850. [5] S. Sugita & P. H. Schultz (2000), *LPSC, XXXI*, #2029. [6] S. Sugita & P. H. Schultz (2003), *JGR*, **108** (E6), 5051, doi:10.1029/2002JE 001959. [7] K. Kurosawa et al. (2007), *LPSC, XXXVIII*, #1629. [8] K. Kurosawa et al., *JTHT*, submitted. [9] K. Fujita & T. Abe (1997), *ISAS Rep.*, **669**. [10] S. Sugita & P. H. Schultz (2003), *JGR*, **108** (E6), 5052, doi:10.1029/2002JE001960. [11] H. Imanaka et al. (2004), *Icarus*, **168**, 344-366. [12] J. T. Wasson & G. W. Kallemeyn (1988), *Phil. Trans. R. Soc. Lond.*, A, **325**, 535-544. [13] R. Stribling & S. L. Miller (1986), *Origins of life*, **17**, 261-273.
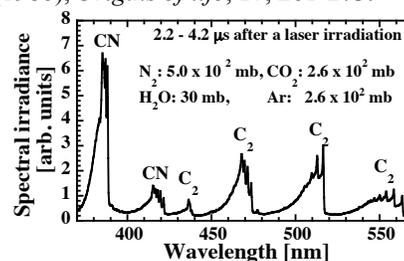

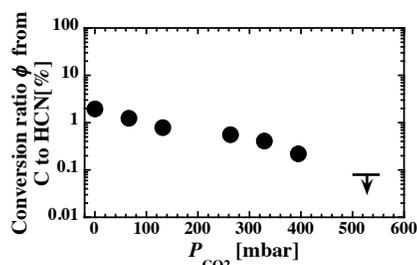**Fig.1** An observed spectrum from laser-induced ablatin vapor.

Fig.2 The conversion ratio ϕ from C to HCN as a function of the partial pressure of CO_2.
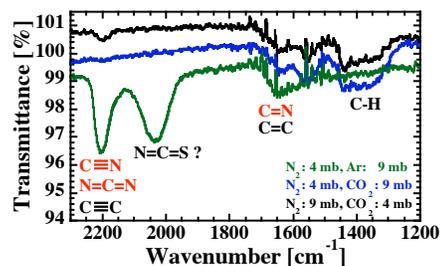

Fig. 3 IR spectra of condensates on deposition plates. The composition of gas mixtures are shown in the figure.