Introduction: Cyanides are considered as one of the most important compounds in the chemical evolution phase of the origin of life [e.g., 1]. However, the efficient production process of cyanides in the surface environment on the early Earth has been highly uncertain because formation of CN bonds highly inefficient in a redox-neutral atmosphere atmosphere (N$_2$-CO$_2$), which are widely accepted as the early Earth’s atmosphere [e.g., 2, 3].

Previous experimental studies on hypervelocity impacts suggest that oblique impacts of carbon-rich asteroids could form CN radicals efficiently in the N$_2$-rich atmosphere due to aerodynamic ablation [4, 5]. Because impact-induced ablation vapor is much more reducing than the ambient atmosphere, the carbon included C-rich meteoritic fragments are converted to CN radicals via interactions with atmospheric N$_2$. These CN radicals are likely to subsequently react with the ambient atmospheric gas species, possibly leading to an efficient cyanide production mechanism.

Kurosawa et al. [6] recently conducted laser ablation experiments in redox-neutral gas mixtures using graphite to assess the fate of CN radicals produced by the oblique impacts. They have found the production of gaseous HCN, which is essential for the formation of amino acids and nucleic acid basis, by chemical reactions between CN radicals and H$_2$O in the gas phase. Nevertheless, the conversion ratio from vaporized solid carbon to gaseous HCN is obtained to be only 0.2 – 2.0% for the partial pressure of CO$_2$ = 0.0 – 4.0 x 10$^5$ mbar; thereby the fate of other CN radicals and highly reactive carbons in the ablation vapor is still a mystery.

In this study, we focus on the condensed products from the laser-induced ablation vapor. We investigate the chemical composition and structure of the condensed products collected from the laser ablation experiments. Finally, we discuss implications of the production of the condensed products including cyanide compounds for the origin of life.

Laser ablation experiments: The laser ablation experimental system and procedure used in this study are given by Kurosawa et al. [6]. In order to collect the condensed products from the laser-induced ablation vapor, we set a CaF$_2$ substrate (25 mm in diameter, 2 mm in thickness) at ~6 cm from the laser spot on the targets.

We used graphite (C: 99.999 wt%) as laboratory analogs of carbon-rich chondrite. We also used Murchison meteorite (CM2) powder (N: 7.8 x 10$^{-2}$ wt%; C: 1.7 wt%) compressed at ~ 4 GPa using a cubic press. In this study, we used gas mixtures of N$_2$, CO$_2$, and Ar for the ambient gas species in the vacuum chamber. The total gas pressure was fixed to be 13 mbar. We varied the partial pressures of N$_2$ in the gas mixtures. The chemically inert Ar gas was used to balance the total pressure in the chamber.

Chemical analysis: We conducted elemental analysis and infrared absorption spectroscopy of the condensed products. Elemental analysis investigates the contents of total nitrogen (TN) and carbon (TC) in the condensed products. Infrared spectroscopic analysis provides the information on the presence of nitrogen-bearing chemical bonds, such as C≡N and C=N in the products. Based on the results of both the elemental and IR analyses, we investigate dependence of the chemical composition and structure on the partial pressure of N$_2$. Elemental analysis was performed with an online system of Finnigan Delta Plus XP isotope-ratio mass spectrometer coupled to a Flash EA1112 elemental analyzer (EA/IRMS system) [7]. Infrared absorption spectroscopy was carried out with a Fourier transform-infrared spectrometer (FT-IR) (ParkinElmer, Spectrum 2000).

Experimental results: The main results of this study are dependence of both TN and absorption depth of CN bonds of the condensed products on the partial pressure of N$_2$ ($P_{N_2}$). We found that nitrogen in the gas phase are efficiently fixed into the solid products condensed from the laser-induced ablation vapor. The absorption depths of CN bonds also increase with the $P_{N_2}$.

The results of elemental analysis of the condensed products from graphite are shown in the left panel of Fig.1. The results show that the chemical composition of products strongly depends on that of the ambient gases. The condensed products are not observed for laser irradiations on a graphite under CO$_2$ gas, suggesting that carbon in the laser-induced ablation vapor is probably oxidized to CO gas by the reactions with the...
ambient CO₂ gas. When we use N₂ as the ambient gas, TN reaches ~10 wt% in the condensed materials. These results suggest that nitrogen in the gas phase is incorporated into the condensed phase (TN ~10 wt%) via chemical reactions with carbon-rich laser-induced ablation vapor.

The IR measurements of the condensed products also support the idea that N₂ in the gas phase is incorporated into the condensed products by reacting with C in the laser-induced ablation vapor. Figure 2 shows IR absorption spectra of the condensed products from graphite under various chemical compositions of the gas mixtures. This figure shows that the depth of absorption bands around 2200 cm⁻¹, which correspond to C≡N, and -N=C=N bonds [e.g., 8], increases with the P₈. The depth of absorption bands around 1600 cm⁻¹ in the IR absorption spectra, which correspond to C≡N bonds, also shows the similar trend with the increase in the P₈. Both the absorption bands around 2200 cm⁻¹ and 1600 cm⁻¹ are also contributed by the presences of C=C and C=C bonds, respectively, in the condensed products. Therefore, the increase in the absorption depth could not be caused only by the formations of C≡N and C=N bonds. Nevertheless, the observed systematic changes in the depth of these absorption bands with the P₈ strongly suggest the presence of C≡N, C=N, and -N=C=N bonds in the condensed products.

Then, we applied this experimental technique to a meteoritic sample. The right panel of Fig. 1 shows the results of elemental analysis using Murchison meteorite. We found that TN of the condensed products about 15 times larger than that of the target before the laser irradiations. This result indicates that nitrogen is efficiently fixed into the condensed products even when we used meteoritic samples containing oxygen.

**Discussion & Conclusions:** Recent theoretical and observational studies for the Late Heavy Bombardment period (LHB) suggest that the most frequent impactors during the LHB are expected to be carbonaceous chondrite like materials [9-11]. Such carbon-rich impactors could supply a large amount of cyanides to the surface environment of early Earth during the LHB by chemical reactions with the atmospheric N₂.

Our experimental results suggest that CN radicals generated by interactions between impactor material and N₂-including atmosphere are fixed into the condensed products efficiently by forming C≡N, -N=C≡N, and C=N bonds in its chemical structure (i.e., cyanides). These cyanides could be supplied to the primitive oceans and/or lakes after the impacts. Such a temporally, concentrated supply of cyanides may have played an important role in the origin of life.


**Fig. 1.** The mass contents of total nitrogen (TN) and carbon (TC) in the condensed products. Pure Ar, and pure N₂ were used in these experiments. The blue and red dotted lines in the right panel indicate TN and TC in the target before the laser irradiations, respectively.

**Fig. 2.** IR absorption spectra of condensed products from graphite targets. The composition of the gas mixtures are indicated in the figure. The green bars show the wavenumbers of the absorption bands of C≡N, -N=C≡N, and C=N.