

Highly isotopically depleted hydrocarbon gases in methane-derived carbonate of the Cretaceous age

A. IJIRI¹, U. TSUNOGAI¹, T. GAMO¹ AND Y. HIKIDA²

¹ Division of Earth and Planetary Sciences, Graduate School of Science, Hokkaido University, N10 W8, Kita-ku, Sapporo, Japan. (iji@ep.sci.hokudai.ac.jp)

² Nakagawa Museum of Natural History, 28-9, Yasukawa, Nakagawa-cho, Hokkaido

We report $\delta^{13}\text{C}$ compositions of the light hydrocarbon gases (methane: C_1 , ethane: C_2 , propane: C_3 , n-butane: n- C_4 , and iso-butane: iso- C_4) included in the Cretaceous methane-derived carbonate rocks. The sample aliquots used for this study was taken from a carbonate lens including fossil seep community found in the upper Cretaceous aged in the Omagari Formation, northern part of Hokkaido, Japan (44°39'26"N, 142°2'25"E). Based on their low $\delta^{13}\text{C}_{\text{carbonate}}$: -41.2~-44.4 (‰ PDB), a major portion of the carbonate seems to be generated by the oxidation of methane, probably during seafloor seeping activities of methane-rich fluids.

Hydrocarbon gas was extracted by the acidification of carbonate sample in a glass vial bottle that had been already crused and flushed by highly purified helium, and $\delta^{13}\text{C}$ of hydrocarbon gas liberated in gas phase of glass vial was analyzed directly by using isotope-ratio-monitoring-gas chromatography / mass spectrometer (irm-GC/MS).

The concentrations of methane were 0.0207~0.434 (ng/g) (nanogram per crushed carbonate) with the $\text{C}_1/[\text{C}_2+\text{C}_3]$ ratios of 1.2~4.2. The $\text{C}_1/[\text{C}_2+\text{C}_3]$ ratios are 2~4 orders of magnitude lower than the typical bacterial hydrocarbons. The $\delta^{13}\text{C}$ values of methane were typical values for bacterial methane (-63.9~-70.2‰). On the other hand, the other hydrocarbon gases showed highly ^{13}C depleted carbon isotopic compositions (C_2 : -55.0~-91.7‰, C_3 : -58.2~-99.4‰, n- C_4 : -91.8~-163.7‰, iso- C_4 : -25.7~-65.4‰). The relationships of the $\delta^{13}\text{C}$ values for these hydrocarbons in each sample showed a pattern of $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 > \delta^{13}\text{C}_3 > \delta^{13}\text{C}_{\text{n-4}}$ which is in contrast to the widely accepted isotope distribution pattern of natural gases. There may be two possibilities to explain such $\delta^{13}\text{C}$ compositions: 1) syntheses of the hydrocarbons by way of polymerization of bacterial methane ($\delta^{13}\text{C}$: -63.9~-70.2‰), 2) fortuitous mixture of thermally generated hydrocarbons ($\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3 < \delta^{13}\text{C}_{\text{n-4}}$) from a highly ^{13}C -depleted precursor organic molecules ($\delta^{13}\text{C}$: ~-160‰) probably produced by methanotrophic and those from ordinary marine organic compounds ($\delta^{13}\text{C}$: ca. -20‰).

Migration and fixation of organic carbon in vegetation – forest soil system

HIDESHI IKEDA, TAKUYA KOBAYASHI, KO NAKAYA, CHIEKO SUZUKI AND SHINJI YASUIKE

Central Research Institute of Electric Power Industry, 1646, Abiko, Abiko-City, CHIBA, Japan, 270-1194
ik@criepi.denken.or.jp

Introduction

Although plant - soil system is a very important factor on carbon(C) cycling in global system, quantitative analysis based on field observations is limited.

Observation site and method

Observation site is located in central Japan, which has altitude with 1400 meters and easy gradient. In this site, organic C storages and fluxes were observed, and mechanism of reaction in soil layer, decay rate, and C supply were analyzed.

Results and Discussion

In throughfall and stem flow samples, organic carbon was enriched by foliar exudation. Vegetation roots and vertical variation of soil water chemistry were not observed in the lapilli layer, which was observed lower than 20cm depth. Then, C cycle in the forest – soil system in this site is conducted between vegetation above ground and surface organic soil with 20cm thickness. C storages in a layer between soil surface and the depth of 5cm were about 35 C-t/ha in July 2002, 15 and 18 C-t/ha in April and December. Supply of organic C as throughfall and litterfall were 0.1 and 1.4 C-t/ha/yr, and soil respiration was 5 C-t/ha/yr. These evaluated values are not coincident with seasonal variations of C storage in soil layer. This deflect is caused by respiration of alive root and decomposition of dead root in soil layer.

Conclusion

In this site, C migration and fixation in organic soil layer was evaluated, and estimated to be a sink of C since 19th Century. In soil layer, C storage showed evident seasonal variation. These seasonal variations are caused by root respiration and decomposition of death root. These results will be applied to some C cycling models, and contribute the investigation whether forest plant – soil system will be the C source or sink in future