Distribution of Ammonium-Bearing Clay Minerals and their $\delta^{15}N$ values Occurred in Shallow-Seafloor Hydrothermal System in Kagoshima bay, Southern Kyushu, Japan.

*Jaeguk Jo[1], Toshiro Yamanaka[2], Youko Miyoshi[3], Jun-ichiro Ishibashi[4], Yoshihiro Kuwahara[4], Hitoshi Chiba[1], Tomoki Kashimura[1]

1. Graduate School of Science, okayama University, 2. Tokyo University of Marine Science and Technology, 3. The National Institute of Advanced Industrial Science and Technology (AIST), 4. Department of Earth and Planetary Sciences, Graduate School of Sciences, Kyushu University, Japan

The seafloor hydrothermal fluids occurred in the arc and back-arc systems where are often covered with thick sediments contained organic matter are characterized by a high concentration of ammonium which is considered to originate from decomposition of the sedimentary organic matter. Under these conditions, ammonium cation can be fixed in interlayer space of 2:1 clay mineral during their formation associated with hydrothermal mineralization. However, the role of this process with respect to the nitrogen cycle around the Earth's surface has not been well understood until today. In this study, we measured ammonium concentrations and their isotopic ratios in the venting hydrothermal fluids and clay fraction in the hydrothermal altered sediments obtained from Kagoshima Bay, southern Kyushu, Japan.
The submarine volcano, Wakamiko, located in the submerged Aira Caldera, which formed during the late Pleistocene (ca. 29 ka) resulting from the huge eruption of the Ito pyroclastic flow, and about 200 m in water depth of depression area as well as it is filled with thick unconsolidated sediment layer up to 80 m. The hydrothermal activity of this area is associated with the Aira magmatism, and the emitting fluid has been characterized by a high ammonium concentration up to 17 mM, respectively.
All of samples were collected around vent expect for typical marine sediments of PC-4 site. Clay minerals were recovered as a clay size fraction (2 μm) by hydraulic elutriation from the core sediments and then samples repeatedly treated by 30 % hydrogen peroxide solution and finally KOBr-KCl solution to remove organic matter and exchangeable ammonium. After that clay fractions were measured by XRD for identification of clay minerals as well as their chemical composition were measured by EPMA. And NH group were detected by FT-IR. Nitrogen contents and their isotopic ratios were measured by EA/irMS. Total nitrogen (TN) contents and inorganic nitrogen (IN) contents were ranging from 0.03 to 0.28 μg/g and from 0.002 to 0.01 μg/g, respectively. And $\delta^{15}N_{TN}$ and $\delta^{15}N_{IN}$ values were ranging from -6.2 to +4.6 ‰(av. +0.3 ‰) and from -1.7 to +5.1 ‰(av. +1.2 ‰), respectively. The $\delta^{15}N$ values of venting hydrothermal fluids and porefluids were ranging from -1.8 to +1.9 ‰(av. -0.2 ‰) and from +2.4 to +2.9 ‰ (av. +2.7 ‰), respectively. Particularly, $\delta^{15}N_{IN}$ values can be divided two groups, relatively 15N-enriched and 15N-depleted. And those trends were consistent with the difference of $\delta^{15}N$ values between hydrothermal fluids and pore fluids. Further study, it is required that understanding of nitrogen fractionation between fluid and mineral in hydrothermal system through the synthesis of ammonium-smectite.

Keywords: seafloor hydrothermal system, nitrogen cycle, 2:1 clay mineral, ammonium, nitrogen isotope

