Microbial CO_2 reduction continuing for millions years in Neogene mudstone resulting in extreme ^{13}C-enrichment

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The Horonobe Underground Research Laboratory (URL) project has been conducted for the generic purposes of geoscientific research and R&D on technologies which will be used during the geological disposal. As part of this project, deep boreholes were drilled to obtain information on the hydrogeological characteristics of the Koetoi and Wakkanai formations. Around the boundary between these formations, saline groundwater was diluted with meteoric water [1].

The Horonobe area is on the eastern margin of a Neogene to Quaternary sedimentary basin which is a region of oil and gas accumulation. $\delta^{13}C$ of paired CH_4 and CO_2 obtained from the project shows relatively heavy values. Previous study [2] reported that CH_4 found in the URL area was affected by microbial secondary oxidation since sedimentation of the Wakkanai Formation. However, another work [3] suggested that CH_4 was produced by microbial CO_2 reduction in a closed system. In this study, we make clear the origin of CH_4.

Our results of $\delta^{13}C - \delta D$ systematics are evidence that CO_2 reduction is the primary source of CH_4 in this area. Possible secondary oxidation [2] may be caused in a sample bottle after sampling due to the artifact. Correlation of $\delta D_{CH4\text{-}H2O}$ also suggests CO_2 reduction, however, $\delta D_{CH4\text{-}H2O}$ around the formation boundary does not match the CO_2 reduction line, which implies that intrusion of meteoric water through fractures would happen relatively recently.

Our results also show that the Koetoi Formation can be assumed an open system regarding to CO_2 supply although the Wakkanai Formation can be a closed system. This is consistent with occurrence of carbonate veins having heavy $\delta^{13}C$ value mostly in the Wakkanai Formation. In this closed environment, CO_2 reduction continuing for millions years would result in extreme ^{13}C-enrichment of CH_4, CO_2, and carbonate.

[1] Ishii *et al*. (2007) *J. Geol. Soc. Jpn* **113** 41-52. [2] Funaki *et al*. (2012) *J. Geograph* **121** 929-945. [3] Tamamura *et al*. (2014) *Chikyukagaku* **48** 39-50.