

## Methane production potential of subsurface microbes in Pleistocene sediments from a water-dissolved natural gas field in central Japan

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As much as 20% of the world's natural gas resources is estimated to be of biogenic origin [1]. This implies that subsurface anaerobic microbes are important producers of natural gas. However, it is unclear when and where the microbes produced methane and what kind of substrates they utilize. To address these issues, we investigated microbial methanogenesis in Pleistocene sediments from Minami-Kanto gas field in central Japan. The gas field is widely distributed in the southern area of the Kanto Plain and the gas dissolved in the formation water consists almost solely of biogenic methane [2]. Mochimaru *et al.* found that methanogens are living in the formation water from production wells [3].

Core sediments from the depth of 287-607 m were obtained by drilling, and sludge sediments were collected from the settling ponds which were located downstream of the gas-water separators. Methane production rates from the sediments were measured in the tracer experiments using [<sup>14</sup>C]-bicarbonate and [2-<sup>14</sup>C]-acetate. Cumulative amounts of methane produced from the sediments were monitored in the long-term (tracer-free) incubation experiments.

The tracer experiments showed that CO<sub>2</sub> reduction was the main pathway of methane production. The highest rate of 1.1 nmol CH<sub>4</sub> cm<sup>-3</sup> day<sup>-1</sup>, obtained from the muddy sediment at 607 m, was comparable with those in the sediments from the Blake Ridge gas-hydrate region [4].

In the long-term incubation experiments, intense methanogenesis occurred and continued for a few months. Mass balance evaluation indicated that most of the methane was derived from kerogen. This study has demonstrated that subsurface microbes can utilize a substantial fraction of the recalcitrant sedimentary organic matter as the source of methane production.

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## *In-situ* iron isotope analysis of pyrite in ca. 3.8 Ga metasediments from Isua supracrustal belt, Greenland

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The timing of emergence of life still remains one of the unresolved questions in the early Earth. Early life could be identified and characterized by its metabolic processes, which must be deposited and preserved in the old rocks. The oldest (*ca.* 3.8Ga) sedimentary rocks on Earth occur in the Isua supracrustal belt (ISB), southern West Greenland. These rocks have been subjected to until amphibolite facies metamorphism [1,2]. Despite the contribution of the intense thermal metamorphism, carbon isotope compositions from the Isua metasediments suggested the evidence for biological carbon fixation [3,4,5]. Microbial dissimilatory iron reduction (DIR) is also considered to be one of the earliest metabolisms on Earth [6,7].  $\delta^{56}\text{Fe}$  value of Fe<sup>2+</sup><sub>aq</sub> generated by DIR is expected to have lower value, whereas negative  $\delta^{56}\text{Fe}$  values lower than -1 ‰ are not found in the sedimentary record prior to 2.9Ga. Here, we report the *in-situ* iron isotope analysis of pyrite in sedimentary rocks from the ISB, using femtosecond laser ablation multi-collector ICP-MS technique (fs-LA-MC-ICP-MS)[8]. We obtained a large variation of iron isotope data from -2.41 to +2.35 ‰ in  $\delta^{56}\text{Fe}$  values, from 212 points of pyrite grains in 15 rock specimens, including metachert, muddy metachert, BIF, carbonate rock and conglomerate. The distribution of  $\delta^{56}\text{Fe}$  values varies depending on the lithology, whereas no correlation could be found between  $\delta^{56}\text{Fe}$  values and the metamorphic zone.

Low  $\delta^{13}\text{C}$  values of graphite in ISB muddy metachert suggested the existence of biological carbon fixation [5].  $\delta^{56}\text{Fe}$  values of pyrite grains from the same samples show lower  $\delta^{56}\text{Fe}$  values, which suggested the occurrence of microbial DIR in the Early Archean.

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