

INVESTIGATION OF *GEM*-ALKANES IN SURFACE SEDIMENTS FROM THREE METHANE-SEEP SEA AREAS OFF JAPAN

Shigenori OGIHARA¹, Yifeng CHEN¹, Ryo MATSUMOTO¹ and Juichiro ASHI²

1. *Earth & Planetary Science, University of Tokyo*, 2, *Ocean Research Institute, University of Tokyo*

Mud samples collected from three methane-seep sites in the sea around Japan were analysed. All samples contain a small amount of pentamethylcosane (PMI) that characterizes anoxic oxidation of methane (AOM). The feature of the three samples is that they contain several kinds of *gem*-alkanes. These are the predominant biomarker compounds in the samples analysed in this study. The composition of these biomarkers is different from the known features of the methane-seep sites.

Samples (1) Surface sediment on top of a mud volcano in the Nankai Trough: Nankai Trough is the subduction margin between the Philippine Sea Plate and the Eurasia Plate. The current accretionary prism is building out from the trench and is increasing in thickness landward. The Kumano forearc basin is located east of the Kii Peninsula and is the forearc basin of the Nankai Trough. The 2002 “DAISINKAI” project investigated the Kumano basin for methane hydrate. KP-2 is the piston core collected from the top of one of the mud volcano in the Kumano basin, and the water depth was 1930 m. (2) Surface sediment covered by a bacterial mat with cold seep in the Ryuyo Canyon: In the eastern Nankai Trough, the accretionary prism formed by offscraping of incoming sediments from the Philippine Sea Plate has been investigated by the French-Japanese project since 1984. The Ryuyo submarine Canyon is located 50 km off Tokai, and is regarded as an antecedent valley. The sample was collected during the 1989 Kaiko-Nankai cruise Dive 821 “Shinkai 2000” at the Ryuyo Canyon (1093 m). The sampling point was covered by a bacterial mat. Some *Calyptogenia* colonies were observed around the sampling point. (3) Surface sediment from methane seeping pot hole from the Umitaka spur off Naoetsu: Large pock marks and mud volcanoes have been observed on a small ridge named the Umitaka spur, at 900-1000 m water depth in the Naoestu basin of the eastern margin on the Japan Sea. An echo-sounding survey revealed a number of magnificent methane plumes, 600-700 m in height, reaching up to shallow waters of 200 to 250 m depth. This area is one of the most active methane-seep sites in the world. The ridge sediments were recovered by 5.5 m long piston cores during the Umitaka-maru 2004 cruise. The sample used in this study is muddy sediment with adjacent gas hydrate and carbonate nodules.

Results: (1) the mud volcano in the Nankai Trough and (3) the Umitaka spur off Naoetsu: 2,2-Dimethylalkanes of even carbon number are the predominant biomarkers in the mud samples from these two areas. The carbon isotope composition of 2,2-dimethylalkanes is between -29.2 and -28.2 per mil. The small amount of other *gem*-alkanes such as, 3-ethyl-3-methylalkane, 3,3-dimethylalkane, 5,5-diethylalkane, 6,6-diethylalkane, 2,2-dimethylalkane, 5-ethyl-5-methylalkane and 5-butyl-5-ethylalkane are present. Another feature is the small amount of alkylcyclopentanes. Neither PMI nor crocetane that characterizes AOM are detected in both samples. (2) Ryuyo Canyon: Alkylcyclopentanes with even number of carbons and 5,5-diethylalkanes following it are present in high quantities in this sample. The carbon isotope composition of 5,5-diethylalkanes is between -31.3 and -24.6 per mil, and alkylcyclopentanes are between -31.9 and 26.3 per mil. Another feature of this sample is that it contains unsaturated PMI with 3 to 5 double bonds. The carbon isotope composition of unsaturated PMIs is between -122 and -109 per mil, which indicates a methanogenic origin.

Discussion: *gem*-Alkanes have been found in sedimentary rocks back to the Precambrian and in hydrothermal fluids (Mycke et al., 1988; Simons et al., 2002; Kenig et al., 2004). Their origin is unknown, however, they may be of autochthonous microbial origin, possibly from bacteria that exploit the redox gradients prevailing in hydrothermal systems (Greenwood et al., 2004). The carbon isotope composition of *gem*-alkanes in this study shows that they are not of methanogenic origin. In our presentation, we will discuss the origin of *gem*-alkanes detected in the sediments of three methane-seep sites in the seas around Japan.

REFERENCES

- Greenwood P. F., Arouri K. R., Longman G. A. and Summons R. E. (2004) Abundance and geochemical significance of C_{2n} dialkylalkanes and highly branched C_{3n} alkanes in diverse Meso- and Neoproterozoic sediments. *Org. Geochem.* **35**, 321-346.
- Kenig F., Simons D.-H., Crich D., Cowen J. P., Ventura G. T., Rehbein-Khalily T., Brown T. C., and Anderson K. B. (2004) Branched aliphatic alkanes with quaternary substituted carbon atoms in modern and ancient geologic samples. *Proc. Natl. Sci. USA* **100**, 12554-12558.
- Mycke B., Michaelis W., and Degens E.T. (1988) Biomarkers in sedimentary sulfides of Precambrian age. *Org. Geochem.* **13**, 619-625.
- Simons D.-H., Kenig F., Crich D., and Schröder-Adams C. J. (2002) Significance of novel branched alkanes with quaternary carbon centers in black shales (abstract). *Geochim. Cosmochim. Acta* **66**, A718.