Quantitative determination of methane and its isotopologues in deep marine sediments at IODP 370 site C0023, off Muroto, Japan

ELLEN LALK[1*,2], DAVID T. WANG[1,3], ARTHUR J. SPIVACK[4], SHUHEI ONO[1]

[1]Department of Earth, Armospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA
[2]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA
[3]ExxonMobil Upstream Research Company, Spring, TX
[4]Graduate School of Oceanography, University of Rhode Island, Narragansett, RI

Methane (CH_4) geochemistry and cycling are of particular interest in regards to deep microbial life because methanogenesis is a terminal process of organic matter decomposition such that it is expected to represent the deepest microbial metabolisms. Standard methods of extracting and determining dissolved CH_4 in sediment cores (e.g. headspace analysis) fail in poorly-competent and gassy sediments due to the formation of gas pockets during core retrieval. Further, no method has been described for extraction of CH_4 from sediments for isotopologue analysis.

During IODP Expedition 370, the Scientific Party collected a set of whole-round core slice samples for gas analysis, which were immediately frozen and maintained at -80°C[1]. Here, we report a method to quantitatively extract CH_4 and other gases from the core slices. Dissolved gases (CH_4, N_2, Ar, O_2) released from sediment core samples upon thawing are measured using a quadrupole gas analyzer. The *in situ* CH_4 concentration can then be estimated by applying corrections to account for both depressurization-induced gas loss during core retrieval, and entrainment of air during subsampling and initial freezing abord D/V *Chikyu*; this method is similar to one previously developed to determine *in situ* CH_4 concentrations from depressurization-associated gas pockets [2].

For samples that yield enough gas for clumped isotopologue analysis (ca. >1 mL, STP), the $^{13}CH_3D$ abundance, as well as apparent equilibrium temperatures calculated from the relative abundance of four methane isotopologues ($^{13}CH_4$, $^{12}CH_4$, $^{12}CH_3D$, and $^{13}CH_3D$), will be reported. Clumped isotopologue analysis can potentially target whether methane found in sediments was formed *in situ* by microbial methanogenesis, or at greater depth by thermal cracking of organic materials, and migrated upward.

[1] Expedition 370 Preliminary Report (2017)
[2] Spivack et al. (2006), *Proceedings of the Ocean Drilling Program 201*