## Tectonically enhanced deep subsurface microbial carbon cycling in the Nankai Trough, Japan

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The occurrence and activity of microbial communities in deep subsurface environments are highly investigated. However, the abundance of microbial life and the source of energy necessary for these microorganisms remain controversial and under explored.

Here we investigate the impact of depositional and tectonic events on those deep microbial processes in sediments at IODP (Integrated Ocean Drilling Program) Site C0006, drilled and sampled during IODP Expedition 316 at the Nankai Trough, Japan. The observed methane isotope profiles indicate that active microbially mediated methane production occurs in sediments below 450 mbsf. This observation is supported by alkalinity measurements, indicating a source of inorganic carbon into the pore water as a by-product of deep in situ methane production. Thus, our data provide evidence for carbon cycling in these deep subsurface sediments. This is likely related to the highly dynamic tectonic regime at Nankai Trough, where tectonically induced temporary temperature increase can re-stimulate organic matter at distinct depths.

While tectonic activity can lead to the reactivation of recalcitrant organic matter, the variable sedimentary system provides niches for microbial abundance. The newly available/accessible organic carbon compounds fuel the microbial community – resulting in an onset of microbial methane production several hundred meters below the seafloor. This process is also captured in the isotope signal of methane, and thus methane isotopes can help us pin down locations of active microbial processes in deeply buried sediments.

## Accurate isotope composition measurements by a miniature LMS system designed for in situ space research

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A miniature laser ablation reflectron time-of-flight mass spectrometer designed for in situ space research for sensitive and accurate measurements of the elemental and isotopic composition of extraterrestrial material is described and its performance for accurate in situ measurements of isotope composition is demonstrated [1-4]. A ns- (266 nm, 5 ns, 20 Hz) [1-2] and a fs-laser ablation ion source (775 nm, 190 fs, 1kHz) [3] were used to investigate figure of merits (mass resolution, dynamic range, detection sensitivity and accuracy of measurements). The studies are performed with a high spatial resolution by focusing the pulsed laser radiation to spot of about Ø20 and 40 µm, respectively on the sample surface. The measurements are conducted with high dynamic range of at least  $10^8$  and a mass resolution (m/ $\Delta$ m) of up to 800-900, as measured at <sup>56</sup>Fe [1]. High detection sensitivity is achieved in measurements of both, metallic and non-metallic elements (tens of ppb) [1]. While ns-laser ablation ion source have to be calibrated with appropriate NIST standard reference materials (SRM), the relative sensitivity coefficients (RSC) were determined to be close to one when the fs-laser ablation ion source was applied [3]. Hence, the coupling of LMS with a fs laser system is preferable and is of considerable interest for the development of standard-less instruments. We developed a measurement procedure, which will be disscussed in detail, that allows LIMS to measure isotope composition of elements, e.g. Ti, Cr, Pb, etc., with a measurement accuracy and precision in the per mille and sub per mille level for the first time and is comparable to the performance of other wellknown and accepted measurement techniques (TIMS, SIMS and LA-ICP-MS) [2-3]. High performance of the LMS instrument offers versatile applications regarding in situ investigations of the chemical composition (elemental and isotopic) of extraterrestrial surface material [1-4].

[1] Riedo et al. (2013) J. Mass Sectrom. 44, 1-15. [2] Riedo et al. (2013) PSS, submitted. [3] Riedo et. al. (2013) JAAS, submitted. doi: 10.1039/C3JA50117E. [4] Tulej et al. (2012) Int. J. Spectros., doi:10.1155/2012/234949.