Thermogenic hydrocarbons in Mid Ocean serpentinites

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The progressive hydration of mantle-derived peridotites is known to support deep microbial ecosystems unrelated to photosynthesis. Relics of endogenic, microbiologically-driven, carbon accumulations have been recently discovered strictly associated to hydrogarnet minerals in serpentinized rocks coming from the MAR 4-6 °N region [1]. The presence of this colonization suggests that the serpentinization byproducts can constitute a valuable source of carbon and metabolic energy for microorganisms held deep in the oceanic lithosphere. We have decided to re-investigate the recently described relics of deep microbial ecosystems to study its fate through ageing and thermal degradation. A set of high resolution micro-imaging techniques (HRTEM, Raman and Fourier-transform infrared microspectroscopy, and STXM at the carbon K-edge) have been applied to characterize the organic carbon speciation and its spatial distribution at the micrometer scale. Our data show that the biologically derived organic matter colocalized with the hydrogarnets has experienced thermal degradation and aromatization while a light fraction constiting of C_6-C_{10} aliphatic compounds associated to carboxylic functional groups wet the surrounding bastite and the late vein network.

Ecosystem-hosting serpentinites can thus be seen as source rocks generating deep thermogenic hydrocarbons which then migrate upward and mix with the complex pool of organic compounds discharged at hydrothermal vents.

This work shows how a combination of complex biological and geochemical processes contribute to the hydrothermal carbon cycle at Mid Ocean Ridges.

[1] Ménez, B., Pasini, V., Brunelli, D., 2012. Life in the hydrated suboceanic mantle. Nature Geoscience 5, 133–137.

Novel Method for Compound Specific Stable Isotope Analysis of contaminated groundwater across the sediment-water interface

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Chlorinated benzenes are toxic contaminants frequently identified in groundwater. Because a variety of bacteria are able to conduct reductive dehalogenation of these compounds, Monitored Natural Attenuation (MNA) is a potentially effective technique for groundwater remediation. Here, we evaluate the potential for Compound Specific Isotope Analysis (CSIA) to detect *in situ* biodegradation of chlorinated benzenes in a historically contaminated site. Groundwater samples were collected during three sampling campaigns in 2009 and 2012 along a contaminant plume that discharged to surface water until a sheet pile barrier was installed in December 2008 and controlled the release. A passive sampling "peeper" method for conducting microscale CSIA sampling at the groundwater - sediment pore water interface, was also tested for its suitability for CSIA.

In the highest concentration zone, the most ^{13}C-depleted carbon isotopic signatures for dichlorobenzenes (DCBs) and 1,2,4-trichlorobenzene (1,2,4-TCB) were measured ranging from -32.4 ± 0.5‰ to -29.6 ± 0.5‰. Downgradient of the plume, moderate (2 to 4 ‰, 1,4-DCB and 1,2,4-TCB) to large (10 ‰, 1,2-DCB) enrichments in the heavy stable carbon isotope were observed with values as enriched as -27.9 ± 0.5‰ (1,4-DCB), -20.5 ± 0.5‰ (1,2-DCB), and -28.2 ± 0.5‰ (1,2,4-TCB) in 2009. A similar trend was confirmed in 2012. The most enriched values were measured close to the groundwater / sediment pore water interface where high microbial activity may have been responsible for biodegradation. A novel method for sampling for CSIA via peeper diffusion sampler with a polysulfone membrane showed promise for collecting chlorinated benzene-bearing water samples without significantly affecting contaminant isotope signatures. This new approach will be used to extend the current field investigation by measuring CSIA trends at a fine spatial resolution across the sediment - pore water interface.