U-Th systematics and chronology of of CH_4-derived $CaCO_3$ crusts of the Barents Sea

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$CaCO_3$ crusts forming due to methane oxidation at seafloor seepage sites serve as archives of past fluid flow and methane discharges into ocean and atmosphere. U incoporation into $CaCO_3$ during precipitation offers the opportunity to date the crust formation and growth via U-Th systematics (e.g., Aharon et a., 1997; Teichert *et al.*, 2003).

We present U-Th and $^{87}Sr/^{86}Sr$ data obtained on such $CaCO_3$ crusts recovered from the Barents Sea floor using a remotely operated vehicle. $CaCO_3$ phases occur in different modes within the crusts – disseminated within the siliclastic matrix, porosity- and late cavity- filling. These $CaCO_3$ domains, sampled by microdrilling, display $[^{230}Th/^{232}Th]_{AR}$ from 0.9 up to ~200 and ^{232}Th concentrations from ~10 to 7000 ppb. Intra-crust U-Th dates range from ~13.1 ± 0.4 to 8.9 ± 0.4 ka. Older dates come from $CaCO_3$ disseminated within the sediment matix while younger dates are from late cavity filling $CaCO_3$. Layered cavity fills yield resolvable growth histories on the order of 1.0 kyr. Combined such dating results can be used to constrain the histories of CH_4 seepage in the Barents Sea.

$^{87}Sr/^{86}Sr$ has been analysed on aliquots drilled adjacent to U-Th sample sites. For the majority of crust samples both $^{87}Sr/^{86}Sr$ and $\delta^{234}U$ are close to expected values for modern/Holcene seawater. In addition, a sample of a matrix-dominated tubestone representing a subsurface carbonatized fluid conduit, has more radiogenic $^{87}Sr/^{86}Sr$ values and $\delta^{234}U$ closer to secular equilibrium. Such contrasts in $^{87}Sr/^{86}Sr$ and initial $\delta^{234}U$ reflect distinctly different fluid chemistries forming surface and subsurface $CaCO_3$ precipitates. These data, together with crust data from from other seeps, demonstrate the utility of U-Th for constraining CH_4 seepage duration and absolute timing.

[1] Aharaon, P., *et al.*, 1997, GSA Bulletin, v. 109, p. 568-579. [2] Teichert, B. M. A., *et al.*, 2003, Geochimica et Cosmochimica Acta, v. 67, p. 3845-3857.

Distribution of Metalloenzymes in Pacific Ocean Environments as Detected by Proteomic Analysis

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The use of mass spectrometry based proteomics has the capability for direct measurement of proteins produced by microbial life. These proteins can include biomarkers for nutrient stress or microbial taxonomy, as well as enzymes that are responsible carrying out biogeochemical reactions. Most biogeochemically-relevant enzymes require one or more metal atoms for catalytic activity. We report on the analyses of samples collected from a range of depths in the Equatorial Pacific and Eastern Tropical South Pacific. Analyses involved total protein extractions, enzymatic digestion, multi-dimensional chromatographic separation, mass spectrometry analyses, peptide mapping by high performance computing, and quantitative estimates. Proteins of interest will be discussed with a particular focus on metalloenzymes that contain nickel, cobalt, copper, and iron.

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