Clumped and Stable Isotope Characterization of Methane Seep Environments

NIVEDITA THIAGARAJAN[1*], ANTOINE CREMIERE[1], CLARA BLÄTTLER[2], JOHN HIGGINS[2] AIVO LEPLAND[3] AND JOHN EILER[1]

[1]CalTech Pasadena, CA 91125 *nivedita@caltech.edu
[2]Princeton University Princeton, NJ 08544
[3]Geological Survey of Norway, 7491 Trondheim, Norway

Marine cold seeps are characterized by methane-rich fluid migration and release at the seafloor, and contain diverse and active microbial communities. A consortium of methane-oxidizing archaea and sulfate reducing bacteria control aneroebic methane oxidation, which is the main methane sink in marine sediments. Methane oxidation coupled with sulfate reduction results in elevated carbonate alkalinity, which promotes carbonate precipitaiton.

We have analyzed a suite of methane-derived authigenic carbonate (MDAC) crusts as well as associated methane from the North and Barents Sea using stable and clumped isotopes ($\delta^{13}C$, $\delta^{18}O$, $\delta^{44}Ca$, δD, Δ_{47}, and Δ_{18}) to characterize the sources of fluids as well as changes in the diagenetic environment. Additionally, we assess the potential of MDACs as a paleotemperature archive.

Under conditions where gas seepage rates are moderate, MDACs form in the subsurface, below the sediment-water interface. In these environments, the HCO_3^- source for MDAC formation is predominantly from methane oxidization. At sites where gas supply is high, MDACs form in the shallow subsurface and incorporate HCO_3^- from two sources: methane oxidation and seawater. We find that MDACs formed in deeper subsurface environments have low $\delta^{13}C$, high $\delta^{44}Ca$, high-Mg-calcite mineralogy and Δ_{47}-temperatures (0-6^{o}C) consistent with subsurface precipitation in isotopic equilibrium. The shallow subsurface MDACs have higher $\delta^{13}C$ values, lower $\delta^{44}Ca$ values, are predominantly aragonite and have a wide range in Δ_{47}-based apparent temperatures (0-25^{o}C) reflecting a failure to attain isotopic equilibrium.

The high apparent temperatures and low $\delta^{44}Ca$ values seen in the aragonite MDACs suggest three kinetic processes: a kinetic isotope effect (KIE) due to the incomplete equilibration of carbon and oxygen isotopes among DIC species from the different sources of DIC (i.e., seawater and methane-sourced DIC), a KIE due to fast, irreversible precipitation, and a third KIE that we hypothesize occurs during methane oxidation, producing CO_2 with anomalously low Δ_{47}-values (hot apparent temperatures).