

## Clumped Isotope Characterization of Authigenic Carbonates and Methane in Cold Seep Environments

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Cold seep environments are characterized by methane-rich fluid migration and release at the seafloor. Methane cold seeps are also intimately linked to diverse microbial communities. A consortia of methane-oxidizing archaea and sulfate reducing bacteria control anaerobic 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 precipitation.

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

At sites where gas seepage rates are moderate, MDACs form at the subsurface, below the sediment-water interface. In these environments, the  $\text{HCO}_3^-$  source for MDAC formation is predominantly from methane oxidation. At sites where gas supply is high, MDACs form at a shallow subsurface and incorporate  $\text{HCO}_3^-$  from two sources: methane oxidation and seawater. We find that MDACs formed in deeper subsurface environments have smaller grain size, low  $\delta^{13}\text{C}$ , high Mg-calcite content and  $\Delta_{47}$ -temperatures (0-6°C) consistent with subsurface precipitation. However, MDACs formed at shallow subsurface have larger grain sizes, higher  $\delta^{13}\text{C}$  values, are predominantly aragonite and have very high  $\Delta_{47}$ -based apparent temperatures (10-25°C). These higher temperatures are consistent with mixing effects on  $\Delta_{47}$  values, caused by mixing of two different  $\text{HCO}_3^-$  sources (seawater and methane oxidation) with distinct bulk and clumped isotope compositions. These data suggest that Mg-calcite MDACs formed in the deeper sub-surface (but not aragonitic MDACs forming close to the seafloor) are promising targets for paleotemperature reconstructions.

We also measure the isotopic composition of methane and find that the methane is consistent with a mixture of biogenic and thermogenic sources in our study area.