

Constraining temperature and reaction chemistry kinetics in cold-water methane seeps using dual-clumped isotopes

PHILIP STAUDIGEL¹, DONG FENG², JÖRN PECKMANN³,
AMELIA J DAVIES¹, MATTIA TAGLIAVENTO¹, MIGUEL
BERNECKER¹ AND JENS FIEBIG¹

¹Goethe University Frankfurt

²South China Sea Institute of Oceanology, Chinese Academy of Sciences

³Universität Hamburg

Presenting Author: staudigel@em.uni-frankfurt.de

Methane seeps represent an important interface between oxidizing and reducing environments, which facilitate multiple exchange reactions, often precipitating copious quantities of carbonate minerals. Constraining the rate of these reactions in modern and ancient systems is critical to understanding the modern and ancient carbon cycles. The geochemistry of the carbonate minerals precipitated in these systems reflects the biogeochemical conditions present during mineralization and could be used to determine factors such as temperature, as well as reaction mechanisms and rates. Previous work applying clumped isotopes towards studying these systems has shown that there are significant kinetic biases which must be addressed before it can be applied unambiguously to ancient systems (Loyd et al., 2016). Application of dual-clumped isotopes represents a unique tool for constraining these kinetic isotope effects, as the ¹⁸O¹³C- and ¹⁸O¹⁸O-substituted isotopologues of DIC (measured as carbonate Δ_{47} and Δ_{48} values, respectively) can behave very differently in kinetically-limited systems (Guo 2020, Bajnai et al., 2020). Using this novel technique alongside numerical models for DIC-water exchange (Watkins and Devriendt, 2022; Guo, 2020), we can constrain the factors that govern the chemical evolution of the methane seep. We present a dataset of carbonate precipitates' Δ_{47} and Δ_{48} values from a modern cold seep in the South China Sea. These samples have variable kinetic offsets from equilibrium, which can be used to accurately calculate the seep temperature. The slope and magnitude of these kinetic offsets contains additional information regarding the rate and mechanisms of methane oxidation.

References:

Loyd et al., (2016) “Methane seep carbonates yield clumped isotope signatures out of equilibrium with formation temperatures” Nat. Com.

Bajnai et al., (2020) “Dual clumped isotope thermometry resolves kinetic biases in carbonate formation temperatures” Nat. Com.

Guo, W. (2020) “Kinetic clumped isotope fractionation in the DIC-H₂O-CO₂ system: Patterns, controls, and implications” Geochim. et Cosmochim. Acta

Watkins, J. Devriendt, L. (2022) “A Combined Model for Kinetic Clumped Isotope Effects in the CaCO₃-DIC-H₂O