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## Clumped Isotope Composition of Cold Seep Carbonates: Patterns and Controls

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### Introduction

The isotopic composition of cold-seep carbonates, which form as a result of anaerobic oxidation of methane (AOM) and other hydrocarbons at marine seep sites, could provide important constraints on the subsurface environmental conditions and AOM activities. However, the presence of disequilibrium isotope effects complicates the application of various geochemical proxies to these carbonates, including the recently developed carbonate clumped isotope thermometer, leading to incorrect estimations of their formation temperatures in some cold-seep carbonates. This project seeks to systematically examine the variations of clumped isotope composition of cold-seep carbonates formed at multiple sites and to determine the environmental controls governing these variations. Particularly, we aim to test the hypothesis that the incorporation of AOM-derived dissolved inorganic carbon (DIC) causes the disequilibrium clumped isotope effects in cold seep carbonates.

### Research Progress

Our research in Yr. 2 builds on the findings of Yr. 1, and focuses on mechanistic understanding of the causes of the disequilibrium clumped isotope effects in cold seep carbonates. Specifically, we have derived the first-order estimation of the clumped isotope composition of AOM-derived CO<sub>2</sub> and investigated how it affects the isotope composition of DIC that gets incorporated into cold-seep carbonates. We have also explored inverse methods to reconstruct the formation environment of cold seep carbonate based on their isotope compositions.

#### *A. Theoretical estimation of clumped isotope composition of CO<sub>2</sub> derived from AOM*

One key component of our research hypothesis is that the DIC derived from AOM are depleted in their clumped isotope composition relative to the expected equilibrium values and lead to the disequilibrium clumped isotope signals in some modern cold-seep carbonates. To test this hypothesis, we estimated for the first time the clumped isotope composition of CO<sub>2</sub> derived from AOM through theoretical calculations. The production of CO<sub>2</sub> is believed to occur during the last step of AOM and is catalyzed by the formylmethanofuran dehydrogenase with the N-carboxymethanofuran ion as the intermediate. However, the exact reaction mechanism involved in the decarboxylation of N-carboxymethanofuran ion is not well constrained. We therefore estimated the isotope composition of CO<sub>2</sub> derived from a similar decarboxylation reaction, pyruvate decarboxylation, whose reaction mechanism is better known. Our calculations based on first-principles transition state theory confirm that CO<sub>2</sub> derived from pyruvate decarboxylation is depleted in clumped isotope composition relative to the expected equilibrium values. This finding thus adds strong support to our research hypothesis.

#### *B. Experimental and theoretical investigation of the clumped isotope fractionations in the DIC-H<sub>2</sub>O-CO<sub>2</sub> system*

To determine how the isotope composition of AOM-derived CO<sub>2</sub> influences the isotope composition of DIC involved in cold seep carbonate formation, we conducted controlled laboratory experiments and numerical modeling to systematically investigate the clumped isotope fractionations among the DIC-H<sub>2</sub>O-

CO<sub>2</sub> system. In these experiments, CO<sub>2</sub> gases with known isotope compositions were exposed to high pH Ba(OH)<sub>2</sub> solutions, leading to rapid formation of BaCO<sub>3</sub> solids. Analysis of these BaCO<sub>3</sub> solids shows that their clumped isotope compositions correlate with the isotope compositions of the CO<sub>2</sub>. Similarly, numerical modeling shows that, under low-medium pH conditions, the clumped isotope composition of DIC exhibits strong correlation with that of CO<sub>2</sub> and then gradually evolves towards the equilibrium values. Together, these findings further support our hypothesis that AOM-derived CO<sub>2</sub> and DIC is the cause of the disequilibrium clumped isotope effects in cold seep carbonates.

### ***C. Reconstruct the formation environment of cold seep carbonate based on their isotope compositions***

In Yr. 1, we developed a reactive transport model to calculate the temporal and spatial evolution of the isotope composition of cold seep fluid, including carbon isotope, oxygen isotope and clumped isotope composition of each dissolved inorganic carbon species in the seep fluid. In Yr. 2 we have used this numerical model to determine the key environmental parameters that control the clumped isotope composition of cold seep carbonates, and explored various methods to reconstruct the formation environment of cold seep carbonates by comparing the experimentally measured isotope composition with the model predictions. Such comparison, with further development in the next grant year, will enable us to place quantitative constraints on the temperature, relative methane flux and other environmental parameters at marine seep sites.

### **Impact on Career Development**

In Yr. 2 this PRF grant has supported 5 guest students: 3 undergraduates (1 female) and 2 graduate students. The project exposed these students (from 3 majors: Geochemistry, Chemistry and Operations Research) to new analytical and modeling techniques, and provided them opportunities to interact with experts in different fields. This project also provided the PI a unique opportunity to thoroughly investigate the physicochemical principles governing stable isotopologue fractionation in the DIC-H<sub>2</sub>O-CO<sub>2</sub> system, and have opened many new research directions.