THE EFFECTS OF PRECIPITATION RATE ON CLUMPED ISOTOPES: RE-EVALUATING THE ACCURACY OF A NEW TECHNIQUE

Sean T. Murray, Peter K. Swart, and Monica Arienzo

PROJECT OBJECTIVES

- Manually precipitate calcium carbonate under varying environmental conditions with a control on all factors that have a role in the final composition.
- To quantify the variation in Δ_{47} CO_2 with changes in precipitation rate in order to evaluate the effect on clumped isotope measurements.

PROJECT RATIONALE

The variation of multiply substituted "clumped" isotopologues in calcium-carbonate, measured as the Δ_{47} of CO_2, has been found to be a precise and easily accessible paleothermometer. The use of this technique has a major advantage because it does not require any knowledge of the original solution from which the carbonate precipitated. This is because the multiple substitution of isotopes into a molecule is strongly dependent on temperature and is not reliant upon the oxygen or carbon composition within the solution. The use of clumped isotopes as a paleothermometer opens up a new realm of possibilities in the variety and age of samples that can be measured.

The ability to accurately measure clumped isotopes is a relatively new and unexplored field of geochemistry. When the paleothermometer based on clumped isotopes was first discovered by Ghosh et al. (2006), it was explained as a simple and elegant approach that could measure any carbonate, biological or inorganic, at any temperature. Consequently many laboratories quickly adopted the technique and utilized it for a multitude of applications without further exploring the development and proper measuring of clumped isotopes. With further research, it was found that clumped isotopes suffer from a few problems characteristic of measurements in most isotope systems:

- The calibration between Δ47 and temperature is only applicable to a small range of temperatures and had to be adjusted to suit more extreme ranges.
- Some carbonates (e.g. deep water corals, speleothems) showed fractionation in their clumped isotope measurements relative to other carbonates.
- The accurate measurement of clumped isotopes is susceptible to many contaminations and drift within the machines that varies with each machine.

In order to explain some of these patterns we will examine the behavior of the Δ_{47} of CO_2 produced from the dissolution of carbonates. For example the effect of precipitation rate on the isotopic composition of carbonates was shown in Romanek et al. (1992) to have a measurable enrichment factor (ε) of 2.7% in aragonite and 1.0% in calcite. While this effect is minimal in $\delta^{13}C$ and $\delta^{18}O$ measurements, its impact on Δ_{47} of CO_2 is magnified many times over and needs to be quantified to increase the accuracy of clumped isotope measurements.

PROJECT DESCRIPTION

The Stable Isotope Laboratory at RSMAS has acquired a Thermo MAT-253 mass spectrometer which is capable of measuring clumped isotopes, making our lab one of less than twenty world-wide. This project entails precipitation of carbonate samples in an apparatus that is capable of controlling the temperature, precipitation rate, precipitate mineralogy, and solution chemistry. The project will follow the methods of Romanek et al. (1992) using a water-jacketed reaction vessel (±0.1 °C).

Each precipitation experiment will be performed at a range of Earth temperatures and in a suite of precipitation rates. The experiment starts with making a stock solution of $NaHCO_3$ dissolved in deionized water plus the addition of CaCl. At this point, an equilibrium between the gaseous and aqueous phases must be reached by the continuous pumping of CO_2/N_2 gas until the solution is supersaturated. To encourage the precipitation of calcite, a known quantity of a seed material of pure $CaCO_3$ will be added to the solution. The presence of the seed will dictate the crystalline structure that is precipitated out ensuring a pure calcite. As the calcite is precipitated out, the solution chemistry will be constantly changing. To control this and keep the environment constant, a computer-controlled system will analyze the environment using pH probes and then add in an equivalent amount of chemical solution to readjust the environment back to the original saturation state. By doing this, each molecule within the precipitated calcite will be formed from the same environmental conditions and the rate of precipitation can be controlled by increasing or decreasing the saturation.

After each experiment, the precipitate will be dried, weighed, and analyzed by x-ray diffraction to check the composition of the sample. These samples will then be processed on our extraction line. They will be digested in a 90 °C phosphoric acid bath, releasing CO_2 gas which will be cleaned using a series of traps and vacuums. The sample will then be measured for its multiply substituted isotopologues on the Thermo MAT-253.

ANTICIPATED FINDINGS

We expect to be able to determine what the variation of precipitation rate has on the carbonate molecular structure. This will be shown if it is found that Δ_{47} values vary at the same temperature when the precipitation rate is different. If it is found that Δ_{47} values are independent of precipitation rate, then further focus on saturation state and the varying forms of high-Mg calcite, low-Mg calcite, and aragonite will be looked at. The overall impact of the experiment will be based on whether a discernible pattern can be found and applied to real life carbonate samples. Because of the possible impacts of the clumped isotope technique on the field of geochemistry, we believe it is well worth the effort to better understand what impacts the measuring of it in samples.

REFERENCES

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