Clumped Isotopes: Application to Diagenesis

Peter K. Swart

Project Purpose

The recognition that clumped isotopes of CO_2 are solely dependent upon temperature and not on the isotopic composition of the fluid from which they are formed has opened significant possibilities in unraveling the temperature and water signal as applied to diagenetic carbonates. The purpose of this project will be to investigate this technique as applied to sedimentary carbonates.

Instrumental Requirement

The first step in performing clumped isotope measurements is the acquisition of an instrument capable of simultaneously measuring mass 44-47. The instrument must also have very sensitive amplifiers at mass 47-49 (to measure the species at these masses). This instrument is being purchased courtesy of a grant from the National Science Foundation and matching financial support from the CSL and the Stable Isotope Laboratory. Once the instrument is installed and works satisfactorily, we will develop procedures to extract the CO_2 from carbonate samples and subsequently purify it without fractionation.



Figure 1. Mass spectrometer able to measure clumped isotopes. The instrument has four collectors and sensitive amplifiers that allow measuring the species at the 44-49 masses.

Project Background and Goal

Ghosh et al. (2006) demonstrated then that the abundance of ${}^{13}C^{18}O^{16}O$ in CO₂ generated from the classical reaction of carbonates with phosphoric acid, is proportional to the abundance of ${}^{13}C^{18}O^{16}O_2{}^{2^-}$ ion species within the minerals. Usually, abundances of mass 47 CO₂ are reported using the variable Δ 47 representing the difference in permil between the measured 47/44 ratio and the expected 47/44 ratio for that sample if its carbon and oxygen isotopes were randomly distributed among all isotopologues. Using this nomenclature any differences in the $\delta^{13}C$ or $\delta^{18}O$ of the water from which the mineral precipitated is taken care of by the expected 47/44 ratio and therefore the difference (Δ 47) is solely dependent upon temperature. To date, this method has been applied to a number of different carbonate systems (Affek, et al., 2008a; Affek, et al., 2008b; Ghosh, et al., 2007a; Ghosh, et al., 2007b), but not been investigated in the service of diagenesis. The first goal of this study will, thus, be to evaluate whether the clumped isotope technique can be applied to diagenetic applications.

Scope of Work

Following the delivery of a new mass spectrometer which is capable of measuring the abundances of masses 47-49, we will start to investigate the clumped signature in naturally occurring carbonates whose temperature of formation is well constrained. In addition, we will artificially produce carbonates at higher temperature in order to ascertain the temperature dependence of the Δ 47 signal in these materials.

Key Deliverables

- 1) Assessment of whether the clumped isotope technique can be applied to diagenetic applications.
- 2) Assessment of temperature dependence of the $\Delta 47$ signal in carbonates.

References

Affek, H. P., et al. 2008a, Glacial/interglacial temperature variations in Soreq cave speleothems as recorded by 'clumped isotope' thermometry, Geochim. Cosmochim. Acta, 72, 5351-5360.

Affek, H. P., et al. 2008b, 'Clumped isotopes' in speleothem carbonate and atmospheric CO2 - Is there a kinetic isotope effect? Geochim. Cosmochim. Acta, 72, A6-A6.

Ghosh, P., et al. 2006, C-13-O-18 bonds in carbonate minerals: A new kind of paleothermometer, Geochim. Cosmochim. Acta, 70, 1439-1456.

Ghosh, P., et al. 2007a, Calibration of the carbonate 'clumped isotope' paleothermometer for otoliths, Geochim. Cosmochim. Acta, 71, 2736-2744.

Ghosh, P., et al. 2007b, Carbonate clumped isotope thermometry of molluscs and its applications to Pleistocene gastropod fossils from South Dakota, Geochim. Cosmochim. Acta, 71, A319-A319.