CLUMPED ISOTOPES: THE FUTURE

Peter K. Swart

PROJECT OBJECTIVES

- Acquisition of the next generation of clumped isotope instrumentation.
- Automation of procedure.
- Understanding of artifacts associated with the procedure.

PROJECT RATIONALE

The clumped isotope method for the direct determination of temperatures in carbonates has only been around for 10 years, yet its influence on the field has been profound! Since the pioneering work of Ghosh et al. (2006) the number of papers per year has increased from ~3 in 2006 to over 50 in 2016 (Fig. 1) and of these papers the predominant application is in the field of carbonate diagenesis. The stable isotope laboratory, which is part of the CSL, has just started to publish its first papers (Murray, 2016; Murray et al., 2016; Swart et al., 2016; Vahrenkamp et al., 2014) on clumped isotopes and in 2016 hosted the 5th international clumped isotope workshop. However, despite the success of the clumped isotope method the principal instrument used for clumped isotopic analyses, the Thermo 253, has an important design flaw, mainly the occurrence of a negative base line at masses 47-49 which seriously impacts the calculation of the Δ_{47} (He et al., 2012). The result of the negative baseline is that there is a positive correlation between $\delta 47$ and Δ_{47}, the slope of which changes with time and varies significantly between different laboratories. Our laboratory has one of the steeper slopes. While it is possible to correct for the base line by measuring the base line adjacent to the mass 47 peak and then adding this to the mass 47 peak, this solution is not ideal and necessitates a significant number of extra analyses of standard gases. An example of the sloping relationship between $\delta 47$ and Δ_{47} and the corrected relationship is shown in Figure 2. The solution to the dilemma is a new generation of instruments such as the Thermo 253 plus and the Nu Perspective, which do not have the negative base line. Instruments such as the Thermo 253 plus also have the added capability of having amplifiers which are an order of magnitude more sensitive allowing smaller samples to be analyzed.

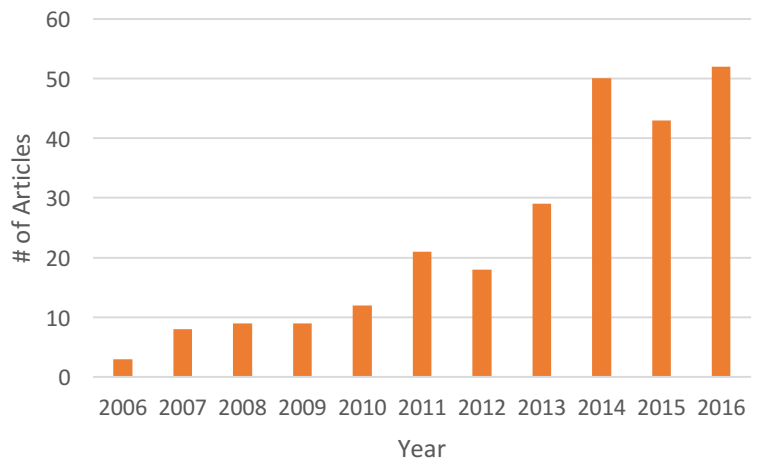

Figure 1: Number of citations in the ISI citation index with the keyword 'clumped isotope' since the first paper was published in 2006 on clumped isotopes in carbonates.

SCOPE OF WORK

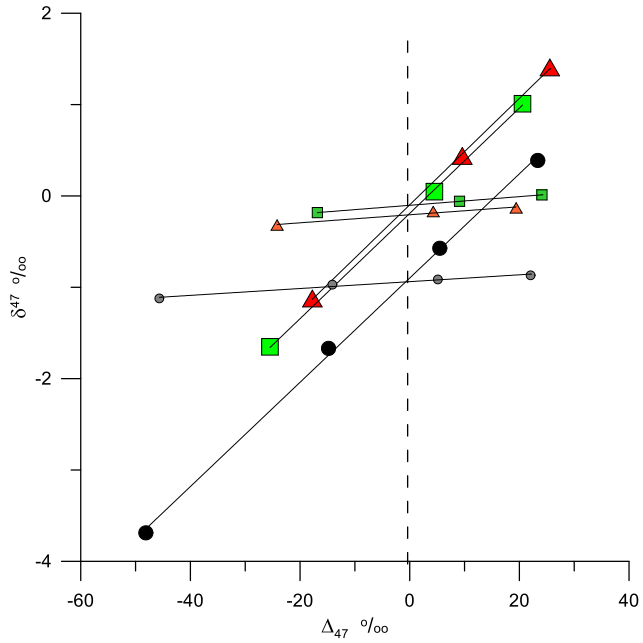

Figure 2: Comparison of the Δ_{47} and δ^{47} relationships with (shallow slope lines) and without (steep slope lines) the correction for the negative base line. The black dots represent the 1000°C heated gases, the green the 50°C equilibrated gases and the red the 25°C equilibrated gases. The correction made by measuring the background makes the relationship approximately horizontal.

We propose to acquire the funding for the purchase a new instrument to be housed at the University of Miami.

The procedure currently employed in our laboratory is completely manual. We can measure about four samples a day, one of which is a standard. With the acquisition of the new instrument we propose to transfer one instrument to an automated system.

There is still a significant uncertainty regarding artifacts associated with the extraction procedures. Notably (a) the isotopic exchange between the CO_2 and the phosphoric acid, (b) the fractionation factors as a function of temperature for different carbonate minerals, and (c) the influence of the extraction method itself upon the $\delta^{18}O$, $\delta^{13}C$, and Δ_{47}.

SIGNIFICANCE

The measurement of Δ_{47} has emerged as an essential tool in any study of carbonate diagenesis and the University of Miami is one of less than 25 laboratories worldwide which is capable of making such measurements. The acquisition of this equipment will be vital for the future of the stable isotope facility and the excellence of the CSL.

REFERENCES

Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W.F., Schauble, E.A., Schrag, D., and Eller, J.M., 2006, C-13-O-18 bonds in carbonate minerals: A new kind of paleothermometer, Geochimica et Cosmochimica Acta, v. 70, p. 1439-1456.

He, B., Olack, G.A., and Colman, A.S., 2012, Pressure baseline correction and high-precision CO2 clumped-isotope (Delta(47)) measurements in bellows and micro-volume modes, Rapid Communications in Mass Spectrometry, v. 26, p. 2837-2853.

Murray, S., 2016, The application of clumped isotopes in the study of dolomitization, University of Miami, Miami, 213 p.

Murray, S. T., Arienzo, M.M., and Swart, P.K., 2016, Determining the Δ47 acid fractionation in dolomites, Geochimica et Cosmochimica Acta, v. 174, p. 42-53.

Swart, P.K., Cantrell, D.L., Arienzo, M.M., and Murray, S.T., 2016, Evidence for high temperature and ^{18}O-enriched fluids in the Arab-D of the Ghawar Field, Saudi Arabia, Sedimentology, v. 63, p. 1739-1752.

Vahrenkamp, V.C., Barata, J., Van Leer, P.J., Swart, P.K., and Murray, S., 2014, Micro Rhombic Calcite of a Giant Barremian (Thamama B) Reservoir Onshore Abu Dhabi - Clumped Isotope Analyses fix Temperature, Water Composition and Timing of Burial Diagenesis, Society of Petroleum Engineers, v. SPE 172033.