ORIGIN OF Δ_{47} AND Δ_{48} DISEQUILIBRIUM IN CARBONATE MINERALS

Peter K. Swart and Chaojin Lu

KEY FINDINGS

- The combination of Δ_{47} and Δ_{48} proxies can be used to ascertain whether carbonates are deposited close to equilibrium or if they are affected by kinetic influences.

INTRODUCTION

The Δ_{47} proxy has caused a revolution in the study of the stable oxygen isotopes in carbonate rocks. By examining the difference between the measured and the theoretical 47/44 ratios, the Δ_{47} value can be determined. This in turn is related to the temperature of formation, both theoretically and experimentally (Wang et al., 2004; Ghosh et al., 2006). Recently, measurement of the Δ_{48} values has also been added (Fiebig et al., 2019; Bajnai et al., 2020; Bajnai et al., 2021; Swart et al., 2021b) to the clumped isotope arsenal, although its application is still in the early stages. As a result of the potential of the Δ_{47} proxy, particularly during Earth's early history (Bergmann et al., 2018) as well as uncertainties regarding the meaning of variations in $\delta^{13}C$ and $\delta^{18}O$ values of these rocks (Swart

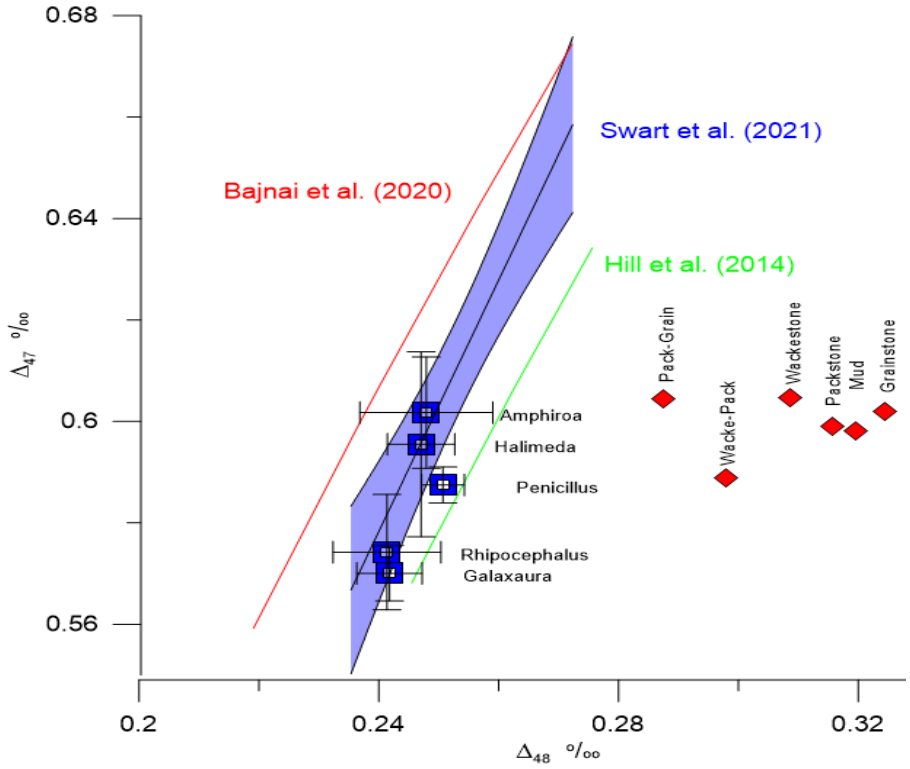

Figure 1: The two calibration lines (Bajnai et al., 2020; Swart et al., 2021b) together with the theoretical line (Hill et al., 2014). The Swart et al. (2021) line is shown together with the 95% confidence limits. Also shown are data from between 5-6 replicates of various calcareous algae: Halimeda sp., Penicillus sp., and Rhipocephalus sp. are green algae and form aragonite, while Amphiroa sp. and Galaxaura sp. are red algae and have HMC skeletons. All the algae data fall close to the equilibrium line based on the calibration of Swart et al. (2021). Also shown are values for non-skeletal material from GBB which show elevated Δ_{48} values, but no relationship between either Δ_{48} or Δ_{47} values and grain size.

and Kennedy, 2012; Hoffman et al., 2021), it is more important than ever to understand how early diagenetic processes affect both the conventional and clumped isotope proxies.

THE NON-EQUILIBRIUM PROBLEM

It is well established that numerous systems precipitate carbonates with Δ_{47} values 'out of equilibrium' (Saenger et al., 2012; Affek and Zaarur, 2014; Davies and John, 2018). Systems in which CO_2 degassing causes the precipitation of carbonates, such as in a speleothem environment (Affek et al., 2008), produce Δ_{47} values which are too negative yielding warmer than expected temperatures, while systems such as corals (Saenger et al., 2012; Spooner et al., 2016) give cooler temperatures. Although both types of non-equilibrium behaviors can be modeled and hence explained (Guo and Zhou, 2019b), it is necessary to use an additional geochemical proxy such as the Δ_{48} value which shows a different type of non-equilibrium behavior to enable the Δ_{47} value to provide temperature information (Guo and Zhou, 2019a; Bajnai et al., 2020). Using the modeled behavior of the Δ_{47} and Δ_{48} values it is theoretically possible to correct both values to equilibrium.

PROPOSED WORK

In order to obtain a better understanding of the behavior of disequilibrium of Δ_{47} and Δ_{48} during early diagenesis, it is necessary to establish base line values for the sedimentary allochems. Here follows some preliminary data on this aspect. We propose to extend this work over the next 12 months.

Calcareous Algae: We show Δ_{47} and Δ_{48} values from algae (red and green) from the Bahamas relative to the calibration lines for Δ_{47} Swart et al. (2019) and Δ_{48} (Swart et al., 2021b) values. Also shown on this figure are the calibrations from Bajnai et al. (2021) and Hill et al. (2014) (Fig. 1). These three lines fall within error of each other. These values plot close to the expected lines of Swart et al. (2021).

Great Bahama Bank Sediments: The origin of sediments on Great Bahama Bank (GBB) are still controversial. The sediments are considered to be mainly non-skeletal in origin, although there is still controversy as to whether the mud is derived from the breakdown of green algae or is a direct precipitate (Shinn et al., 1989) perhaps induced by cyanobacteria (Robbins et al., 1997) and fertilized by dust (Swart et al., 2014). The majority of the sediments on GBB are peloids, which based on their $\delta^{13}C$ and $\delta^{18}O$ values, are similar to the muds therefore suggesting a common origin (Swart et al., 2009). The Δ_{47} values of the sediments are close to equilibrium (Atasoy, 2014), while the Δ_{48} values appear to be slightly elevated (Fig.1).

Speleothems: Previous students at UM have studied the $\delta^{13}C$ and $\delta^{18}O$ values of speleothems through the use of precipitation plates placed under stalagmites (Arienzo et al., 2016). During the precipitation periods water samples and temperature measurements were collected. The calcites precipitated on these plates within several months and yielded calcite with a wide range of $\delta^{13}C$ and $\delta^{18}O$ values with the central axis of the stalagmite clearly being out of equilibrium. We also measured the Δ_{47} and Δ_{48} values of some of these materials and determined that the Δ_{47} values were too negative and the Δ_{48} values too positive in the central region.

Corals: Corals are known to precipitate skeletons with respect to $\delta^{13}C$, $\delta^{18}O$, and Δ_{47} values (Saenger et al., 2012). In order to study this in more detail we examined an eight-year record from the skeleton of *Copophyllia* sp., collected from the island of Tobago. Sampling the coral at a resolution of four samples a year we measured an annual cycle in the Δ_{47} values and showed the offset documented by Saenger et al. (2012). As a test of the Δ_{48} proxy we measured the same coral again over one year and not only reproduced the values measured previously but showed lower than expected Δ_{48} values.

SIGNIFICANCE

This study will establish base line values for the Δ_{47} and Δ_{48} values of Modern sediments as well as casting light on the origin on some of the more controversial sediments, such as the muds from the surface sediments of Great Bahama Bank.

REFERENCES

Affek, H. P., Bar-Matthews, M., Ayalon, A., Matthews, A. and Eiler, J. M., 2008. Glacial/interglacial temperature variations in Soreq cave speleothems as recorded by 'clumped isotope' thermometry: Geochimica et Cosmochimica Acta, v. 72, no. 22, p. 5351-5360.

Affek, H. P. and Zaarur, S., 2014. Kinetic isotope effect in CO2 degassing: Insight from clumped and oxygen isotopes in laboratory precipitation experiments: Geochimica Et Cosmochimica Acta, v. 143, p. 319-330.

Arienzo, M., Swart, P. K., Pourmand, A., Broad, K., Clement, A. C., Murphy, L., Vonhof, H. B. and Kakuk, B., 2016. Bahamian speleothem reveals temperature decrease associated with Heinrich stadials: Earth and Planetary Science Letters., v. 430, p. 377-386.

Atasoy, D., 2014. Clumped isotope signals of biogenic and non-biogenic carbonates [MS: University of Miami, 130 p.

Bajnai, D., Coplen, T. B., Methner, K., Loffler, N., Krsnik, E. and Fiebig, J., 2021. Devils Hole Calcite Was Precipitated at +/- 1 degrees C Stable Aquifer Temperatures During the Last Half Million Years: Geophysical Research Letters, v. 48, no. 11.

Bajnai, D., Guo, W. F., Spotl, C., Coplen, T. B., Methner, K., Loffler, N., Krsnik, E., Gischler, E., Hansen, M., Henkel, D., Price, G. D., Raddatz, J., Scholz, D. and Fiebig, J., 2020. Dual clumped isotope thermometry resolves kinetic biases in carbonate formation temperatures: Nature Communications, v. 11, no. 1.

Bergmann, K. D., Al Balushi, S. A. K., Mackey, T. J., Grotzinger, J. P. and Eiler, J. M., 2018. A 600-million-year carbonate clumped-isotope record from the Sultanate of Oman: Journal of Sedimentary Research, v. 88, no. 8, p. 960-979.

Davies, A. J. and John, C. M., 2018. The clumped (13C-18O) isotope composition of echinoid calcite: further evidence for "vital effects" in the clumped isotope proxy: Geochimica et Cosmochimica Acta.

Fiebig, J., Bajnai, D., Löffler, N., Methner, K., Krsnik, E., Mulch, A. and Hofmann, S., 2019. Combined high-precision Δ48 and Δ47 analysis of carbonates: Chemical Geology, v. 522, p. 186-191.

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, no. 6, p. 1439-1456.

Guo, W. and Zhou, C., 2019a. D48 fractionation in carbonates and its implications for clumped isotope thermometry, in Proceedings 7th International Clumped Isotope Workshop, Long Beach, CA.

Guo, W. and Zhou, C., 2019b. Patterns and Controls of Disequilibrium Isotope Effects in Speleothems: Insights from An Isotope-Enabled Diffusion-Reaction Model and Implications for Quantitative Thermometry: Geochimica et Cosmochimica Acta.

Hill, P. S., Tripati, A. K. and Schauble, E. A., 2014. Theoretical constraints on the effects of pH, salinity, and temperature on clumped isotope signatures of dissolved inorganic carbon species and precipitating carbonate minerals: Geochimica et Cosmochimica Acta, v. 125, p. 610-652.

Hoffman, P. F., Halverson, G. P., Schrag, D. P., Higgins, J. A., Domack, E. W., Macdonald, F. A., Pruss, S. B., Blättler, C. L., Crockford, P. W., Hodgin, E. B., Bellefroid, E. J., Johnson, B. W., Hodgskiss, M. S. W., Lamothe, K. G., LoBianco, S. J. C., Busch, J. F., Howes, B. J., Greenman, J. W. and Nelson, L. L., 2021. Snowballs in Africa: sectioning a long-lived Neoproterozoic carbonate platform and its bathyal foreslope (NW Namibia): Earth-Science Reviews, v. 219, p. 103616.

Robbins, L. L., Tao, Y. and Evans, C. A., 1997. Temporal and spatial distribution of whitings on Great Bahama Bank and a new lime budget: Geology, v. 25, no. 10, p. 947-950.

Saenger, C., Affek, H. P., Felis, T., Thiagarajan, N., Lough, J. M. and Holcomb, M., 2012. Carbonate clumped isotope variability in shallow water corals: Temperature dependence and growth-related vital effects: Geochimica et Cosmochimica Acta, v. 99, no. 0, p. 224-242.

Shinn, E. A., Steinen, R. P., Lidz, B. H. and Swart, P. K., 1989. Whitings, a sedimentologic dilemma: Journal of Sedimentary Petrology, v. 59, p. 147 - 161.

Spooner, P. T., Guo, W., Robinson, L. F., Thiagarajan, N., Hendry, K., Rosenheim, B. E. and Leng, M. J., 2016. Clumped Isotope Composition of Cold-Water Corals: A Role for Vital Effects?: Geochimica et Cosmochimica Acta.

Swart, P. K. and Kennedy, M. J., 2012. Does the global stratigraphic reproducibility of d13C in Neoproterozoic carbonates require a marine origin? A Pliocene-Pleistocene comparison: Geology, v. 40, no. 1, p. 87-90.

Swart, P. K., Lu, C., Moore, E. W., Smith, M. E., Murray, S. T. and Staudigel, P. T., 2021. A calibration equation between Δ48 values of carbonate and temperature: Rapid Communications in Mass Spectrometry, v. 35, no. 17, p. e9147.

Swart, P. K., Murray, S. T., Staudigel, P. T. and Hodell, D. A., 2019. Oxygen Isotopic Exchange Between CO2 and Phosphoric Acid: Implications for the Measurement of Clumped Isotopes in Carbonates: Geochemistry, Geophysics, Geosystems, v. 20, p. 3730-3750.

Swart, P. K., Oehlert, A. M., Mackenzie, G. J., Eberli, G. P. and Reijmer, J. J. G., 2014. The Fertilization of the Bahamas by Saharan Dust: A trigger for carbonate precipitation?: Geology, v. 42, p. 671-674.

Swart, P. K., Reijmer, J. J. and Otto, R., 2009. A reevaluation of facies on Great Bahama Bank II: Variations in the d13C, d18O and mineralogy of surface sediments, in Swart, P. K., Eberli, G. P., and McKenzie, J. A., eds., Perspectives in Carbonate Geology: A Tribute to the Career of Robert Nathan Ginsburg, IAS Special Publication, Volume 41: Oxford, Wiley-Blackwell, p. 47-60.

Wang, Z. G., Schauble, E. A. and Eiler, J. M., 2004. Equilibrium thermodynamics of multiply substituted isotopologues of molecular gases: Geochimica Et Cosmochimica Acta, v. 68, no. 23, p. 4779-4797.