DIAGENETIC ISOTOPE SIGNALS IN BORON, MAGNESIUM, & CALCIUM ISOTOPES?

Peter K. Swart, Chris Holmden[1], Gavin Foster[2], and John Higgins[3]
[1] *University of Saskatchewan Saskatoon, SK*
[2] *University of Southampton*
[3] *Princeton University*

PROJECT PURPOSE

A fundamental argument used to support the idea that large changes in the C isotopic record during specific periods of time are related to changes in the global carbon cycle is that similar changes in the C isotopic signals are seen on a global basis during ancient time periods. However, we have shown in a recently published paper that this is not the case (Swart and Kennedy, 2012). In fact similar changes in the C isotopic composition were evident in Pleistocene carbonates collected from both the Pacific and the Atlantic which are related to freshwater diagenesis connected to sea-level changes and not global changes in the carbon cycle. They appear to be similar in nature to C isotope patterns observed in the Neoproterozoic which have been interpreted as being original in nature. Within the Neoproterozoic sections other isotope systems (B, Mg, and Ca) have also been investigated and suggested to be original in nature. The purpose of the project outlined here will be to investigate how changes in other isotopic systems (Ca, Mg, and B-isotopes) in the well-known diagenetic zones are documented in comparatively recent rocks (Pleistocene-Miocene) and ascertain whether these systems can be usefully applied to the other geological time periods. The results of this study will be of use in applying these new isotope systems towards the understanding of diagenesis in carbonates.

PROJECT RATIONALE

We have already analyzed the stable C and O isotopic composition of shallow water carbonates from several cores in the Bahamas. These show a characteristic change in stable C and O isotopic composition from isotopically negative values associated with meteoric diagenesis to heavy values associated with marine processes (Melim et al., 2002). We also have extensively studied processes of dolomitization in what we consider to be relatively well constrained environments (Swart and Melim, 2000). The goal will be to resample these materials and analyze variation in B-isotope (Foster), Ca-isotopes (Holmden), and Mg-isotopes (Higgins) within the context of the observed C and O isotope changes. The results of this work would then be applied to ancient geological sections not only including the Neoproterozoic, but also younger geological materials.

PROJECT DESCRIPTION

Large carbon isotope excursions occur stratigraphically beneath erosion/exposure surfaces throughout the geological record. In the Neoproterozoic these changes are widely believed to record changes in the global carbon cycle even though they are commonly associated with evidence of diagenetic alteration including, textural evidence of karst and carbonate neomorphism, dolomitization and covariation between $\delta^{13}C$ and $\delta^{18}O$ within some data sets. In spite of such evidence, a marine origin for C isotope values remains the consensus view based on 1) the recurrence of excursions in lithologically similar successions in multiple basins, 2) replication of the C isotopic values in some sections within basins (where others do not conform, they have been

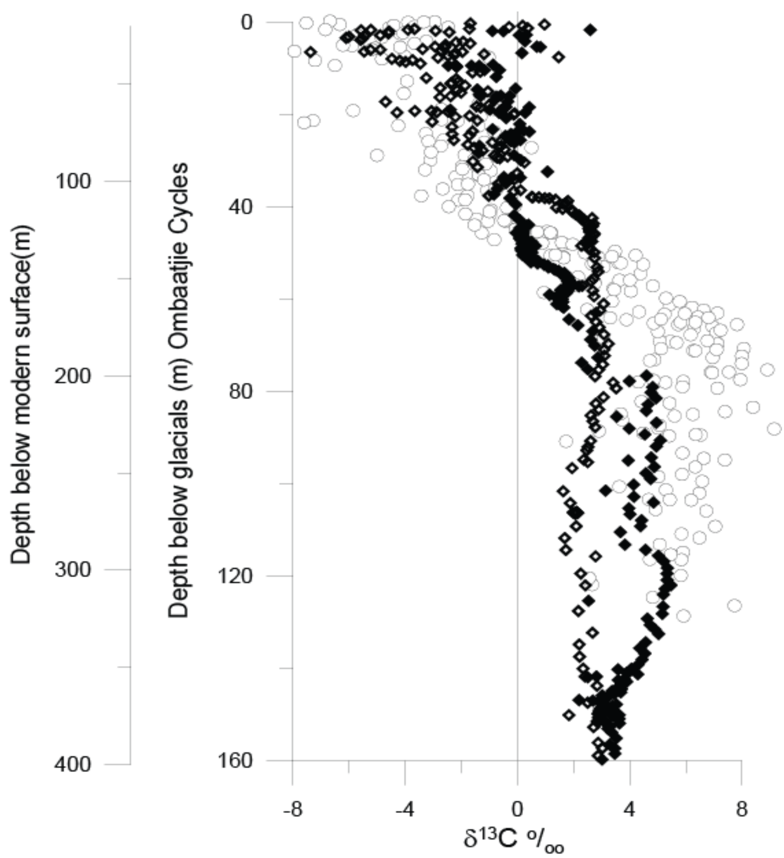

Figure 1. Comparison of the C isotopic profile from Clino (closed diamonds) and Unda (solid diamonds) with data from the Ombaatije formation (circles) in Namibia. Note the similarity of the profile and the range (Swart and Kennedy, 2012).

assumed to be incomplete as a result of erosion, 3) the distinctive magnitude (both positive and negative) of the values perceived to be limited to this period of Earth history, 4) step-wise development of values to define peaks, and 5) a perception that $\delta^{13}C$ values are robust to diagenetic change because pore fluids and interbedded organic carbon do not contain sufficient carbon to affect a mass balance dominated by marine material. By comparing the pattern of changes seen in the Pleistocene, where the diagenetic history is well constrained, we have been able to draw similarities to the Neoproterozoic (Figure 1). By inference we proposed that the Neoproterozoic changes are also diagenetic in origin. Within these same Neoproterozoic sections, various workers have started to utilize other isotope systems (Ca, Mg, and B) to make interpretations regarding changes in the chemistry of the Neoproterozoic oceans. Are these changes original or do they also reflect diagenesis? In the proposed work we intend examine the behavior of these isotopes under well constrained diagenetic systems.

<u>B Isotopes</u>: The two stable isotopes of boron occur in seawater as either borate ion, $B(OH)_4^-$ (enriched in ^{10}B) or boric acid, $B(OH)_3$ (enriched in ^{11}B). At low pH levels, all dissolved boron is in the form of $B(OH)_3$; at high pH levels, both ^{10}B and ^{11}B are in the form of $B(OH)_4^-$. The ratio of the two isotopes has been proposed as a paleo pH proxy and been applied to recent and modern carbonates (Hemming and Hanson, 1992) as well as very old examples (Neoproterozoic) (Kasemann et al., 2010; Sansjofre et al., 2011).

<u>Mg Isotopes</u>: Magnesium has three stable isotopes (24, 25, and 26). Although there has not been a great amount of work in this area there are suggestion from preliminary data that the ratio of 26/24 may be characteristic of the type of dolomitization (Carder et al., 2005)(Higgins and Swart, unpublished).

<u>Ca Isotopes</u>: Calcium has multiple stable isotopes (40, 42, 43, 44, 46, and 48). The ratio of 44/40 has recently been used in a number of studies to ascertain temperature (Hippler et al., 2006)and the diagenetic process (Holmden, 2009).

ANTICIPATED FINDINGS

In the case of these isotope systems, the behavior of the isotopes during early diagenesis is poorly constrained and the interpretation controversial. However, they all have the potential to reveal new information about diagenetic systems. Our work will take materials from well characterized diagenetic environments and examine the changes that take place in the calcium and boron isotopic systems.

REFERENCES

Carder, E. A., Galy, A., McKenzie, J. A., Vasconcelos, C., and Elderfield, H. E., 2005, Magnesium isotopes in bacterial dolomites: A novel approach to the dolomite problem: Geochimica et Cosmochimica Acta, v. 69, no. 10, p. A213-A213.

Hemming, N. G., and Hanson, G. N., 1992, Boron isotopic composition and concentration in modern marine carbonates: Geochimica et Cosmochimica Acta, v. 56, no. 1, p. 537-543.

Hippler, D., Eisenhauer, A., and Nagler, T. F., 2006, Tropical Atlantic SST history inferred from Ca isotope thermometry over the last 140ka: Geochimica et Cosmochimica Acta, v. 70, no. 1, p. 90-100.

Holmden, C., 2009, Ca isotope study of Ordovician dolomite, limestone, and anhydrite in the Williston Basin: Implications for subsurface dolomitization and local Ca cycling: Chemical Geology, v. 268, no. 3-4, p. 180-188.

Kasemann, S. A., Prave, A. R., Fallick, A. E., Hawkesworth, C. J., and Hoffmann, K.-H., 2010, Neoproterozoic ice ages, boron isotopes, and ocean acidification: Implications for a snowball Earth: Geology, v. 38, no. 9, p. 775-778.

Melim, L. A., Westphal, H., Swart, P. K., Eberli, G. P., and Munnecke, A., 2002, Questioning carbonate diagenetic paradigms: evidence from the Neogene of the Bahamas: Marine Geology, v. 185, no. 1-2, p. 27-53.

Sansjofre, P., Ader, M., Trindade, R. I. F., Elie, M., Lyons, J., Cartigny, P., and Nogueira, A. C. R., 2011, A carbon isotope challenge to the snowball Earth: Nature, v. 478, no. 7367, p. 93-U103.

Swart, P. K., and Kennedy, M., 2012, Large and systematic Pleistocene carbon isotope excursions indicate Neoproterozoic mega-excursions do not record global changes in the carbon cycle: Geology, v. 40, p. 87-90.

Swart, P. K., and Melim, L. A., 2000, The origin of dolomites in Tertiary sediments from the margin of Great Bahama Bank: Journal of Sedimentary Research, v. 70, no. 3, p. 738-748.