Does the global stratigraphic reproducibility of $\delta^{13}C$ in Neoproterozoic carbonates require a marine origin? A Pliocene–Pleistocene comparison

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ABSTRACT

The large and systematic negative shifts in the $\delta^{13}C$ values (>12‰) of carbonate-dominated rocks that preceded Neoproterozoic glacial successions have been interpreted to record a dramatic series of global environmental and evolutionary events. These values are widely considered to be marine rather than diagenetic in origin because stratigraphic patterns of change are systematic and reproducible from basin to basin, distinct in magnitude, and associated with recognizable stratigraphic markers such as glacial deposits. In contrast, diagenetic systems are commonly considered to have a more local and stochastic influence on $\delta^{13}C$ values. Cores taken in Quaternary carbonate platform sediments, however, reveal a curious similarity in magnitude, thickness, and core to core reproducibility where diagenetic alteration has occurred in response to sea-level fall. Sea-level changes produced similar $\delta^{13}C$ and $\delta^{18}O$ stratigraphic records at globally disparate locations, which are unrelated to the global marine $\delta^{13}C$ signal and bear no relation to the global carbon cycle. By analogy with the Pliocene–Pleistocene, we propose that spatial reproducibility of $\delta^{13}C$ in some Neoproterozoic successions might be attributed to causes other than secular variation of the global carbon cycle, including diagenesis. This observation does not negate the stratigraphic utility of the carbon isotopic values, only the origin of the signal.

INTRODUCTION

The $\delta^{13}C$ record of sedimentary carbonates plays an important role in understanding the complex series of Neoproterozoic events leading up to the advent of multicellular life (Bjerrum and Canfield, 2011; Fike et al., 2006; Hoffman et al., 1998; Swanson-Hysell et al., 2010). The synthesized marine $\delta^{13}C$ record of the Neoproterozoic shows extreme variation from values >+6‰ to <-6‰. The largest of these excursions are used to construct the Neoproterozoic stratigraphic framework because the magnitude of these events makes the otherwise binary signal of carbon isotopes recognizable across isolated sections. In some studies, specific carbon isotopic values serve directly as a datum from which the stratigraphy is established (Halverson et al., 2002). The $\delta^{13}C$ values of carbonates are also interpreted to record changes in the biosphere propagated through the global carbon cycle (Hayes et al., 1999). Fundamental in the use of $\delta^{13}C$ for both correlation and carbon cycle models in general is that these values retain the original seawater $\delta^{13}C$ value recorded from an isotopically homogeneous portion of the ocean that is consistent between basins and that is representative of the ocean-atmosphere system. However, the $\delta^{13}C$ values of carbonates might not record open-ocean values. They could be deposited in restricted and/or stratified water bodies or even under lacustrine conditions or reflect carbonates produced with inherently different isotopic values (Swart and Eberli, 2005) or be diagenetically altered (Allan and Matthews, 1977; Derry, 2010; Fairchild et al., 1990; Gross, 1964; Knauth and Kennedy, 2009; Loyd and Corsetti, 2010). Although some degree of diagenesis should be expected in the transformation of metastable carbonate precipitates to carbonate rocks, many authors consider that the Neoproterozoic $\delta^{13}C$ values are difficult to alter because there is insufficient dissolved carbon in diageneric fluids (Veizer et al., 1999).

The most common line of evidence offered for retention of marine values through diagenesis is the global spatial reproducibility. Where trends in $\delta^{13}C$ values can be reproduced and similar patterns reoccur between basins, secular variation of marine water is considered to be the exclusive mechanism operating on this scale (Bjerrum and Canfield, 2011; Halverson et al., 2002, 2005; Swanson-Hysell et al., 2010). Furthermore, these trends are often composed of values that show a progressive shift that forms a broader pattern. By inference, diageneric systems are considered to show more localized effects on the scale of groundwater systems.

Here we compare one of the most stratigraphically prominent negative carbon isotopic excursions in the Neoproterozoic record with the pattern of demonstrably $\delta^{13}C$-altered Quaternary platform sediments to determine if reproducibility, magnitude, and progressive development of a signal are adequate tests to eliminate postdepositional alteration.

A NEOPROTEROZOIC PREGLACIAL CARBON ISOTOPE ANOMALY

Unlike the Phanerozoic where independent dating of carbon isotope excursions is based on biostratigraphy, independent evidence of synchronicity of $\delta^{13}C$ excursions is more difficult to establish in Neoproterozoic successions. As partial confirmation, patterns in $\delta^{13}C$ have been correlated between sections in association with glacial features that may record global ice ages (snowball Earth events) (Harland, 1964; Hoffman et al., 1998). Excursions in $\delta^{13}C$ beneath Marinoan glacial sediments are documented from at least six basins globally, including Namibia, China, Canada, Scotland, and Greenland (Brasier and Shields, 2000; Halverson et al., 2002; Narbonne et al., 1994; Xiao et al., 2004). On the basis of correlation of these successions, the preceding $\delta^{13}C$ excursion has been identified as a biogeochemical event and named the Trezona Excursion after initial observations of strongly depleded values in the Trezona Formation of South Australia (McKirdy et al., 2001). The Trezona Excursion immediately underlies glacial sediments correlated with the Marinoan ice age and is assigned an absolute age by lithologic and chemostratigraphic correlation to a radiometric date in the postglacial succession (cap carbonate) in China and Namibia at ca. 635 Ma (Condon et al., 2005; Hoffmann et al., 2004). The reproducibility of the successions is probably best documented in nine sections distributed over ~80 km of the Ombaatjie Formation in Namibia, a carbonate platform that underlies glacial deposits of the Ghaub Formation. Here, more than seven sequence boundaries stack into a subglacial unconformity characterized by erosional truncation and silification (Halverson et al., 2002; Hoffmann et al., 1998), potentially recording the glacio-eustatic effects of the growth of an ice sheet at higher latitudes. The most negative $\delta^{13}C$ value of the Trezona Excursion within the Ombaatjie Formation varies between 0‰ and ~8‰, and thickness varies between 10 m and 60 m. Halverson et al. (2002) correlated these sections using a $\delta^{13}C$ datum (0‰). These authors considered the section to be incomplete where values did not decline below 0‰. By contrast, Kennedy et al. (1998) attributed the $\delta^{13}C$ variation of the excursion to variable degrees of meteoric alteration at a karstified subglacial exposure surface. In details of magnitude, sample to sample variability, and thickness, the Trezona Excursion is also not uniform globally. The Trezona Excursion...
within the Trezona Formation itself is not just a simple negative excursion, but rather shows a prolonged positive trajectory by returning from $-9^{\circ}$ to $-3^{\circ}$ $\delta^{13}$C over the upper ~150 m before the base of the Marinoan glacial event (Swanson-Hysell et al., 2010).

**COMPARISON WITH THE PLIOCENE–PLEISTOCENE**

As a basis for comparison, we present $\delta^{13}$C and $\delta^{18}$O data from four cores that sampled Pliocene–Pleistocene carbonates from the Bahamas, Florida, and the Pacific (Melim et al., 2004; Quinn, 1991) (Fig. 1). The sediments at these locations were subjected to between 4 and 11 major sea-level changes (depending on the location of the core) leaving sections of rocks, >100 m thick, highly depleted in $\delta^{13}$C and $\delta^{18}$O values overlying a section with relatively positive $\delta^{13}$C values, similar to Neoproterozoic sections used to construct the Trezona anomaly (Fig. 2). The origin of $\delta^{13}$C and $\delta^{18}$O changes in these cores can be succinctly described by the model proposed by Allan and Matthews (1982). Upper portions of the cores, which are composed of relatively unaltered modern nonskeletal sediments most similar to Neoproterozoic carbonate grains, have $\delta^{13}$C values as high as $+6^{\circ}$ in the Bahamas (Swart et al., 2009). In the Pacific, where the grains are mainly skeletal in nature, values are only $+2^{\circ}$.

Below the unaltered zone, $\delta^{13}$C values associated with subaerial exposure surfaces become as negative as $-10^{\circ}$. The negative $\delta^{13}$C values associated with these horizons and the entire meteorically altered sequence is derived from the oxidation of organic material. The thick sequence of the isotopically negative values reflects repeated changes in sea level throughout the Pleistocene and repeated exposure to meteoric lenses (Melim et al., 2001). The $\delta^{18}$O values of these altered carbonates are negative throughout, deriving their values from the $\delta^{18}$O of the local meteoric waters. These $\delta^{13}$C and $\delta^{18}$O negative values are underlain by a zone of carbonates where the positive $\delta^{13}$C and $\delta^{18}$O values represent carbonates that have not been exposed to meteoric water and record the strongly $\delta^{13}$C-enriched values of the unaltered sediments. This transition between the portion of the section altered by fresh water and that in which marine diagenesis predominates is characterized by a progressive zone in which the $\delta^{13}$C and $\delta^{18}$O values are often correlated as a result of proportional mixing between these two end members. In shape and magnitude, the $\delta^{13}$C and $\delta^{18}$O pattern reproduces itself from section to section, broadly timed through a common influence, sea-level fall. In detail, these Pleistocene isotope features are diachronous, with isotopic values determined in each section by differences in sedimentation rates, the specifics of local aquifers, and subsidence rates. While covariation between $\delta^{13}$C and $\delta^{18}$O is common in Pleistocene sections where mixing between meteoric and marine influences occurs, a similar

![Figure 1. Comparisons of the carbon isotopic records of four Pliocene–Pleistocene cores taken from Caribbean (Melim et al., 2004, 2002) and Pacific (Quinn, 1991) shallow-water carbonate platforms; symbols are plotted every second point. The oceanic (pelagic) record is shown in gray from Zachos et al. (2001) in each example and has been scaled to the approximate sedimentation rate. The right-hand panel shows data from five Neoproterozoic examples preceding the Marinoan glaciation that have been used to show stratigraphic reproducibility of the carbon isotope excursion, including sections from Namibia and Svalbard representing approximately similar spacing as for the Pliocene–Pleistocene Caribbean sections (between 20 and 60 km). Ombaatjie Formation (black); Fransfontein Ridge (Kennedy et al., 1998) (dark blue); Tweelingskop section at Huab Ridge (green); Keiserfontein section at Makalani Ridge (Halverson et al., 2002) (orange); Sveanor (light blue); Sore Russoya (pink) sections from Svalbard in the Russoya Member of the Elbobreen Formation (Halverson et al., 2004).](image-url)
might be envisaged in the Neoproterozoic where exposed surfaces were inhabited by a primitive land biota composed of protists (Horodyski and Knauth, 1994; Kennedy et al., 2006; Prave, 2002), before the advent of vascular plants.

**EXTREME RANGE OF ISOTOPIC VALUES**

An argument suggested for the primary origin of the $\delta^{13}C$ signals in the Neoproterozoic is that their extreme range of values is not matched in more recent carbonates, and that the Neoproterozoic carbonates do not show as much scatter as the Pliocene–Pleistocene samples. It is true that Pliocene–Pleistocene carbonates do not reproduce exactly the same magnitude of change, but the ranges are not as dissimilar as suggested. For example, modern nonskeletal sediments in the Bahamas have $\delta^{13}C$ values as positive as $+6\%e$ (Swart et al., 2009), only $2\%e$–$3\%e$ more negative than typical maximum values reported for the Trezona Excursion. The relatively positive values for these carbonates are actually exactly what would be expected from marine aragonite precipitated in equilibrium (Romanek et al., 1992) with the relatively positive $\delta^{13}C$ for the dissolved inorganic carbon ($\delta^{13}C_{DIC}$) found in the shallow waters of the Bahamas (Swart et al., 2009). In modern restricted shallow-water carbonate environments, this positive $\delta^{13}C_{DIC}$ signature arises as a result of high amounts of photosynthesis. Neoproterozoic carbonates deposited in shallow-water, restricted environments might behave in a similar manner. The difference in the absolute $\delta^{13}C$ values between the modern and the Neoproterozoic could be associated with a modest secular change in the $\delta^{13}C_{DIC}$ of Neoproterozoic seawater or the absence of skeletal material maintaining more depleted $\delta^{13}C$ open-ocean values. The most depleted $\delta^{13}C$ values for bulk samples in the Pleistocene are $-8\%e$ to $-10\%e$, once again not vastly different compared to the most depleted Neoproterozoic examples. Most importantly, both the Pliocene–Pleistocene and Neoproterozoic examples presented here (Figs. 1 and 2) record a similar progression from positive to negative $\delta^{13}C$ values of similar magnitude and over similar depth intervals. In addition it should be noted that the carbonates that made up the Neoproterozoic sediments were probably mainly fine-grained aragonite that recrystallized quickly compared to the skeletal allochems in the Pleistocene. This feature would tend to make the $\delta^{13}C$ signal in fine-grained Neoproterozoic carbonates less variable compared to the Pliocene–Pleistocene.

**CONCLUSIONS**

The comparison presented in this paper clearly shows that global changes in the $\delta^{13}C$ signal of Pliocene–Pleistocene carbonates, which are similar in character to the Neoproterozoic, can be generated by changes in sea level. These changes are not related to variations in the global carbon cycle as recorded in the deep-sea record. In addition, the extent of the range in $\delta^{13}C$ values and the magnitude of change of the values seen in the Neoproterozoic is not unique. There is no question that diagenesis is responsible for recent variation in carbonate platforms, and therefore there is a strong likelihood that it could have also been a causative mechanism in governing $\delta^{13}C$ changes prior to the Neoproterozoic glaciations. This observation, however, does not negate the utility of the carbon isotopic record for stratigraphic correlation purposes.

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