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On the significance of δ^{13}C correlations in ancient sediments

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ABSTRACT

A graphical analysis of the correlations between δ_c and ε_{TOC} was introduced by Rothman et al. (2003) to obtain estimates of the carbon isotopic composition of inputs to the oceans and the organic carbon burial fraction. Applied to Cenozoic data, the method agrees with independent estimates, but with Neoproterozoic data the method yields results that cannot be accommodated with standard models of sedimentary carbon isotope mass balance. We explore the sensitivity of the graphical correlation method and find that the variance ratio between δ_c and δ_o is an important control on the correlation of δ_c and ε. If the variance ratio $\sigma_c/\sigma_o \geq 1$ highly correlated arrays very similar to those obtained from the data are produced from independent random variables. The Neoproterozoic data shows such variance patterns, and the regression parameters for the Neoproterozoic data are statistically indistinguishable from the randomized model at the 95% confidence interval. The projection of the data into δ_c–ε space cannot distinguish between signal and noise, such as post-depositional alteration, under these circumstances. There appears to be no need to invoke unusual carbon cycle dynamics to explain the Neoproterozoic δ_c–ε array. The Cenozoic data have $\sigma_c/\sigma_o < 1$ and the δ_c vs. ε correlation is probably geologically significant, but the analyzed sample size is too small to yield statistically significant results.

1. Introduction

Various biogeochemical processes lead to correlations between stable isotopes of carbon in sedimentary carbonate and organic carbon records, and also between the carbon, oxygen and sulfur isotope systems. Identifying the significance of those correlations and the processes that cause them is an ongoing challenge. Rothman et al. (2003) herein referred to as RHS, introduced a graphical analysis of the variation in δ_c and ε_{TOC}, where $\varepsilon_{TOC} = \delta_c - \delta_o$ and is the isotopic difference between carbonate and organic carbon records preserved in buried sediments ($\delta_c = \delta^{13}$C measured in sedimentary carbonate, $\delta_o = \delta^{13}$C measured in sedimentary organic matter). They considered the steady state carbon isotope mass balance equation for a single reservoir:

$$\delta_c = \delta_{in} + F_{org} \bullet \varepsilon_{TOC} \tag{1a}$$

$$\varepsilon_{TOC} = \delta_c - \delta_o \tag{1b}$$

where $\delta_{in} = \delta^{13}$C of the mean inputs of carbon to the oceans and F_{org} is the global burial fraction of organic carbon (Hayes et al., 1999). By fitting regressions to paired data for δ_c and ε_{TOC} they were able to obtain an estimate of both the mean F_{org} from the slope of a plot of δ_c vs. ε_{TOC} and δ_{in} from the intercept for three different intervals they examined. For the two Phanerozoic intervals RHS examined they obtained similar results, with F_{org} near 0.3 for both the lower Cambrian and the Cenozoic. For the Cenozoic they obtained an estimate of $\delta_{in} = -6.1$‰, in agreement with previous estimates of the isotopic composition of the mean inputs to the oceans (Derry et al., 1992; Derry and France-Lanord, 1996; Hayes et al., 1999). This is an important result because it derives an estimate of the mean input directly from a statistical treatment of multiple observations of δ^{13}C values in carbonates and organic matter through time. For the Precambrian–Cambrian boundary interval the estimate of $\delta_{in} = -8.1$‰, but sample size was quite small ($n = 9$ pairs) and the result is unlikely to be significantly different from the Cenozoic.

However, application of the graphical analysis to Neoproterozoic samples yield a very different result, with implied $F_{org} > 0.9$ and $\delta_{in} \approx -24$‰, values that cannot be consistent with the steady state model described by Eqs. (1a) and (1b) (Fig. 1a,b). RHS considered several hypotheses to explain the Neoproterozoic data, including the possibility that fortuitous or spurious correlations drove the δ_c vs. ε correlation. They argued that these were not likely explanations, and concluded that the Neoproterozoic data reflected a non-steady state carbon cycle operating quite differently from the Phanerozoic, with a time constant for an active reservoir of dissolved organic carbon (DOC) that was significantly longer than the time constant for the dissolved inorganic carbon (DIC) reservoir. RHS suggested that the Neoproterozoic oceans had a large reservoir of DOC, and dynamical interactions of this reservoir with the DIC reservoir gave rise to the large fluctuations observed in the carbon isotope data. This hypothesis has been influential, in particular

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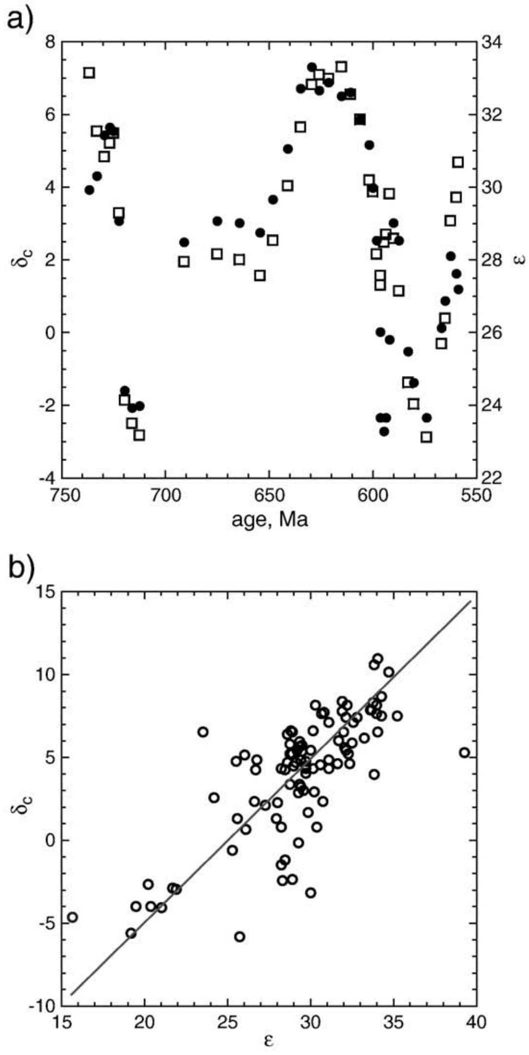

Fig. 1. a. Neoproterozoic δ_c (●) and ε_{TOC} δ_c– δ_o (□) as plotted by Rothman et al. (2003). The data were averaged from records compiled and filtered by Hayes et al., 1999, b. Correlation of δ_c with ε_{TOC} from Rothman et al. (2003) with RMA linear fit ($n=98$, $f=0.88$ [0.85, 1.15], $b=-24.6$ [$-30.5,-20.7$], $r=0.76$[0.64, 0.85]). Square brackets enclose 95% confidence limits.

because it appears to suggest an explanation for some of the anomalously low δ_c in the Neoproterozoic. Gradual oxidation of a large DOC reservoir has been proposed as a mechanism to produce the very low δ_c values (down to −12‰) observed in some late Neoproterozoic sections (Fike et al., 2006; McFadden et al., 2008).

Given the influence of the hypothesis of a non-steady state carbon cycle with large oceanic DOC reservoir we wish to reexamine the kinds of processes that could produce the δ_c–ε correlation. In particular, recent work suggests that sample alteration could have significantly impacted the records of δ^{13}C in Neoproterozoic carbonates (Ader et al., 2009; Knauth and Kennedy, 2009; Derry, 2010). To what extent could sample alteration be responsible for the correlation observed in Fig. 1b? Projections of the data such as Fig. 1b show a high degree of cross-correlation, and can show apparently impressive correlations that may not be geochemically significant. In real data both δ_c and δ_o vary for several reasons. Time dependent variation in the burial fraction of organic carbon (F_{org}) is one. Other sources of variation can cause decoupling of the δ_c and δ_o records. If the photosynthetic fractionation varies as a function of time ε will not be constant. For example, ε decreases during the Cenozoic, and this decrease is believed to result from declining pCO$_2$ that in turn decreases the kinetic isotope effect during photosynthetic carbon assimilation (Freeman and Hayes, 1992). Diagenesis can both add noise to and bias the δ_c and/or the δ_o records. In general there is no reason to expect that diagenesis will always affect both records equally, or even in the same direction, so diagenesis will also tend to decouple the records.

While carbon isotope variations during the Cenozoic are well known from multiple records with good biostratigraphic control, further back in time we may expect alteration to have a greater impact on the records, and be less easy to recognize. Recognition of a diagenetic signal is particularly challenging in the Precambrian because of the lack of good biostratigraphic correlations makes it difficult to objectively assess the degree to which a given sample has been altered. Given that the stable isotope systematics of carbonates can be substantially altered by post-depositional processes, it raises the question of whether the δ_{carb}–ε_{TOC} array defined by the Neoproterozoic data reflects primary oceanic processes or could be substantially influenced by sample alteration. In sediments of this age essentially all data are expected to include at least some signal from post-depositional processes. While there are a number of empirical techniques for sample "screening" (using δ^{18}O, Mn/Sr, H/C etc.), none of these provide a quantitative estimate of the magnitude of alteration of the δ^{13}C signal in either carbonate or organic carbon samples. Essentially, the signal-to-noise ratio in these records is poorly known and currently not well quantified. Given this uncertainty we wish to investigate the sensitivity of the graphical analysis approach to "noise" produced by alteration.

2. Regression of δ_c and ε

As noted above, striking features of the Neoproterozoic data analyzed by RHS are the steep slopes (f) and low intercepts (b), as well as high correlation coefficients (r). The regressed variables are $\varepsilon=\delta_c-\delta_o$ vs. δ_c. We wish to consider the influence of the variance structure of the data on the regression coefficients f and b. Because δ_c and δ_o are coupled by the isotopic fractionation associated with photosynthesis, in the simplest case we would expect the two records to be offset by a constant ε value. In that case δ_c and δ_o need not be constant but will covary perfectly in phase and amplitude. However real data are not perfectly coupled, and we may consider two illustrative end member cases. If δ_o is constant (i.e. all the variance is in δ_c) the plot reduces to δ_c vs. δ_c, and both the slope and correlation coefficient will equal unity, while $b=-\varepsilon$. On the other hand, if δ_c is constant and all the variance is in δ_o, f and $r=0$, while $b=\delta_c$. For geological examples the values should lie between these two idealized end members, but this simple thought experiment suggests that the ratio between the variances in the carbonate and organic carbon records should be important in determining the regression parameters.

Given that there are uncertainties in both variables, ordinary least squares (OLS) may not be the most appropriate regression technique. RHS chose a regression technique that allows for uncertainty in each variable, reduced major axis (RMA) regression that is widely used in biometry, for example. Rather than minimize the sum of squared deviations parallel to the y-axis as in OLS, RMA minimizes the sum of the product of deviation in both the x and y directions. Smith, (2009) provides an extensive recent review of the relative merits of OLS vs. RMA regressions.

The RMA regression slope (f_{RMA}) depends only on the sign of the correlation coefficient r and the ratio of the variances in the regressed variables (Sokal and Rohlf, 1995):

$$f_{RMA}=sign(r)\sqrt{\frac{Var(\delta_c)}{Var(\varepsilon)}} \tag{2}$$