

# Marine carbon reservoir, $C_{\text{org}}-C_{\text{carb}}$ coupling, and the evolution of the Proterozoic carbon cycle

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## ABSTRACT

The post-2.0 Ga Proterozoic C isotope record reveals two distinct, yet interrelated trends: a stepwise increase in average  $\delta^{13}\text{C}$  from  $\sim 0\text{‰}$  (calculated with respect to the Peedee belemnite isotope standard) prior to ca. 1.3 Ga to  $>+5\text{‰}$  in the Neoproterozoic, and a concomitant increase in the magnitude of isotopic excursions. Steady-state and non-steady-state models suggest that these fundamental changes are best explained by a combination of evolving burial fluxes and a secular decrease in the size of the marine dissolved inorganic carbon (DIC) reservoir. The DIC reservoir size affects the sensitivity of the isotopic system to biogeochemical perturbation. Major rearrangements of carbon cycling during the Proterozoic, in part related to the evolving marine carbon reservoir, permit elevated  $\delta^{13}\text{C}$  values to be sustained for geologically long time spans. Recognition of this dependence on DIC reservoir size provides, for the first time, a direct link between changing carbonate precipitation styles and the marine C isotope record and may help constrain estimates of Proterozoic  $p\text{CO}_2$ .

**Keywords:** Proterozoic, carbon cycle, dissolved inorganic carbon, C isotopes, model.

## PROTEROZOIC CARBON ISOTOPE RECORD

Isotopic evolution of the Proterozoic C cycle, as recorded in carbonates and coeval organic matter, can be subdivided into two primary intervals, characterized by differences in both average  $\delta^{13}\text{C}$  and in the magnitude of observed isotopic excursions. With the exception of a large positive excursion ca. 2.3–2.0 Ga (Karhu and Holland, 1996), the pre-1.3 Ga global C isotope record has  $\delta^{13}\text{C}$  values near 0‰ with excursions  $<2\text{‰}$  (Buick et al., 1995; Knoll et al., 1995; Frank et al., 1997; Xiao et al., 1997; Lindsay and Brasier, 2000). In contrast, late Mesoproterozoic strata record positive  $\delta^{13}\text{C}$  values ( $+3.5\text{‰}$ ) with higher-amplitude (4‰–5‰) excursions (Kah et al., 1999; Bartley et al., 2001), and Neoproterozoic strata record  $\delta^{13}\text{C}$  values near  $+6\text{‰}$  and excursions to 10‰ (Kaufman and Knoll, 1995).

Observed shifts toward more positive  $\delta^{13}\text{C}$  values reflect reorganizations of the global C cycle that resulted in increases in steady-state burial flux of organic carbon ( $C_{\text{org}}$ ) relative to carbonate carbon ( $C_{\text{carb}}$ ). These changes have been attributed to major tectonic events, such as the initial assembly and subsequent breakup of Rodinia that correspond broadly to the mid-Mesoproterozoic (Kah et al., 1999; Bartley et al., 2001), and later Neoproterozoic rise in  $\delta^{13}\text{C}$  values, respectively (Knoll et al., 1986; Kaufman et al., 1993). Biological evolution may have affected global carbon cycling as well. Perhaps driven by changes in availability of redox-sensitive bioessential nutrients (Anbar and Knoll, 2002), eukaryotic complexity

and diversity increased dramatically ca. 1.3 Ga (Knoll, 1994; Butterfield, 2000), perhaps further stimulating  $C_{\text{org}}$  production and burial.

By contrast, isotopic excursions record short-term C-cycle perturbations, perhaps caused by changes in  $C_{\text{org}}$  production and burial (Magaritz, 1989; Frank et al., 2003), marine stratification and overturn (Knoll et al., 1996; Bartley et al., 1998),  $C_{\text{org}}$  remineralization (Rothman et al., 2003), or methane hydrate activity (Dickens et al., 1995). The short time scale of perturbations demands a mechanism that is oceanographic in nature; however, there is no reason to suspect that the magnitude of the perturbations has changed through time.

Because short-term perturbations reflect non-steady-state behavior of the marine isotopic system, they depend not only on relative fluxes of  $C_{\text{org}}$  and  $C_{\text{carb}}$ , but also on the size of the marine dissolved inorganic carbon (DIC) reservoir. A long-term decrease in Proterozoic marine carbonate saturation is suggested by changing carbonate depositional styles (Grotzinger, 1989; Kah and Knoll, 1996; Bartley et al., 2000). Because Proterozoic carbonate production must balance alkalinity input to the global ocean, higher  $\text{CaCO}_3$  saturation indicates a larger DIC reservoir and, by extension, higher marine alkalinity. In turn, a larger DIC reservoir affects the response of the marine C cycle to isotopic change.

## CONCEPTUAL MODEL Steady State

Changes in average  $\delta^{13}\text{C}$  values reflect fundamental differences in the  $C_{\text{org}}:C_{\text{carb}}$  ratio

over geologic time. At steady state, marine  $\delta^{13}\text{C}$  can be described by an isotopic mass balance (variables defined in Table 1):

$$\delta_{\text{carb}} = \delta_{\text{w}} - (\Delta\delta \times f_{\text{org}}). \quad (1)$$

Table 1 shows single-variable and two-variable changes that could account for a  $+3.5\text{‰}$  shift in  $\delta^{13}\text{C}$ , such as those observed in the Mesoproterozoic and Neoproterozoic. A 3.5‰ change in  $\delta_{\text{w}}$  would produce a commensurate 3.5‰ change in  $\delta_{\text{carb}}$ . Such a shift is unlikely because  $\delta_{\text{w}}$  is equivalent over long time scales to  $\delta^{13}\text{C}$  of bulk terrestrial C. Similarly, a decrease in  $\Delta\delta$  could produce this pattern; however, the  $C_{\text{org}}$  record refutes this possibility (Des Marais, 1994). However, a 50% increase in  $f_{\text{org}}$ , caused by doubling organic burial flux ( $F_{\text{o}}$ ), halving carbonate burial flux ( $F_{\text{i}}$ ), or some combination of the two, could also generate such a shift.

## Non-Steady-State Behavior

In contrast to the long-term C isotope composition of the oceans, short-term isotopic excursions are functions not only of input and output fluxes, but also of C reservoir size (approximated by DIC). These relationships can be described by using a time-dependent mass-balance model that permits imbalances between input and output fluxes and results in changes in both  $\delta^{13}\text{C}$  and reservoir size over multimillennial time scales (Kump and Arthur, 1999):

$$\frac{d\delta_{\text{carb}}}{dt} = \frac{F_{\text{w}}(\delta_{\text{w}} - \delta_{\text{carb}}) - F_{\text{o}}\Delta\delta}{M_{\text{o}}}, \quad (2)$$

where  $F_{\text{w}}$  is the total input flux of C, and  $M_{\text{o}}$  is the reservoir size. In this model, the rate of isotopic change varies dramatically with changes in both  $f_{\text{org}}$  and  $M_{\text{o}}$  (Fig. 1). At present-day DIC levels, a 50% increase in  $f_{\text{org}}$  results in a maximum rate of change of 17.5‰/m.y., suggesting that the modern DIC reservoir does not provide an effective buffer against isotopic change. The relative isotopic stability observed in the modern ocean (Veizer et al., 1999) must therefore be attributable to variables other than reservoir size.

If the Proterozoic DIC reservoir were only five times larger than at present, the same 50% increase in  $f_{\text{org}}$  would produce a maximum rate of change of 3.5‰/m.y. A DIC reservoir

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TABLE 1. STEADY-STATE MODEL FOR PROTEROZOIC C ISOTOPE CHANGE

Name	$\delta_w$	$\Delta\delta$	$F_o$	$F_i$	$f_{org}$	$\delta_{carb}$
Initial values	-5.0	-25.0	10,000	40,000	0.2	0.0
Change in $\delta_w$	<b>-1.5</b>	-25.0	10,000	40,000	0.2	3.5
Change in $\Delta\delta$	-5.0	<b>-42.5</b>	10,000	40,000	0.2	3.5
Change in $F_o$	-5.0	-25.0	<b>20,608</b>	40,000	0.3	3.5
Change in $F_i$	-5.0	-25.0	10,000	<b>19,410</b>	0.3	3.5
Change in $\Delta\delta$ and $F_o$	-5.0	<b>-30.0</b>	<b>15,750</b>	40,000	0.3	3.5
Change in $F_i$ and $F_o$	-5.0	-25.0	<b>15,000</b>	<b>29,000</b>	0.3	3.5
Change in $\delta_w$ and $F_i$	<b>-3.0</b>	-25.0	10,000	<b>28,500</b>	0.3	3.5

Note: Single-variable and two-variable changes that could account for a  $\pm 3.5\%$  shift in marine  $\delta^{13}\text{C}$  values. Values in bold indicate variables changed from initial model values (Kump and Arthur, 1999).  $\delta_w$  =  $\delta^{13}\text{C}$  value of input C (‰, PDB);  $\Delta\delta$  = biological fractionation (‰, PDB);  $F_o$ ,  $F_i$  = burial flux of organic and carbonate C, respectively ( $10^{12}$  mol C/yr);  $f_{org}$  = relative flux of organic C ( $F_o/(F_o + F_i)$ );  $\delta_{carb}$  =  $\delta^{13}\text{C}$  value of carbonate C (‰, PDB). PDB is Peedee belemnite.

10 times larger than at present would permit a maximum rate of change of only 1.7‰/m.y. In either case, high DIC provides an effective buffer against even large perturbations of the C cycle.

### $C_{org}$ - $C_{carb}$ Coupling

The sensitivity of the marine C cycle to isotopic change is further affected by the degree of coupling between C fluxes, i.e., the extent to which  $C_{org}$  and  $C_{carb}$  are produced, buried, and exhumed together. Throughout Earth history, a certain degree of geochemical control has been exerted over both  $C_{org}$  and  $C_{carb}$  fluxes. For example, weathering exerts a first-order control on both  $C_{org}$  production, via P input to the oceans, and on  $C_{carb}$  burial, via alkalinity flux. Such controls must have been in place for the entire history of the carbon cycle. Beyond these controls, however, the modern marine C cycle is characterized by biological coupling in which  $C_{org}$  and  $C_{carb}$  are linked through enzymatic production of  $\text{CaCO}_3$  skeletons. As a result, perturbations that affect  $C_{org}$  production and burial (e.g., extinction events) also affect  $C_{carb}$  production and burial, effectively reducing the range of values for  $f_{org}$  in the global ocean. In the Proterozoic, however,  $C_{org}$  was produced by non-skeletal prokaryotic and eukaryotic autotrophs and  $C_{carb}$  was produced by nonenzymatic processes (Brasier, 1986). Thus, the Proterozoic system was subject to a largely geochemical control on  $C_{carb}$  and an ecological control of  $C_{org}$ . Under these circumstances,  $C_{org}$  and  $C_{carb}$  would have behaved as independent variables, and the DIC reservoir size would have played the primary role in determining the isotopic sensitivity of the global ocean.

## EVOLUTION OF THE MARINE CARBON CYCLE

### Late Paleoproterozoic–Early Mesoproterozoic

Atmospheric models suggest elevated Proterozoic  $p\text{CO}_2$ , which would result in elevated marine DIC and extreme carbonate supersaturation (Grotzinger and Kasting, 1993). This

interpretation is supported by observations of extensive benthic precipitation of abiotic crystalline carbonate in a range of peritidal to deep-shelf environments (Grotzinger, 1989; Sami and James, 1996; Xiao et al., 1997). Production of open-water carbonate appears to have been greatly reduced at this time, perhaps as a result of lower planktic productivity (Anbar and Knoll, 2002) and a lack of suitable carbonate nucleation sites. In this scenario, any benthic production and deposition of  $C_{org}$  on continental shelves would have coincided with  $C_{carb}$  production and deposition (Fig. 2A). The degree to which  $C_{org}$  and  $C_{carb}$  production and deposition overlap spatially therefore results in an environmental coupling that may constrain  $f_{org}$  and, ultimately, the steady-state fluxes of  $C_{org}$  and  $C_{carb}$ . Thus, a model involving changes in the DIC reservoir size provides a link between petrographic observations and the marine C isotope record: elevated DIC should result in elevated carbonate saturation, increased ease of abiotic carbonate precipitation, and decreased sensitivity of the marine C isotope system to perturbation.

The C isotope record from ca. 2.0–1.3 Ga strata reveals a monotonous signature of  $\delta^{13}\text{C}$  values near 0.0‰. The relative absence of isotopic variation has been interpreted to reflect either tectonic quiescence (Brasier and Lindsay, 1998), unlikely given known tectonic activity during this interval (reviewed in Bartley et al., 2001), or low biological productivity (Buick et al., 1995). Low biological productivity, plausibly driven by nutrient limitation, would be expected to reduce export of  $C_{org}$  and result in a relatively small isotopic gradient in DIC with depth (Anbar and Knoll, 2002). Although low productivity may play a role in restricting the magnitude of isotopic excursions driven by marine upwelling or ocean overturn, mass-balance considerations require that  $f_{org}$  at this time was broadly similar to modern  $f_{org}$  ( $\sim 0.20$ ) in order to sustain average isotopic values of 0‰. We therefore suggest that the relative insensitivity of a high-DIC system to short-term perturbation was the primary factor in reducing isotopic

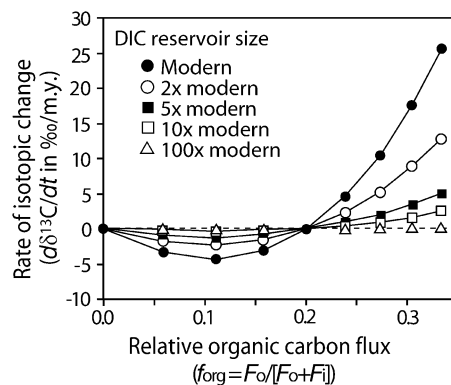


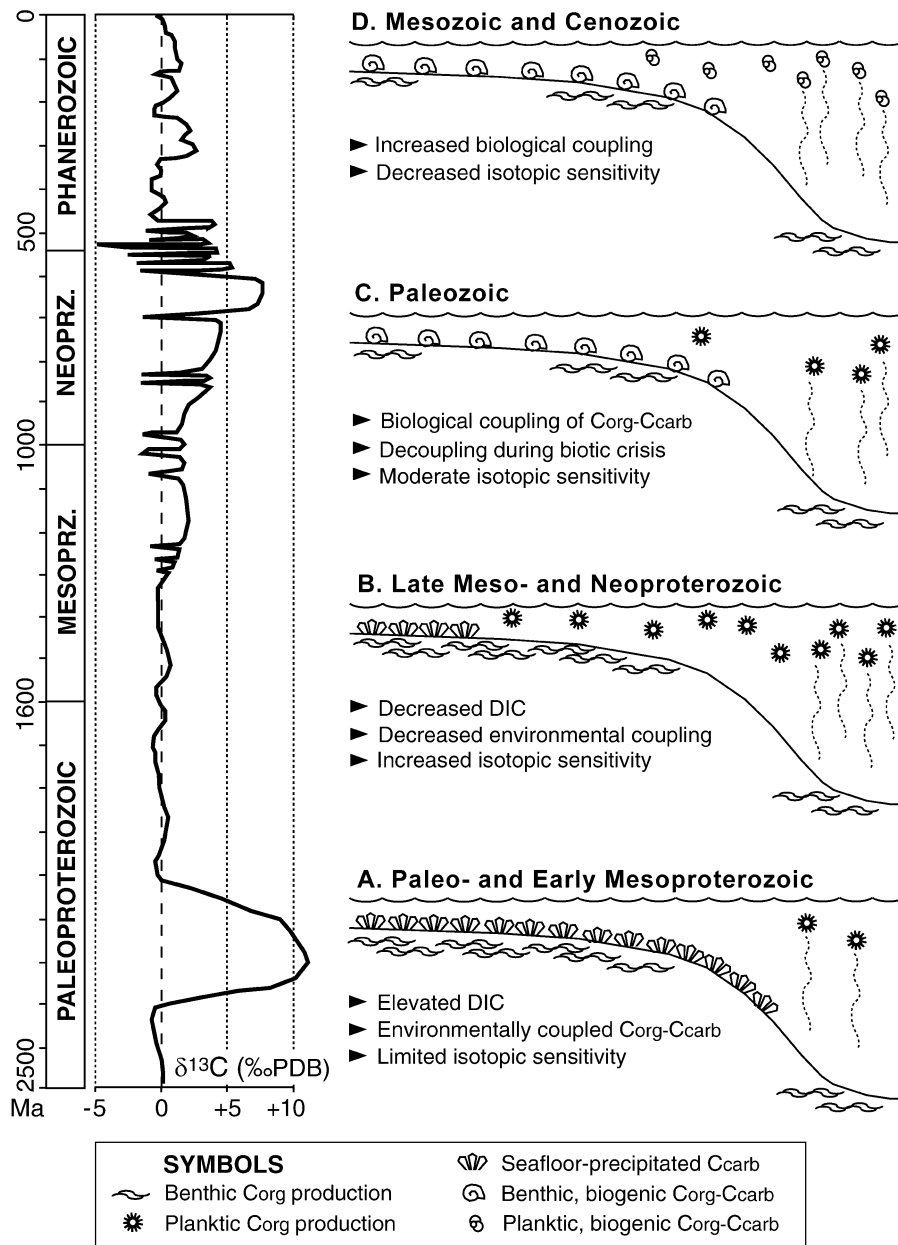
Figure 1. Sensitivity of marine C isotope system based on time-dependent mass-balance model.  $F_w$ ,  $F_i$ ,  $\delta_w$ , and  $\Delta\delta$  were held constant (initial values given in Table 1; Kump and Arthur, 1999).  $\delta_{carb}$  was allowed to vary as input parameters were altered. Maximum rates of isotopic change are plotted as function of  $f_{org}$  for dissolved inorganic carbon (DIC) reservoirs varying from modern to 100 times modern reservoir size.

variability during this interval. Short-term fluctuation in  $C_{org}$  production and export likely occurred, yet remained unrecognizable in the marine C isotope record. High marine DIC therefore acted to ensure that isotopic stasis would be maintained as long as perturbations were not large enough to carry the system to a new equilibrium state.

### Late Mesoproterozoic–Neoproterozoic

The transition from Paleoproterozoic and early Mesoproterozoic isotopic stasis to elevated average  $\delta^{13}\text{C}$  values and excursions of moderate magnitude in the late Mesoproterozoic occurred over  $\sim 30$  m.y. (Frank et al., 2003). This transition may reflect an “unstable steady-state” (Kump, 1989), during which marine  $\delta^{13}\text{C}$  values moved rapidly to a new equilibrium. Elevated  $\delta^{13}\text{C}$  values require an increase in  $f_{org}$  that was plausibly driven by secular changes in  $C_{org}$  production and burial (Frank et al., 2003); however, if  $C_{org}$  burial alone were responsible for the observed 3.5‰ change in  $\delta^{13}\text{C}$  values at this time, then mass-balance considerations require an  $\sim 50\%$  increase in  $f_{org}$  without a compensating change in  $C_{carb}$  cycling. A similar, additional increase of  $f_{org}$  would be required to obtain the highly positive average  $\delta^{13}\text{C}$  values observed in the Neoproterozoic. In addition, increased storage and remineralization of dissolved organic matter may contribute to the exceptional variability of the Neoproterozoic record (Rothman et al., 2003).

Such large changes in average  $\delta^{13}\text{C}$  are unlikely to be controlled simply by organic evolution and increased  $C_{org}$  productivity over extended time intervals. For example, the paleobiological record indicates that eukary-



**Figure 2. Marine C isotope curve, modified from Brasier and Lindsay (1998), and sketches illustrating effects of decreasing dissolved inorganic carbon (DIC) and  $C_{org}$ - $C_{carb}$  coupling on evolution of isotopic record. A: Paleoproterozoic and early Mesoproterozoic— $C_{carb}$  was produced primarily as abiotic seafloor cements. B: Late Mesoproterozoic to Neoproterozoic—marine DIC concentration decreased, carbonate-precipitation loci became increasingly restricted, and planktic  $C_{org}$  production expanded with diversification of eukaryotes. C: Paleozoic—with advent of abundant skeleton-forming organisms,  $C_{org}$  and  $C_{carb}$  production became highly coupled in shallow seas, but remained less so in open-marine environments. D: Mesozoic–Cenozoic— $C_{org}$  and  $C_{carb}$  production became more strongly coupled through expansion of calcareous plankton.**

otic diversification occurred primarily in the Neoproterozoic (Knoll, 1994), nearly 400 m.y. after the 3.5‰ shift in  $\delta^{13}C$  in the mid-Mesoproterozoic. If, however, the coincidence of positive  $\delta^{13}C$  values and increased excursion magnitude is related to decreasing DIC reservoir size, then the observed isotopic shift ca. 1.3 Ga may be partly attributable to changing loci of  $C_{carb}$  production and deposition (Fig. 2B). By the late Mesoproterozoic, car-

bonate precipitation had become largely restricted to the shallow shelf, and export of carbonate to the deeper shelf was restricted by rapid lithification of carbonate substrates (Bartley et al., 2000; Kah and Knoll, 1996). Restriction of  $C_{carb}$  production and deposition to shallow shelves resulted in strong environmental coupling in shallow-water environments, yet allowed  $C_{org}$  production in the deep-shelf region to remain uncompensated

by  $C_{carb}$ , thereby resulting in an increase in  $f_{org}$ . Such spatial decoupling of  $C_{org}$  and  $C_{carb}$  production and burial is consistent with observations regarding the style, timing, and locus of carbonate deposition, and provides a mechanism for  $f_{org}$  increases to be sustained over extended intervals of time.

Similarly, the anomalously high average  $\delta^{13}C$  values and dramatic isotopic excursions of the Neoproterozoic plausibly reflect more extensive decoupling of shelf and basin environments in combination with Neoproterozoic evolutionary, tectonic, or climatic events (Kaufman et al., 1993; Knoll, 1994; Hoffman et al., 1998). Extreme isotopic variability during this interval further suggests that DIC (and  $pCO_2$ ) at this time was lower than has been previously suggested (cf. Kasting [1987], who suggested that  $pCO_2$  was at least 10 times present levels in the Neoproterozoic and >100 times present levels at 2.5 Ga). Neoproterozoic excursions of >10‰, in particular, suggest extreme isotopic sensitivity and thus a relatively small DIC reservoir, perhaps approaching modern levels (Fig. 1).

#### Phanerozoic to Recent

The Phanerozoic C isotope record can be divided into two main parts: a Paleozoic component with average  $\delta^{13}C$  values near 0‰ and both positive and negative isotopic excursions of moderate intensity ( $\pm 4\%$ ), often associated with episodes of biotic crisis (Saltzman et al., 1995), and a Mesozoic–Cenozoic component characterized by average  $\delta^{13}C$  values near 0‰ and only limited isotopic variability, even during times of extreme biotic crisis (Magaritz, 1989; Veizer et al., 1999). This Phanerozoic pattern of variation may also be directly linked to the degree of  $C_{org}$ - $C_{carb}$  coupling in the global ocean.

During the Paleozoic, biological productivity and carbonate production is primarily attributed to benthic skeletal organisms, resulting in strong coupling of  $C_{org}$  and  $C_{carb}$  production and burial. However, open-water production was dominated by nonskeletal plankton, providing a potential source of  $C_{org}$  production and burial uncoupled from  $C_{carb}$  production and burial (Fig. 2C). When shelf biota underwent environmental crisis,  $C_{org}$  and  $C_{carb}$  production and burial may have been dominated by decoupled processes. Combined with a relatively small DIC reservoir, this decoupling left the system sensitive to perturbations. With the expansion of calcareous nannoplankton in the Mesozoic, however, both open-water and shelf  $C_{org}$  and  $C_{carb}$  production and burial become inextricably linked (Fig. 2D), which would have strengthened biological coupling and effectively buff-

ered the global isotopic system against all but the most severe biotic crises.

## CONCLUSIONS

The role of DIC in controlling the C isotope character of seawater can be evaluated by using a time-dependent carbon-cycle model. Field and petrographic observations suggest that marine carbonate saturation, and thus DIC reservoir size, decreased through the Proterozoic. Such a decrease would have resulted in a progressive increase in the sensitivity of the isotopic system to short-term biogeochemical perturbations. Reduction in DIC reservoir size would also shift the locus of carbonate precipitation onshore, resulting in spatial decoupling of  $C_{org}$  and  $C_{carb}$  fluxes and further sensitizing the system to isotopic change. In this model, the absence of significant C isotope variation prior to ca. 1.3 Ga need not reflect tectonic, environmental, or evolutionary stasis, but rather the inability of the marine C isotope system to record biogeochemical perturbation. In light of this model, the >10‰ positive  $\delta^{13}C$  excursion ca. 2.3–2.1 Ga (Karhu and Holland, 1996) represents an isotopic event of extraordinary magnitude. During the latter half of the Proterozoic, a stepwise evolution of the marine C isotope system likely records a combination of biological evolution and a decrease in marine DIC reservoir size, which affected both the isotopic sensitivity of the system and the steady-state relationship between  $C_{org}$  and  $C_{carb}$  fluxes, allowing elevated  $\delta^{13}C$  values to be sustained for geologically long time spans. With the advent of abundant skeleton-forming organisms, biological  $C_{org}$ - $C_{carb}$  coupling came to dominate the marine carbon cycle, providing a new mechanism for increased isotopic stability and resulting in dampened isotopic response to perturbations, particularly during the Mesozoic and Cenozoic.

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