Constraints on early Cambrian carbon cycling from the duration of the Nemakit-Daldynian–Tommotian boundary $\delta^{13}C$ shift, Morocco

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ABSTRACT

The Nemakit-Daldynian–Tommotian (ND-T) boundary marks the first appearance of metazoan reefs and calcite biomineralizers and is associated with the largest $\delta^{13}C$ shift during the Phanerozoic Eon. Biological transitions in Earth history are often accompanied by excursions in the carbon isotopic composition ($\delta^{13}C$) of the ocean, where $\delta^{13}C$ variability is interpreted to reflect changes in the global carbon cycle. The duration and thus rate of these $\delta^{13}C$ anomalies are rarely known, making it difficult to constrain their possible causes and their relationship, if any, to biologic transitions. We report sedimentological and $\delta^{13}C$ data from a new 2.5-km-thick section that spans the early Cambrian evolutionary "explosion" in the Moroccan Anti-Atlas Mountains. Three new zircon ^{206}Pb-^{238}U ages from tuffs within the stratigraphy constrain the timing of the ND-T boundary to 524.84 ± 0.09 Ma. Two of the tuffs exactly bracket the ND-T transition and constrain the duration of the –8‰ $\delta^{13}C$ shift to 506 ± 126 k.y. With a simple box model, we explore a range of geochemical processes that could account for such a rapid ND-T $\delta^{13}C$ shift, and conclude that metamorphic and/or volcanic fluxes of carbon may have been sustained at levels 4–16 times higher than today for millions of years.

INTRODUCTION

At the end of the Ediacaran Period, ca. 542 Ma (Bowring et al., 2007), a global carbonate carbon isotope excursion to –6‰ marks the abrupt last appearance of the soft-bodied Ediacaran organisms and the calcified animals *Cloudina* and *Namacalathus* (e.g., Knoll et al., 2006). During the ensuing Nemakit-Daldynian Stage of the early Cambrian, animals began to dig deeper burrows and new calcifying animal taxa appeared (e.g., Marshall, 2006). Large-amplitude oscillations in seawater $\delta^{13}C$ characterize the Nemakit-Daldynian, culminating in a pair of 9‰ positive $\delta^{13}C$ excursions that lasted 1–3 m.y. each (Maloof et al., 2005).

Globally, near the Nemakit-Daldynian–Tommotian (ND-T) boundary, a negative $\delta^{13}C$ shift from +5‰ to mean values of –1‰ to –3‰ corresponds to the first appearance of archaeocyaths and an abrupt dampening of $\delta^{13}C$ volatility (Maloof et al., 2005). Smaller 1‰–3‰ $\delta^{13}C$ oscillations characterize the Tommotian and Atdabanian Stages, as trilobites, brachiopods, and echinoderms first appear. The pair of large pre–ND-T positive $\delta^{13}C$ excursions and the subsequent negative $\delta^{13}C$ shift in Morocco also are found in Siberia (e.g., Kouchinsky et al., 2007), and in less detail in south China (Ishikawa et al., 2008; Brasier et al., 1990) and Mongolia (Brasier et al., 1996), suggesting that shallow-water carbonate regions around the world underwent similar changes in the carbon isotope composition of seawater.

GEOLOGY AND GEOCHRONOLOGY

Rifting of the western Anti-Atlas margin of Morocco associated with initial stages of Rheic Ocean (Nance et al., 2010) opening took place between 577 and 560 Ma and is represented by Ouarzazarte Group lavas and volcaniclastic sediments (Maloof et al., 2005). Following the cessation of rift volcanism, the region subsided and underwent marine transgression. The 2.5-km-thick package of marine carbonates of the Taroudant Group (Adoudounian and Lie de Vin Formations) and the Tata Group (Igoudine, Amouslek, and Issafene Formations; Fig. 1) represents the most expanded record of early Cambrian carbonate deposition in the world.

The first marine carbonates and sandstones of the Tabia Member of the Adoudounian Formation filled fault-bound basins. The overlying Tifnout Member of the Adoudounian Formation represents thermal subsidence–dominated sedimentation on the Anti-Atlas margin. The Tifnout Member is composed of meter-scale shallowing-upward parasequences (e.g., Fig. 2). Typical parasequences begin with silt or marl overlying a flooding surface, and grade up into wavy-laminated dolosiltite, followed by laterally equivalent grainstones and stromatolites, and are capped with supratidal microbialaminites. In the northeast-southwest–oriented trough between the towns of Tiout and Aguerd (Fig. 1A), where the Tifnout Member is 2–5 times thicker than elsewhere, the parasequences tend to be 2–10 m thick, with less frequent evidence of subaerial exposure.

A crosscutting relationship with the Jbel Boho Syenite constrains the lower Tifnout Member to be older than the multigrain U-Pb isotope dilution–thermal ionization–mass spectrometry (ID-TIMS) upper-intercept age of 534 ± 10 Ma (Ducrot and Lancelot, 1977). The upper Tifnout Member contains at least two green tuffs speckled with euhedral feldspar phenocrysts found within 5–30-m-thick microbialite buildups. Tuff M223 is 60 cm thick, at a stratigraphic height of 614 m in Oued Sdas (Figs. 1B and 2). We initially reported a date of 525.38 ± 0.46 Ma for M223 that we interpreted as the depositional age (Maloof et al., 2005). Here we refine this age to be 525.343 ± 0.088 Ma (mean square of weighted deviates, MSWD = 0.33) with three new analyses and an improved U-Pb tracer calibration (Table 1; Fig. 3). Tuff M231 is 50 cm thick, at a stratigraphic height of 764 m in Oued Sdas (Fig. 2); we report a new weighted mean $^{206}Pb/^{238}U$ date of 524.837 ± 0.092 (MSWD = 0.72) (Table 1; Fig. 3).

The Lie de Vin Formation overlies the Adoudounian Formation transitionally and represents a seaward tilting of the Anti-Atlas margin. In the Tiout-Aguerd trough, Adoudounian Formation peritidal dolostones transition into sublittoral couplets of purple argillite and biohermal thrombolitic and stromatolitic limestones. Outside of the Tiout-Aguerd trough, the Lie de Vin Formation is a prograding fluvial sandstone likely responsible for the increase in siliciclastic input to the basin. Thrombolites in the upper half of the Lie de Vin Formation contain calcified remains of algae such as *Renalcis* (Latham and Riding, 1990), and associated grainstones often contain vertical burrows such as *Diplocraterion*. Tuff M234 is 10 cm thick, within an 80-cm-thick microbialite in Oued Sdas at a stratigraphic height of 1031 m (Fig. 2); we report a weighted mean $^{206}Pb/^{238}U$ date of 523.17 ± 0.16 Ma (MSWD = 1.2) (Table 1; Fig. 3). At 1540 m (Fig. 1B) in the upper Lie de Vin Formation at Tiout (MS-6; Fig. 1A), a tuff yielded a weighted mean $^{206}Pb/^{238}U$ ID-TIMS date of 522.4 2.5 Ma using both single zircon and multigrain techniques (Landing et al., 1998; Compston et al., 1992). Here we refine this age by dating M236, a 5-cm-thick tuff within a 2.2-m-thick thrombolite bioherm at a stratigraphic height of 1536 m in Oued Sdas (Fig. 1B). This tuff is located

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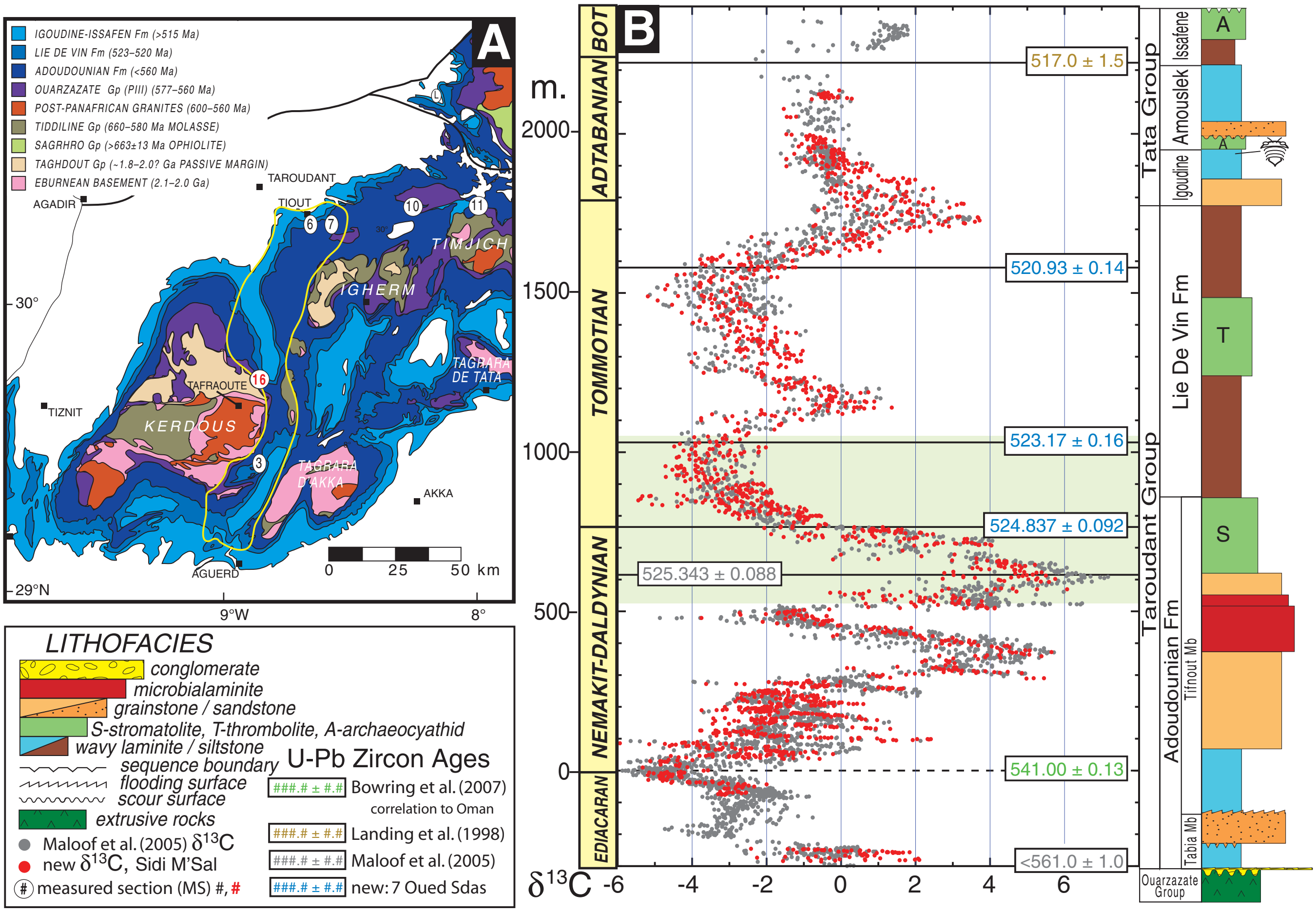

Figure 1. A: Geologic map (after Saadi et al., 1985) of Tiout-Aguerd trough (yellow outline) along early Cambrian margin of western Anti-Atlas Mountains (FM—formation; GP—group). B: Summary $\delta^{13}C$ record of Taroudant and Tata Groups. BOT—Bottomian Stage. The sedimentology is simplified to represent the dominant lithologies. Light green region highlights stratigraphic range depicted in Figure 2.

at approximately the same stratigraphic level (±25 m) as the tuff reported a decade ago from Tiout (Landing et al., 1998; MS6: Fig. 1A), and has a weighted mean $^{206}Pb/^{238}U$ date of 520.93 ± 0.14 Ma (MSWD = 0.42) (Table 1; Fig. 3) as its depositional age.

The overlying Tata Group represents the remainder of early Cambrian strata and a transition to more energetic marine conditions than those found in the Taroudant Group. The Upper Igoudine Formation contains the oldest known skeletal fossils from Morocco and includes trilobites, archaeocyaths, brachiopods, and chancelloriids (Geyer and Landing, 1995). A tuff from the equivalent to the lower Issafene Formation in the Lemdad syncline (High Atlas; L in Fig. 1A) provides a weighted mean $^{207}Pb/^{206}Pb$ ID-TIMS date of 517 ± 1.5 Ma for the upper Tata Group (Landing et al., 1998).

ND-T BOUNDARY

The ND-T boundary is defined as the base of Bed 8 in the Ust-Yudoma Formation at the Ulukhan Sulugur section in the Aldan River, southeastern Siberia (Rozanov, 1984). This horizon was chosen because it marks the first appearance of archaeocyaths and a diverse assemblage of small shelly fossils (Rozanov, 1984). However, attempts to identify the ND-T boundary elsewhere based on biostratigraphic correlation have been frustrated by the fact that fossil appearances are controlled by the distribution of taphofacies and unconformities (e.g., Knoll et al., 1995). The ND-T boundary in the stratotype section is marked by a karstic unconformity that concentrates fauna of varying ages into transgressive base-Tommotian Pestrotsvet Formation beds (Knoll et al., 1995) and even grainstone-filled cavities below the unconformity within the Ust-Yudoma Formation (Khomentovsky and Karlova, 1993).

No Nemakit-Daldynian or Tommotian small shelly fossils have been found in Morocco, and the oldest Moroccan archaeocyaths are Atdabanian in age (Fig. 1B; Geyer and Landing, 1995), so the ND-T boundary in Morocco and Siberia cannot be compared biostratigraphically. Although carbon isotope records may be truncated by stratigraphic hiatuses, the morphology of $\delta^{13}C$ curves between hiatuses remains intact and may be compared from section to section (Maloof et al., 2005). We mapped the carbon isotope records from Ulakhan-Sulugur (Brasier et al., 1993) and Dvortsy (Repina and Rozanov, 1992) onto the $\delta^{13}C$ curve from Morocco (Maloof et al., 2005), and located the ND-T boundary at the zero crossing in the record of declining $\delta^{13}C$ after the last positive anomaly (Fig. 1B). This placement is consistent with combined biostratigraphic and $\delta^{13}C$ data from Mongolia (Brasier et al., 1996), China (e.g., Brasier et al., 1990), and the rest of Siberia (e.g., Kouchinsky et al., 2007).

CHEMOSTRATIGRAPHY

We reproduce structured $\delta^{13}C$ variability as small as 2‰ across 100 km of the western Anti-Atlas Mountains (Fig. 1) without any $\delta^{13}C$ dependence on lithofacies (Fig. 2) or $\delta^{13}C$ covariation with $\delta^{18}O$ (Fig. DR1 in the GSA Data Repository[1]). Furthermore, $\delta^{13}C$ variability from the early Cambrian of Morocco and Siberia can be matched peak for peak without violating

[1]GSA Data Repository item 2010168, methods and results, is available online at www.geosociety.org/pubs/ft2010.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

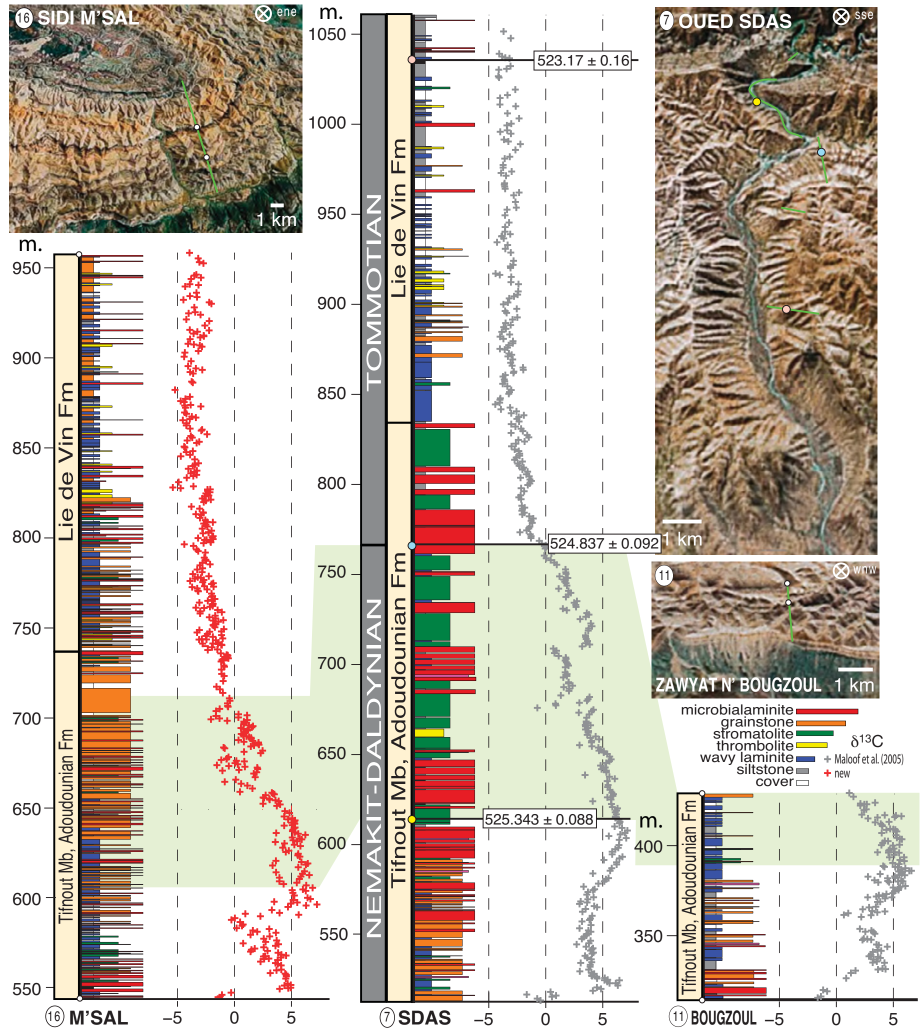

Figure 2. Detailed stratigraphy of Nemakit-Daldynian–Tommotian (ND-T) $\delta^{13}C$ transition. Oued Sdas (MS7) is 70 km northeast of Sidi M'Sal (MS16) and 50 km west of Zawyat N'Bougzoul (MS11). Complete sections are labeled with green lines on Google Earth™ images, with white dots representing the beginning and end of the stratigraphic detail shown in this figure, and colored dots depicting locations of three new single zircon U-Pb ages. Mb—member; Fm—formation.

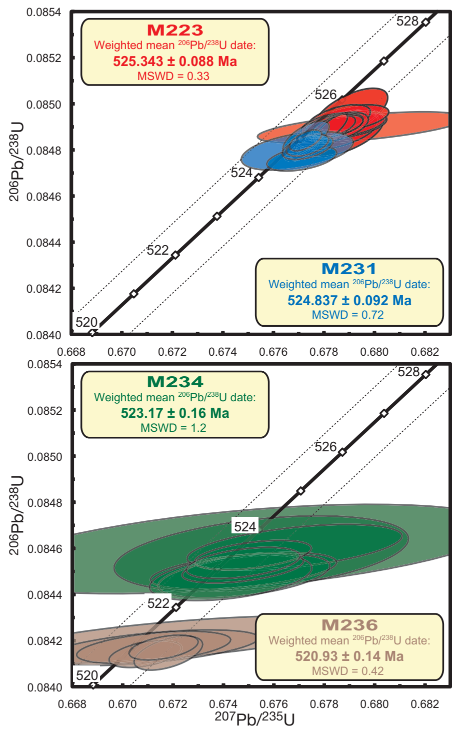

Figure 3. U-Pb concordia diagrams for two Adoudounian Formation tuffs (red—M223; blue—M231) and two Lie de Vin Formation tuffs (green—M234; brown—M236) plotted with the same scale and range. Error ellipses represent 2σ uncertainty with internal errors only. Dashed lines parallel to solid black concordia represent 95% confidence envelope associated with uncertainty in the uranium decay constants. MSWD—mean square of weighted deviates.

TABLE 1. SUMMARY OF CALCULATED U-Pb AGES AND THEIR UNCERTAINTIES

Sample	$^{206}Pb/^{238}U$ age	Error (2σ)			MSWD	$^{207}Pb/^{235}U$ Age	Error (2σ)			MSWD	$^{207}Pb/^{206}Pb$ age	Error (2σ)		MSWD
		X	Y	Z			X	Y	Z			X	Z	
M223	525.343	0.088	0.35	0.93	0.33	525.86	0.17	0.43	1.0	0.27	528.09	0.71	1.3	0.23
M231	524.837	0.092	0.35	0.93	0.72	525.07	0.13	0.39	0.97	0.15	525.99	0.58	1.2	0.25
M234	523.17	0.16	0.42	1.0	1.2	523.62	0.47	0.73	1.3	0.26	525.6	2.3	2.9	0.22
M236	520.93	0.14	0.40	0.97	0.42	521.57	0.37	0.63	1.2	0.30	524.6	1.8	2.4	0.34

Note: MSWD—mean square of weighted deviates.
X—internal (analytical) uncertainty in the absence of all external or systematic errors; Y—-incorporates the U-Pb tracer calibration error; Z—includes X and Y as well as the decay constant errors (Data Repository [see footnote 1]).

biostratigraphic or geochronological constraints (Maloof et al., 2005). Such consistent intrabasinal and interbasinal reproducibility across large environmental and sedimentation-rate gradients suggests that these carbonates are recording primary signals in well-mixed dissolved inorganic carbon (DIC) of the global ocean.

The ND-T in Morocco is characterized by a drop from mean $\delta^{13}C$ values of +5‰ down to 0‰ in 50–150 m and 506 ± 126 k.y., and then a continued decline over 25–75 m and <1 m.y. to a new mean of –3‰ that persists for 4 m.y. (Fig. 2). On >100 k.y. time scales, negative shifts of even a few per mil are difficult to explain with methane or organic carbon release scenarios (e.g., Higgins and Schrag, 2006) because finite reservoirs are depleted quickly. Also, the ND-T transition represents a sudden shift between two states, not a brief $\delta^{13}C$ excursion. For the ND-T $\delta^{13}C$ shift, which lasted just longer than the relaxation time of the ocean-atmosphere carbon cycle (currently ~100 k.y.; Holser et al., 1988), we consider the carbon isotopic mass balance for the bulk Earth:

$$\delta^{13}C_i = \left(1-f_{org}\right)\delta^{13}C_c + \left(f_{org}\right)\left(\delta^{13}C_c - \varepsilon\right), \qquad (1)$$

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where $\delta^{13}C_i$ is the isotopic composition of DIC entering the ocean (approximately mantle), $\delta^{13}C_c$ is the isotopic composition of the oceanic DIC pool, ε is the fractionation between DIC and organic carbon, and $f_{org} = C_{org}/C_{total}$ is the fraction of carbon buried that is organic (Kump, 1991). Changes in f_{org} will cause shifts in $\delta^{13}C$ by relying on changes in the fluxes of oxidized and reduced carbon species, rather than changes in finite reservoirs. Saltzman (2005) and Maloof et al. (2005) developed conceptual models that linked Paleozoic $\delta^{13}C$ variability to changes in f_{org} associated with oceanic redox conditions, carbon to phosphorous ratios in buried organic matter, and phosphate versus nitrate limitation. In this paper we focus on the process constraints afforded by new U-Pb zircon–derived rates of $\delta^{13}C$ change.

Preliminary $\delta^{13}C(C_{org})$ of bulk organic matter from the same dolostones we measured for $\delta^{13}C(CaCO_3)$ suggest ε of 27.5 ± 1.5 spanning the ND-T transition. If $\delta^{13}C_i$ and ε are held constant, a simple way to simulate a negative $\delta^{13}C(CaCO_3)$ isotope shift while maintaining steady state is to allow a drastic decrease in f_{org}. In Figure 4, we plot response times to a step change in f_{org} from 0.4 to 0.14 for various DIC, and carbon burial (F_b), and input fluxes (F_i, where for time scales >100 k.y., $F_i = F_b$ should reflect volcanic [e.g., Berner et al., 1983] and metamorphic [e.g., Evans et al., 2008] outgassing rates of CO_2). For F_b and DIC similar to the modern oceans, the change in f_{org} could cause the 8‰ negative excursion in 3.5 m.y. (Fig. 4).

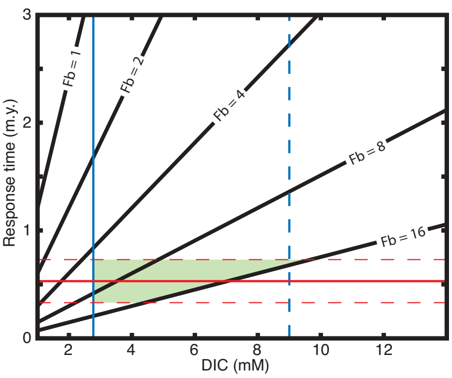

Figure 4. Steady-state model where response time of $\delta^{13}C$ varies depending on size of dissolved inorganic carbon reservoir in ocean ([DIC]) and burial flux of carbon (F_b, as multiple of modern burial flux). Response time is defined as the time it takes $\delta^{13}C_c$ to change from +5‰ to a value within 1‰ of target –3‰ after a step decrease in f_{org} (fraction of carbon carbon buried that is organic) from 0.4 to 0.14. Horizontal solid and dashed red lines depict U-Pb duration and 2σ error bars, respectively, for the Nemakit-Daldynian–Tommotian (ND-T) $\delta^{13}C$ shift. Vertical solid and dashed blue lines depict sizes of the modern and approximate Cambrian DIC reservoirs, respectively. Green region reflects allowable range of parameters for steady-state interpretation of the ND-T transition.

Larger DIC and/or smaller F_b lead to more sluggish response times (Bartley and Kah, 2004). A steady-state model of the ND-T negative $\delta^{13}C$ shift constrained to last 380–632 k.y. will only work for modern values of DIC if F_b is four times larger than today, or the change in f_{org} was much more extreme than the beginning and ending values for $\delta^{13}C$ suggest. Furthermore, the early Cambrian likely had elevated DIC to compensate for a 5% weaker sun and to explain the lack of glaciation. For DIC ~9 mM (Berner et al., 1983), an F_b 16 times larger than modern carbon burial flux is required to generate the observed $\delta^{13}C$ shift in 500 k.y.

Biological events often are associated with $\delta^{13}C$ anomalies, even if the causal relationship is uncertain. The amplitude and duration of $\delta^{13}C$ changes recorded in carbonates are as much a function of the long-term (>1 m.y.) residence time of carbon (DIC/ F_i) as they are a function of the magnitude of the f_{org} perturbation. Perhaps elevated volcanic and/or orogenic fluxes of CO_2 allowed changes in f_{org} to be recorded as large $\delta^{13}C$ anomalies in early Cambrian carbonates, even if these perturbations to f_{org} were no more significant than those associated with biological events later in the Phanerozoic.

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