THE SULPHATE CAPACITOR HYPOTHESIS FOR CARBON CYCLE DYANMICS AT THE DAWN OF LIFE

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Global Carbon Cycle

Important processes to the modern global carbon cycle (Fig. 1):

- **Tectonic timescales (>10^6 yr)**
  - **Plate tectonics**
  - **Weathering (silicate, carbonate, organic carbon)**
  - **Volcanism**
  - **Burial (carbonate, organic carbon)**
- **Orbital (10^4–10^5 yr) and millennial timescales (10^2–10^4 yr)**
  - **Ocean circulation**
  - **Biosphere**
  - **Climate**
- **Anthropogenic timescale (since industrial revolution)**
  - **Fossil fuel burning**
  - **Land use change**

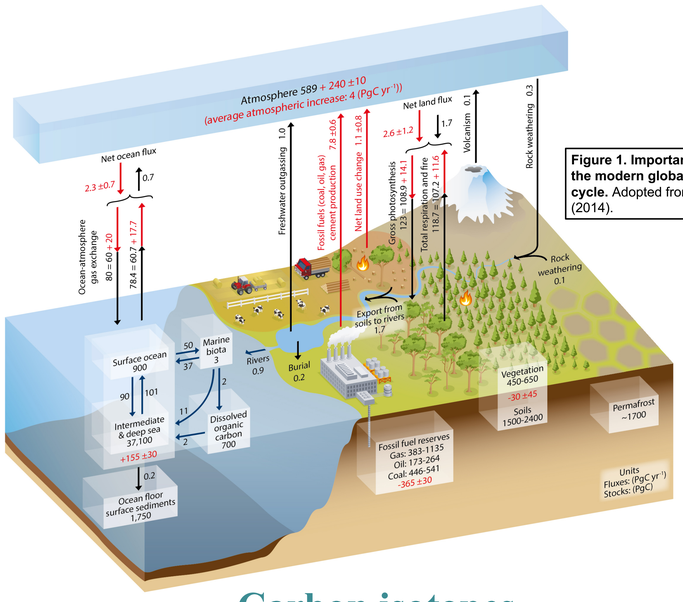


Figure 1. Important fluxes of the modern global carbon cycle. Adopted from IPCC (2014).

Carbon isotopes

- **Carbon isotopes are used to investigate ancient carbon cycle dynamics (Fig. 2)**
- **Carbonate rocks (e.g., limestone) record the seawater ratio of ^{13}C to ^{12}C at the time of formation**
- **This ratio ($\delta^{13}C$; Eq. 1) is controlled by long-term changes in 'tectonic-scale' processes, such as weathering and volcanism**

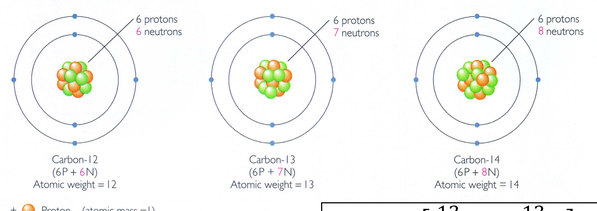


Figure 2. Visual representations of three carbon isotopes. Adopted from Press et al. (2004).

Equation 1.

$$\delta^{13}C = \left[\frac{\frac{^{13}C}{^{12}C_{sa}} - \frac{^{13}C}{^{12}C_{std}}}{\frac{^{13}C}{^{12}C_{std}}} \right] * 1000$$

My Research

The Precambrian–Cambrian transition was an incredibly dynamic period of Earth history in terms of both oceanic and biological evolution. The isotopic signature of carbon ($\delta^{13}C$) is often employed to better understand this evolution, characterizing trends in both the global carbon cycle and ocean chemistry. However, traditional carbon cycle dynamics have failed to fully explain variations in $\delta^{13}C$ documented in this interval. Our research aims to tackle this problem, leading to a greater understanding of both the Precambrian–Cambrian carbon cycle, as well as $\delta^{13}C$ records more generally. We have developed a 'sulphate capacitor' hypothesis for this period of Earth history, potentially explaining large magnitude variations that are irreconcilable with traditional carbon cycle dynamics. Our work offers a new explanation to the interval of greatest $\delta^{13}C$ variability in Earth history, while also introducing a new carbon cycle perturbation mechanism.

This project closely relates to the rest of my dissertation research, which aims to apply a new numerical correlation algorithm to important Precambrian–Cambrian $\delta^{13}C$ records. I am also working to develop a model to better understand smaller, local-scale variations due to depositional histories in $\delta^{13}C$ records. Ultimately, I aim to combine these two numerical algorithms to improve $\delta^{13}C$ correlations and interpretations. As a test, I will apply both algorithms to data I collected in Death Valley (CA) to aid in interpretation. In sum, this research will lead to a deeper understanding of the fundamental controls, fidelity, and heterogeneity in Precambrian–Cambrian $\delta^{13}C$ sequences.

Precambrian Dynamics

- **Neoproterozoic (1000–541 Ma) carbonate rocks host a succession of globally synchronous, large amplitude negative excursions (< -5‰) in $\delta^{13}C$ (Fig. 3)**
- **Previous explanations: a large dissolved organic carbon (DOC) capacitor (e.g., Bjerrum and Canfield, 2011; Shields, 2017) or significant changes to carbon cycle dynamics (e.g., Johnston et al., 2012; Rothman et al., 2003)**
- **Geochemical data (e.g., Sperling et al., 2015; Lyons et al., 2009) depict an anoxic Neoproterozoic ocean subject to brief episodes of localized sulphate-depletion and oxygenation (Sahoo et al., 2016)**

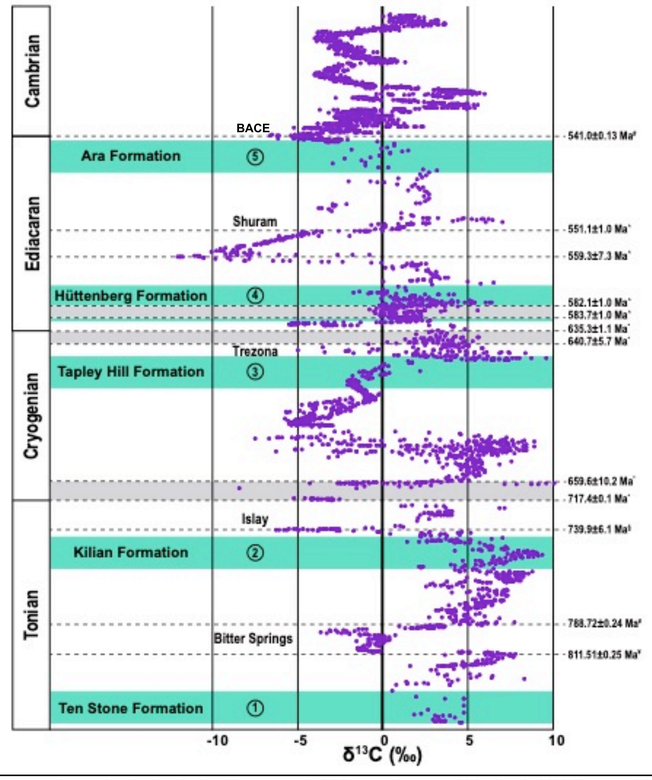


Figure 3. Neoproterozoic geochemical evolution. Neoproterozoic $\delta^{13}C$ composite curve (Maloof et al., 2010; Turner and Bekker, 2016; Fike et al., 2006; Halverson et al., 2005; Amthor et al., 2003; purple) with the position of large amplitude excursions indicated in black. Grey intervals indicate the position of 'snowball' glaciations. Numbered teal intervals indicate the position of bedded sulphate-rich evaporite deposits referred to in the text (Turner and Bekker, 2016). Geochronologic tie points shown in black: ¥ (Halverson et al., 2007); § (Strauss et al., 2014), * (Rooney et al., 2015); ^ (Macdonald et al., 2013); # (Bowring et al., 2007).

Sulphate Capacitor Hypothesis

- ***We hypothesize that dissolution of sulphate evaporite—by sea level rise or erosion—could deliver sulphate to an oxidant-limited, methane-rich Neoproterozoic ocean, driving large amplitude $\delta^{13}C$ excursions via an-aerobic oxidation of methane (AOM) coupled to sulphate reduction (Fig. 4)***
- **We developed a simplified steady-state box model for the Neoproterozoic global carbon cycle to test this hypothesis (Fig. 5; Table 1) and demonstrate that the dissolution of an enormous sulphate evaporite mass can drive a -12‰ model $\delta^{13}C$ excursion (Fig. 6)**

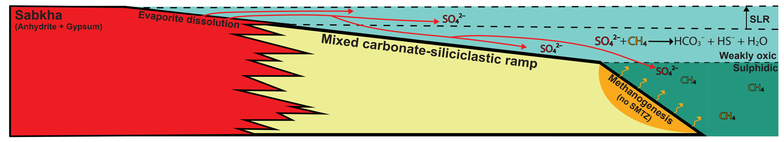
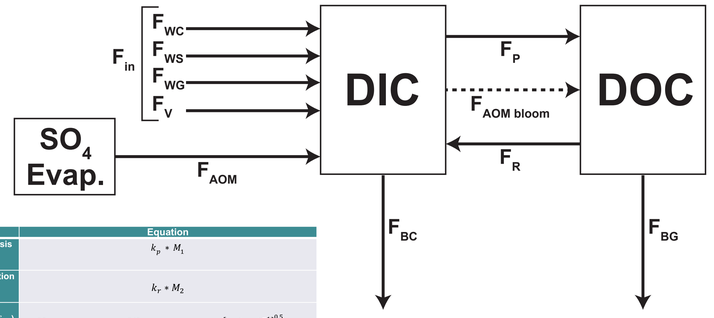


Figure 4 (above). Conceptual visualization of the evaporate dissolution mechanism. During sea level rise or erosion exposed sulphate evaporite is dissolved and delivered to a sulphidic ocean, where it oxidizes free methane in the water column via AOM, adding isotopically light carbon to the DIC reservoir and driving a negative $\delta^{13}C$ excursion.



Flux	Equation
Photosynthesis (F_P)	$k_p * M_1$
Remineralization (F_R)	$k_r * M_2$
Silicate weathering (F_{WS})	$f_{AFER}^{0.5}[1 + RUN * (T - T_0)]^{0.65} * \exp[ACT(T - T_0)] * \left[M_3(M_{3,0})^{-1}\right]^{0.5} * F_{WS,0}$
Carbonate weathering (F_{WC})	$f_{AFER}^{0.2}[1 + 0.087(T - T_0)][M_3(M_{3,0})^{-1}]^{0.5} * F_{WC,0}$
Organic carbon weathering (F_{WG})	$f_{AF} f_{BF} k_{org} M_{org}$
Degassing (F_V)	$9*10^{12}$
Carbonate burial (F_{BC})	$(1 - f_B) * (F_{WS} + F_{WC} + F_{WG} + F_V)$
Organic carbon burial (F_{BG})	$f_B * (F_{WS} + F_{WC} + F_{WG} + F_V)$
Sulphate flux (F_{AOM})	$(EM_R * SP) * EDR$
Oceanic DIC reservoir (M_1)	$\frac{d(M_1)}{dt} = F_{WS} + F_{WC} + F_{WG} + F_V + F_R + F_{AOM} - F_P - F_{BC}$
Oceanic DOC reservoir (M_2)	$\frac{d(M_2)}{dt} = F_P - F_R - F_{BG}$

Figure 5 (above). Neoproterozoic carbon cycle model flow diagram. F_{WC} = carbonate weathering; F_{WS} = silicate weathering; F_{WG} = organic carbon weathering; F_V = volcanism; F_{AOM} = AOM-derived isotopically light bicarbonate; F_{BC} = carbonate burial; F_P = photosynthetic; F_{AOM} = AOM-consortium bacteria bloom; F_R = remineralization; F_{BG} = organic carbon burial; DIC = dissolved inorganic carbon reservoir; DOC = dissolved organic carbon reservoir; SO_4 Evap. = sulphate evaporite reservoir.

Table 1 (left). Reservoirs and fluxes for our simplified Neoproterozoic carbon cycle model. We adopted flux equations from previous work and defined the output fluxes in such a way to maintain steady state in the DIC and DOC reservoirs.

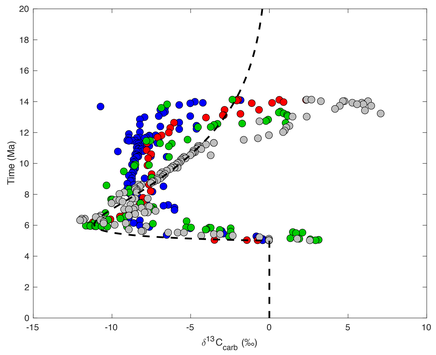


Figure 6 (right). Modeled $\delta^{13}C$ excursion versus published data. Dashed black line is the 'best-fit' model $\delta^{13}C$ excursion (evaporite dissolution begins at 5 Ma). Grey data from the Shuram Formation, Oman; green data from the Johnnie Formation, California; blue data from the Doushantuo Formation, South China; red data from the Wonoka Formation, Australia.

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Acknowledgments

We thank K.S. Dawson, D.A. Fike, C.E. Reimers, and K.R. Jay for helpful feedback. C.J.H. acknowledges support from the NSF GRFP and the ARCS Foundation, J.R.C. and A.C.M. from Oregon State University.

Author contributions: C.J.H. developed the conceptual idea and wrote and executed the MATLAB script for the numerical modelling with input from J.R.C. and A.C.M. All authors contributed to the technical analysis and writing of the manuscript.