Addressing the "Negative δ^{13}C arms" puzzle pre- and post-Neoproterozoic glaciations

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The oceanic dissolved organic carbon (DOC) inventory, estimated at approximately 660 gigatons (Gt),[1] is equivalent to that of atmospheric carbon reservoir. Interaction between the two leads to essential climate change.[2] However, investigations of oceanic DOC extend over a relatively brief temporal span, rendering our understanding of how DOC fluctuations might affect long-term climate variations is inadequately developed and potentially disregarded. Alternatively, paleoceanographic and paleo-environmental records, which may span hundreds of millions of years, offer invaluable opportunities to enhance our understanding and assemble a more comprehensive depiction of the potential significance of DOC in climate change. During the well-known Neoproterozoic "Snowball Earth" glaciations,[2] distinctive two-stage negative excursions of carbonate δ^{13}C ("Negative δ$^{13}C_{carb}$ Arms", Figure 1) are observed. While existing hypotheses fail to provide a reasonable explanation for this phenomenon, this paper introduces a new hypothesis addressing the role of the degradability of DOC in the Negative δ$^{13}C_{carb}$ Arms puzzle.We propose that the degradability of DOC (DOCD), regulated by factors such as O_2 accessibility and temperature-dependent enzyme activity, plays a pivotal role in Neoproterozoic carbon dynamics. This hypothesis offers an encompassing framework for understanding the deep-time carbon cycle, shedding light on the overlooked significance of DOC in Earth's long-term carbon cycle-climate interactions, with broad implications for the planet's dynamic carbon cycle and habitability.

SNOWBALL EARTH EVENTS ASSOCIATED WITH THE "NEGATIVE δ$^{13}C_{carb}$ ARMS"

The Neoproterozoic period, spanning from 1,000 to 540 million years ago (Ma), is a geological epoch nearly equivalent in duration to the Phanerozoic era, characterized by the resurgence of glacial episodes after a billion-year absence.[3] Among these glacial events, the Sturtian (~720 Ma) and the Marinoan (~635 Ma) elicit considerable fascination from both the scientific community and the public, as paleomagnetic evidence suggests that equatorial oceans likely received discharge from extensive continental ice sheets during these events, which is why these occurrences are commonly referred to as the "Snowball Earth" events.[3] The tropical glaciation distinguishes the Neoproterozoic glaciations as fundamentally distinct from the Pleistocene glacial periods, during which ice sheets were predominantly confined to mid- to high-latitudes.

In addition to the wild-spread ice sheet, the covariation of the climate and carbon cycle during the Snowball Earth events adds anotherintriguing facet to the topic.[2] The stable isotopic composition of carbon (denoted as δ^{13}C) preserved in the geological record provides a window to the operation of Earth's carbon cycle. In the geological past, the shift of carbonate δ^{13}C (δ$^{13}C_{carb}$) could hint at the perturbation of carbon budget among different reservoirs. For instance, during the Pleistocene glacial periods, a gradual and relatively modest decrease in the δ^{13}C of the dissolved inorganic carbon, typically less than 1 ‰, is observed, which is often attributed to the input of glacial land biomass (100 to 1000 Gt C) into the ocean. As the land biomass holds a rather low δ^{13}C imprint, remineralization of organic carbon from terrestrial sources results in the release of ^{12}C, leading to a reduction in δ^{13}C values during glacial periods, subsequently returning to higher values during deglacials.

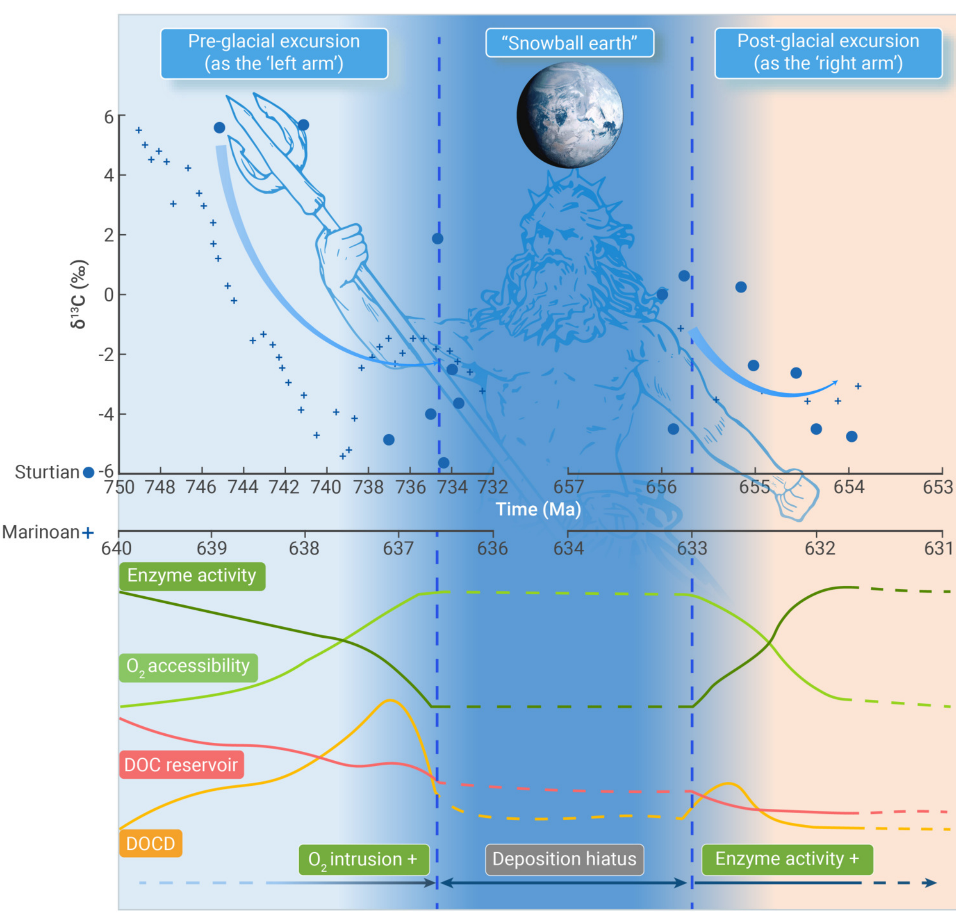

Figure 1. The DOCD hypothesis associated with the "Negative Arms" of the Neoproterozoic glaciations The upper panel displays δ^{13}C changes during both the Sturtian glaciation (indicated by 'o') and the Marinoan glaciation (indicated by '+'), with data from Pierrehumbert et al., (2011) and the references therein. Note that age estimations are based on original stratigraphy, serving the sole purpose of facilitating data comparability. The lower panel provides a conceptual diagram for the hypothesized variations in temperature-dependent enzyme activity and the accessibility of O_2 influenced by ocean stratification. These factors jointly regulate DOCD over time, resulting in two distinct peaks during the pre- and post-glacial phases, respectively. This, in turn, leads to stepwise depletion of the DOC reservoir and consequently the pre- and post-glacial negative excursion of δ$^{13}C_{carb}$.

The Neoproterozoic "Snowball Earth" events present a fundamentally distinct $\delta^{13}C_{carb}$ scenario (Figure 1). The extensive ice sheet coverage during these glaciations leads to a cessation of carbonate deposition. However, records exhibit that in addition to the initial negative shift in $\delta^{13}C_{carb}$ at the beginning of glaciation, there is a continued decrease in $\delta^{13}C_{carb}$ (instead of a return to pre-glacial levels) when carbonate deposition resumes at the end of the glaciation. This distinctive pattern marks a stepwise excursion in $\delta^{13}C_{carb}$. The negative shifts in $\delta^{13}C_{carb}$ values before and after the glaciers are therefore referred to as the "Negative Arms" (Figure 1).

CONNECTING DOC DEGRADABILITY (DOCD) WITH THE NEGATIVE ARMS

The $\delta^{13}C_{carb}$ excursions observed in the context of the Negative Arms can be attributed to potential mechanisms involving both inorganic and organic processes. Carbon input (primarily CO_2), characterized by a $\delta^{13}C$ value of approximately -6‰, originating from deep outgassing (e.g., volcanic emissions), may result in lower $\delta^{13}C$ values through direct mixing with the existing carbon reservoirs. However, the pre- and post-glacial excursions reaching values of nearly -10‰ at the end of the glaciations tends to discount inorganic input as the primary driving force behind these excursions.

Generally, organic carbon exhibits a considerably lower $\delta^{13}C$ signature due to carbon isotopic fractionation during photosynthesis. Therefore, an increased rate of remineralization would retain a higher proportion of ^{12}C in the ocean, causing a decline in $\delta^{13}C_{carb}$. Another case, the oxidation of methane, with extremely low $\delta^{13}C$ values, can lead to significant negative excursions in $\delta^{13}C_{carb}$ values during methane oxidation processes. However, this effect depends on the reservoir of ^{13}C generated during methanogenesis being isolated from remixing with the newly deposited inorganic carbon.

While existing hypotheses are not mutually exclusive, a significant challenge remains in explaining why $\delta^{13}C_{carb}$ values continue to decrease even after the major glacial phase when the climate becomes warmer. An alternative theory has emerged, suggesting that during the Proterozoic, there might exist a large DOC reservoir.[4] With sufficient oxidants, the DOC inventory would be more susceptible to oxidation than the deposited organic matters. We therefore propose a novel hypothesis to elucidate the Negative $\delta^{13}C$ Arms observed during the Neoproterozoic glaciations, which is based on changes in the oceanic dissolved organic carbon degradability (DOCD).

Instead of being defined chemically, DOCD can be viewed as a variable representing the degree of the biodegradability of DOC. It is contingent upon factors such as the molecular composition of DOC, its source, and the prevailing environmental conditions that govern enzyme activity.[5] Generally, oceanic DOC can be classed into three pools: labile DOC, semi-labile DOC and refractory DOC. Labile DOC can be used by heterotrophic microbes within days or even hours, semi-labile DOC can persist for months to years, while refractory DOC is resistant to microbial decomposition and can persist for thousands of years in the ocean.[1] Subsequent research has suggested that lower (higher) DOCD can lead to an increase (reduction) in the DOC inventory, impacting $\delta^{13}C_{carb}$ and pCO_2 during the orbital time scales.[5]

With this conceptual framework, we propose that variations in DOCD may serve as a primary driver for the Negative $\delta^{13}C$ Arms observed both before and after the Snowball Earth events. This hypothesis is founded on two essential conditions: (a) the presence of a sufficiently large DOC pool, or a significantly higher ratio of DOC to DIC in the ancient ocean than is observed today;[4] (b) a non-glacial Neoproterozoic ocean that was predominantly well-stratified.[3] Condition (a) ensures that the amplitude of the $\delta^{13}C_{carb}$ excursion is appropriate. Condition (b) implies limited vertical mixing of water masses, which would hinder DOC remineralization due to extremely slow rates of diapycnal mixing, despite uncertainties related to ocean circulation under distinct continental configurations.

DOCD is consequently regulated by two factors: accessibility to oxidants (e.g., primarily O_2), and temperature-dependent enzyme activity.[5] Throughout the full course of glaciation, alterations in the physical and biogeochemical characteristics of the ocean lead to subtle variations in DOCD, thereby impacting $\delta^{13}C_{carb}$ (Figure 1). In non-glacial conditions, the combination of low atmospheric oxygen level (pO_2)[3] and ocean stratification results in the development of extensive anoxic or euxinic water masses, with limited oxic/suboxic surface waters. The physical separation between the deep-seated DOC and oxidants strongly favors low DOCD, facilitating the accumulation of the DOC reservoir. When glaciation commences, deficiencies in oxidants may diminish due to the breakdown of stratification. As cooling intensifies, it leads to enhanced local convection, and substantial brine rejection further weakens stratification during the expansion of ice sheets and/or sea ice. These processes enhance DOCD and promote the oxidation of the DOC pool through intensified global convection.

Conversely, enzyme activity decreases in response to cooling. As O_2 infiltrates the deep waters and becomes less constrained, the rate of DOC oxidation is dictated by enzyme activity. The influx of O_2 initially lowers $\delta^{13}C$ values at the beginning of glaciation when enzyme activity sustains. However, enzyme-driven oxidation is expected to decrease or become negligible if the ocean cools sufficiently, leading to suppressed DOCD, as is likely the case for the ocean beneath the thick ice of a Snowball Earth. The post-glacial or deglacial phase of the Neoproterozoic is associated with the reestablishment of ocean stratification in response to a warming climate. At this juncture, DOCD could be considerably elevated due to the availability of O_2 accumulated during the pre-glacial O_2 influx combined with the gradually increasing enzyme activity driven by rising temperatures. The continuous consumption of DOC during this period leads to the post-glacial $\delta^{13}C$ excursion.

OUTLOOK

As in an out-of-the-box paper, we presented a novel, non-exclusive hypothesis that seeks to explain the two-stage $\delta^{13}C$ excursion observed before and after the Neoproterozoic glaciations by invoking variations in the DOCD. At present, certain inorganic parameters within the oceanic carbonate system can be reconstructed using paleoceanographic archives. However, the DOC reservoir lacks a robust proxy, resulting in significant uncertainties regarding its storage, distribution, production, and consumption. We posit that the importance of the DOCD, hence the oceanic DOC inventory on the long-term evolution of the carbon cycle, may have been underestimated. We advocate for coordinated multidisciplinary endeavors to address this gap. Specifically, there is an urgent need to identify suitable samples, or at the very least, appropriate proxies, to validate hypotheses regarding the deep-time DOC reservoir. Additionally, it is crucial to conduct in-situ observations and laboratory testing to assess variations in the DOCD. Furthermore, integrating model modules that depict DOCD behaviors into ocean-biogeochemical models is essential for achieving a systematic understanding of these processes. Such collaborative efforts hold the promise of unveiling the intricate role of DOC in Earth's history and its broader implications for the planet's dynamic carbon cycle and habitability.

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AUTHOR CONTRIBUTIONS

NZJ conceptualizes the study and leads in the writing and revision of the manuscript. All the authors contributed to the analysis of the data, writing of the initial version of the manuscript, and revision of the paper.

DECLARATION OF INTERESTS

Nianzhi Jiao is an Editorial Board member of The Innovation Geoscience and was blinded from reviewing or making final decisions on the manuscript. Peer review was handled independently of this member and their research group. The other authors declare no conflicts of interest.