

Modeling the Shuram $\delta^{13}\text{C}$ Excursion as the onset of calcium carbonate biomineralization by acritarchs

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Abstract

The Shuram excursion, an extremely negative and prolonged carbonate $\delta^{13}\text{C}$ anomaly, is recorded globally in late Ediacaran shallow-water marine sedimentary sequences and coincided with a time of increasing ocean oxygenation. Marine planktonic microorganisms with organic cell walls, known as acritarchs, were common in the Ediacaran Period. The onset of the Shuram excursion occurred during a time of rapid acritarch cell wall diversification, and the excursion's resolution was followed by the appearance of macroscopic calcium carbonate biomineralizing metazoans in the late Ediacaran. Accordingly, I consider that the Shuram excursion may be attributed to sedimentary accumulations of material sourced from weakly calcified acritarchs, which primitively biomineralized their cell walls by precipitating ^{13}C -enriched marine carbonate onto ^{13}C -depleted organic carbon. Decay of this organic carbon to authigenic carbonate after burial may have produced the low $\delta^{13}\text{C}_{\text{carb}}$ values. The carbon isotope mass balance of global carbon cycle reservoirs permits this effect to produce a Shuram excursion of any duration. An initial organic fraction of ~ 0.6 is required in the acritarch-derived phase, in agreement with fossil evidence that the earliest biomineralized structures contained a major fraction of organic carbon. I will discuss how fossil, petrographic and geochemical observations are consistent with this hypothesis. During the excursion, a peak globally averaged organic carbon burial fraction of ~ 0.4 is predicted. Burial sequestration of organic carbon in organic-rich biomineralized calcium carbonate could account for the rise in oxygen associated with the Shuram excursion.

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Introduction

The Neoproterozoic Era (1000-541 million years ago) witnessed several major biological evolutionary breakthroughs. Appearing in the fossil record during this time were the first known macroscopic animals, as well as the first animals known to biomineralize calcium carbonate (CaCO_3), prior to the so-called "explosion" in diversity of calcium carbonate biomineralized forms beginning in the Cambrian period around 541 Ma. These evolutionary developments occurred amid dramatic cycles of global glaciation.

In the middle-late Neoproterozoic Era, around 570 Ma, a major geochemical event is recorded in Earth's marine records. Rooney et al. (2020) showed that two unusual effects occurred simultaneously: (1) Atmospheric oxygen suddenly rose from approximately 10% of present-day levels, to levels around or slightly below present-day levels. (2) Widespread carbonates appeared in marine records which today show carbon-13 abundance substantially below the expected minimum $\delta^{13}\text{C}$ values expected by carbon cycle models (around -6 per mil—all values expressed relative to the PDB and SMOW standards). The expression of this carbon-13-depleted carbonate was most pronounced during a global event known as the *Shuram excursion*, during which carbonate $\delta^{13}\text{C}$ values dropped to extremely low values of -12 per mil in some globally scattered shallow-water marine sequences.

Suggested explanations for the Shuram isotope anomaly in carbonates have included extreme deviations from carbon cycle behavior understood to be typical across Earth's history (e.g. Rothman et al. 2003) or else alteration processes that, for some reason, have preferentially affected Neoproterozoic rocks (e.g. Derry et al. 2010, Schrag et al. 2013). The latter possibility, post-depositional alteration, appears to be supported by carbon and oxygen isotope data indicating that the ^{13}C depletion in carbonates is associated with ^{18}O depletion suggestive of alteration by meteoric porewater (e.g. Knauth & Kennedy 2009, Derry et al. 2010). However, geochemical evidence suggests some Shuram excursion-recording rocks have experienced only limited recrystallization (e.g. Fike et al. 2006, Bergmann 2013), suggesting that the Shuram excursion could not have been caused by dissolution and reprecipitation of primary marine carbonate in the presence of water that was enriched with isotopically light organic carbon.

A new hypothesis for the Shuram excursion

At the same time as the Shuram $\delta^{13}\text{C}$ excursion in carbonates, a type of plankton known as **acanthomorphic acritarchs** (hereafter *acanth*s) became widespread in the oceans. Widespread sedimentary deposits of acanth are seen worldwide in mid-late Neoproterozoic shallow-water marine sequences. Fike et al. (2006) pointed out the simultaneous occurrence of acanth with the Shuram excursion, and suggested that the global oxygenation happening around this time allowed them to flourish—a suggestion that was contested (Grey & Calver, 2007) based on the imperfect correspondence between acanth and ^{13}C -depleted carbonate. C. Yang et al. (2021) recently showed, however, that diversifications of acanth were associated with expressions of ^{13}C -depleted carbonate, suggesting a potential causal link between the geochemical perturbation and the diversifications of acanth.

These works have all stopped short of suggesting that the acanth actually caused the $\delta^{13}\text{C}$ anomaly in carbonates. This is the hypothesis explored here, and a specific mechanism for the late Neoproterozoic geochemical effects is now suggested.

Acanth skeletons combined organic carbon (Grey & Willman 2009) and calcium carbonate (H. Wen et al. 2016). The calcium carbonate component is often not discussed, in part because many important studies of these microfossils have used acid preparation treatments that destroy the mineral part of the skeletons. The "skeletons" retrieved by these techniques are actually just the organic component of the originally mineralized skeleton.

Another reason the calcium carbonate biomineralizing nature of acanth is often not discussed is that the fossils of these organisms have only been reported as occurring within chert or phosphorite, and are never found with the original calcium carbonate mineralogy intact. A recent petrographic study by Wen et al. (2016) showed that the original skeletal mineralogy was calcium carbonate, making acanth some of the earliest eukaryotes known to make calcium carbonate skeletons. All known morphologically preserved fossils of these organisms underwent special burial conditions that converted the original calcium carbonate in the skeletons to chert and phosphorite. In other words, there are no reports of acanth fossils with a mostly intact original calcium carbonate mineralogy. Taphonomic replacement of the carbonate in the skeletons with chert or phosphorite is therefore apparently necessary for acanth skeletons to be preserved as morphologically recognizable fossils with the organic carbon component surviving intact to the present day.

As chert and phosphorite-converted acritarch deposits are commonly found associated with Shuram excursion sequences (despite the special conditions needed for mineral conversion), a surprising possible conclusion is that a substantial fraction of the marine carbonate deposited during the Shuram excursion may have originated as acritarch skeletons. Fossils of these plankton are especially common in biologically productive shallow-water marine zones at warm equatorial paleolatitudes, suggesting they may have dominated carbonate deposition in regions where the Shuram isotope effect is most strongly expressed.

Model methodology

Overview of carbon cycle model:

A standard model for global carbon cycle reservoirs (e.g. Kump and Arthur 1999) is adapted to characterize the global carbon fluxes required for acanth to produce the excursion by the proposed effect (which is discussed in the section on the bottom left). The classic Shuram formation sequence from the Migrat-1 well as studied by Fike et al. (2006) was used as input to the model.

The model assumes a steady-state balance of carbon fluxes, reflecting typical long-term behavior of the carbon cycle. Many other models alternatively suggest the Shuram excursion is a rare exception to this usual steady-state behavior of the carbon cycle.

Oxygen release:

The net O_2 release is integrated over time, accounting for the stoichiometric relationship of oxygen to carbon during both organic carbon production and subsequent oxidative decay. A duration of about 11 million years is assumed for the Shuram excursion based on the recent geochronological constraints of Rooney et al. (2020). A total carbon burial flux of 20×10^{12} mol C per year follows established models for typical carbon cycle behavior (e.g. Kump 1991). The net oxygen release is integrated over time based on the globally averaged organic burial fraction and assuming a 1:1 stoichiometric ratio of C to O_2 . Oxidative decay of organic carbon to carbonate ions also has a 1:1 ratio because a water molecule provides the third oxygen atom in the reaction. The O_2 release is estimated for a range of decay half-lives of organic carbon.

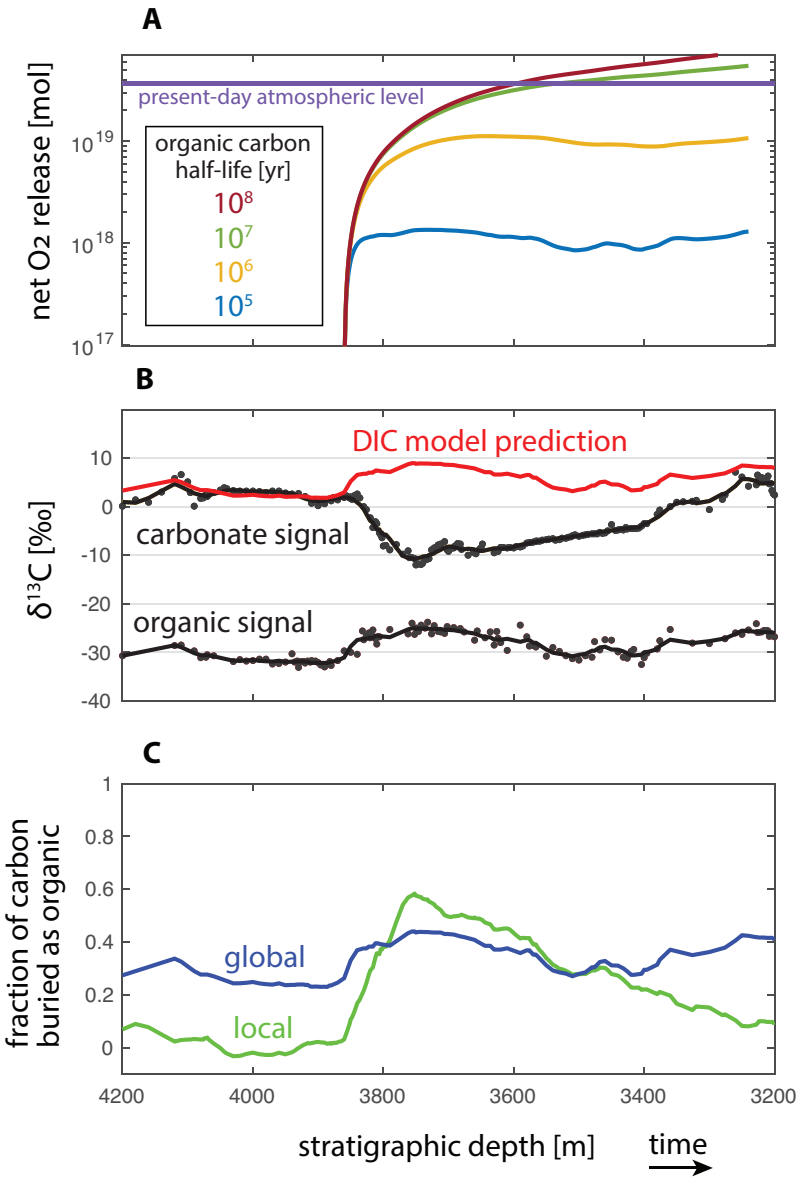
Authigenic carbonate formation (defined as any carbonate forming after burial in the sediment) has been broadly suggested before as a possible mechanism for the Shuram anomaly (e.g. Schrag et al. 2013, Derry 2010). This work considers the possibility that the isotope effect reflects formation of ^{13}C -depleted authigenic carbonate derived from the organic carbon in acanth shells. This explanation is consistent with the observation pointed out by Knauth & Kennedy (2009) that the ^{13}C -depleted carbonate also shows ^{18}O depletion suggestive of interaction with meteoric water.

This hypothesis is also consistent with current petrographic observations and Secondary Ion Mass Spectrometry (SIMS) analyses (e.g. Husson et al. 2020, Xiao et al. 2020; see also Cui et al. 2017 for relevant isotope analysis of distinct co-occurring carbonate phases without using SIMS), which have generally attributed the ^{13}C depletion in bulk samples of Neoproterozoic carbonate to detrital ^{13}C -depleted grains within the bulk carbonate rock. This finding is consistent with an origin of such grains as detrital skeletal remains. At some localities, these ^{13}C -depleted grains coexist in the same rock with a relatively ^{13}C - and ^{18}O -enriched carbonate phase suggestive of seawater composition.

Given this enhanced burial of organic material in acritarch skeletons, net oxygen release would be expected if the oxidative decay of organic carbon in the skeletons was sufficiently slow. A sufficiently long decay half-life to allow oxygen accumulation appears supported by fossil studies (e.g. Ehrlich et al. 2013) demonstrating that chitin, the ubiquitous scaffolding molecule of calcium carbonate shells, can survive at least half a billion years in fortunate cases of preservation. The long-term survival of the organic skeleton material in well-preserved acanth fossils also points to a prolonged decay half-life of the organics.

References Rooney et al. 2020 / Fike et al. 2006, Nature 444(7120) / Rothman et al. (2003) / Schrag et al. (2013) / Bergmann 2013 / Grey & Calver 2007 Nature 450 E17 / Grey & Willman 2009 Palaios 24(4) / C. Yang et al. 2021, Science Adv. 7, 45. / Wen et al. 2016 Chemical Geology 430 / Schrag et al. 2013 Science 339(6119) / Derry 2010 EPSL 294, 1-2 / Husson et al. 2020 Global and Planetary Change (206) / Xiao et al. 2020 Precambrian Research 343 / Cui et al. 2017 Chemical Geology 450, 5 / Ehrlich et al. 2013 Scientific Reports 3(3497) / Kump and Arthur 1999 Chemical Geology 161, 1-3 / Kump 1991 Geology 19(4)

Geochemical mass balance model



- Approximate total oxygen release from sequestration of organic carbon in buried acanthomorph skeletons.
- Carbon isotope input to the model (black) and predicted isotope ratio of dissolved inorganic carbon (DIC) during this time (red).
- Green: predicted organic carbon burial fraction recorded locally in regions with the maximum Shuram isotope effect. Blue: predicted globally averaged organic carbon burial fraction.

Conclusions

As Shuram excursion carbonates tend to be organic-poor, a massive organic carbon burial event has not generally been considered likely. However, this possibility needs to be reevaluated given that the Shuram excursion coincided with an explosion of biomineralizing plankton that had a substantial fraction of organic carbon in their shells.

Many carbonate-biomineralizing marine invertebrates from the Cambrian Period onward have substantially less organic carbon in their skeletons/shells compared to these primitive skeletal plankton. While this evolutionary advancement may account for the lack of a globally widespread Shuram-like effect following the late Neoproterozoic, the continued use of organic carbon, particularly the decay-resistant (e.g. Allison 1989, Ehrlich et al. 2013) and ubiquitous polysaccharide chitin, to build biomineralized marine invertebrate skeletons (Lowenstam & Weiner 1989) can account for the scattered instances of ^{13}C depletion noted by Knauth & Kennedy (2009) to continue from the Neoproterozoic throughout the entire Phanerozoic. While Knauth and Kennedy (2009) suggested the effect was due to alteration of carbonates by organic-charged runoff due to a blooming of Precambrian land plants, there is little evidence for such an evolutionary event during this time. Given that biomineralizing animals first made a widespread appearance in the Neoproterozoic fossil record, the ongoing, scattered ^{13}C -depletion seen in marine carbonates since this time more likely reflects the continued signature of marine carbonate biomineralization.

Moreover, a troubling geochemical problem has been the gradual systematic increase in $\delta^{18}\text{O}$ seen in marine carbonates since the Cambrian—an effect which has been troublingly ascribed to drastic changes in ocean temperature or chemistry. Gradual decay of organics in skeletal limestones since the Phanerozoic offers another explanation for this effect. The widespread use of some biomineralized shells as a proxy for marine isotopic composition may therefore need adjustment for the effect of authigenic carbonate formation from organic carbon within skeletal carbonate.

Further tests

As the model provides testable predictions for the ratio of fluxes of buried organic carbon versus carbonate, constraints on the mass of the organic carbon component of well-preserved acanth skeletons should offer one means of further testing this hypothesis. The maximum organic carbon burial fraction of ~60% at Shuram-recording sequences should be approximately reflected by the relative fraction of organic carbon and minerals in the well-preserved acanth-specimens (i.e. chert- and phosphorite-converted cases), unless a substantial fraction of the organic carbon has also decayed in these cases.

In Shuram-recording rocks, grains with elevated $\delta^{13}\text{C}$ that coexist within the same rock as extremely ^{13}C -depleted carbonate were suggested by Husson et al. 2020 to reflect precipitation from two separate carbon reservoirs. This model suggests that the ^{13}C -enriched grains are simply reflecting seawater composition (either precipitation directly from seawater as might be the case for the ^{13}C -enriched phase found in the Doushantuo Formation by Cui et al. (2017), or early authigenesis in the case of the rhomboid dolomite crystals such as those observed by Husson et al. 2020). If this hypothesis is correct, vast improvements in our ability to cross-correlate late Neoproterozoic stratigraphy may come from extensive further SIMS analysis of Shuram-recording rocks to reveal the variation of marine C and O isotopes throughout the event, as recorded in non-skeletal marine carbonate that is mixed in with skeletal carbonate at some localities.

Nitrogen isotope data (D. Xu et al. 2021) have recently suggested water column denitrification concurrent with the Shuram excursion. This would be consistent with production of chitin $(\text{C}_6\text{H}_{13}\text{O}_5\text{N})_n$ in large volumes by biomineralizing invertebrates. Further studies of nitrogen cycling at high stratigraphic resolution, and comparison to isotope and fossil data, may offer continued insights as to the validity of this hypothesis. Ultimately, an improved understanding of taphonomic decay rates of organic skeletal frameworks in a variety of organisms and preservational settings may be needed to confirm the hypothesis as it relates to the ongoing Phanerozoic marine carbonate record.