

# Enhanced primary productivity in the aftermath of the rise of atmospheric oxygen

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Fluctuations in organic carbon (OC) burial control the redox state of the ocean-atmosphere system and are linked with major geochemical and biological evolutionary events. Carbon isotopes in marine carbonates are generally assumed to track the extent of OC burial and are therefore the most widely used proxy for change in the carbon cycle through time. Variations in the C isotope composition of marine carbonates throughout Earth's history are typically small ( $|\delta^{13}\text{C}| = 5\text{‰}$ ) and short-lived ( $< 20$  myrs), a pattern typically attributed to the stability of the Earth's biogeochemical cycles. A significant deviation may have occurred ca. 2.3-2.1 Ga following the rise in atmospheric oxygen; carbonates of this age have markedly positive carbon isotope values commonly reaching  $+10\text{‰}$ , and unprecedented values peaking above  $+20\text{‰}$  (1-2). If these carbon isotope values capture the primary composition of marine dissolved inorganic carbon, this event, commonly referred to as the Lomagundi excursion, represents the most severe and long-lived perturbation of the global carbon cycle in Earth's history and likely reflects greatly enhanced organic carbon burial. Alternatively, some researchers attribute these values to widespread diagenetic overprints associated with methanogenesis within the sediments, possibly linked more broadly with Earth's redox evolution (e.g. ref. 3). Here, we present a coupled carbon and sulfate isotope study of Lomagundi excursion carbonates that points to primary productivity rather than carbonate formation in the methanic zone as the underlying mechanism for this excursion.

Dissolved inorganic carbon C and sulfate S isotopes show consistent trends in modern marine sediments. Specifically, sulfate  $\delta^{34}\text{S}$  increases with depth due to fractionations associated with bacterial sulfate reduction (BSR), while DIC-C isotopes show an initial decrease and then a shift to markedly positive values in the methanic zone. Sulfate is structurally substituted into the carbonate lattice during carbonate precipitation, and therefore a coupled C-S isotope approach can be used to test for diagenetic influence on carbonate precipitation. Sulfate is essentially depleted before the onset of methanogenesis and carbonate-associated sulfate (CAS) incorporated during precipitation in the methanic zone will have extremely positive  $\delta^{34}\text{S}$  values coincident with the very high  $\delta^{13}\text{C}$  values.

CAS from eight different formations deposited during the Lomagundi excursion have  $\delta^{34}\text{S}$  values ranging from +4 to +29‰ (mean +14‰, n=105). Relative to what we expect in porewaters during diagenesis, this is a narrow range of low S isotope values—inconsistent with those expected in the methanic zone. CAS concentrations typically range from 50 to 500 ppm, which is higher than most Precambrian carbonates. Since CAS concentration scales with ambient sulfate concentration during carbonate precipitation, these values also indicate carbonate precipitation did not occur in the methanic zone. Our method has been tested to ensure that sulfide oxidation during CAS extraction is insignificant. Consequently, Lomagundi excursion carbonates appear to trap seawater C-S isotope signatures and can thus improve our understanding of biogeochemical cycles.

In the Lomagundi Formation, the falling limb of the carbon isotope excursion is marked by an up-section increase in the  $\delta^{34}\text{S}$  values of CAS. An inverse temporal (stratigraphic) relationship in these isotope systems (which are tracking seawater sulfate and DIC) is enigmatic, since the burial rates of reduced carbon and sulfur are positively coupled in modern marine environments through BSR. However, it is possible — given a sufficient flux of organic matter — to decouple the seawater sulfate and DIC isotope records associated with burial of pyrite and organic matter. Specifically, a shift away from spatially widespread environments with nearly quantitative sulfate reduction promoted by an abundance of organic matter delivery could cause a decrease in the carbon isotope values of DIC due to waning OC burial, while the  $\delta^{34}\text{S}$  of seawater sulfate increases due to larger net fractionations in many settings. A scenario of shifting sediment organic matter loading on a global scale appears to be the best explanation for the well-developed negative correlation between carbonate C and CAS-S isotopes in the Lomagundi Formation. Moreover, prolonged periods of high organic matter loading can explain relative abundance of light  $\delta^{34}\text{S}$  values seen at all of our sections.

The inverse C-S relationship in the Lomagundi Formation carbonates is not simply the result of severe sulfate limitation. The sulfate evaporite record in successions approximately coeval with the Lomagundi Formation indicate that sulfate concentrations were higher than 2.5 mmol (4). Additionally, there is a lower rate of isotopic variability for seawater sulfate (inferred from CAS) during the Lomagundi excursion than during early Phanerozoic positive carbon isotope excursions (5), where the isotopic records of the sulfate and DIC pools are positively coupled. Low CAS variability in the Paleoproterozoic is interesting because the temporal variability in sulfate has been shown to effectively track the size of the marine sulfate reservoir (5). In conclusion, a combined C-S isotope study reveals that the Lomagundi excursion is linked with high sediment organic matter loading rather than methanic diagenesis and challenges us to unravel how the marine system sustained unusually high levels of primary productivity at the dawn of atmospheric oxygenation.

## References

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