

Paired Sulfur and Phosphorus Biogeochemical Cycling Show Bottom- Water Anoxia Preceded the Toarcian Ocean Anoxic Event

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Disturbances in the global carbon cycle led to widespread organic carbon burial events termed ocean anoxic events (OAEs) during the Mesozoic era. Increased hydrological cycling paired with increased continental weathering promoted nutrient influx to the oceans. Surplus nutrients, including phosphorus (P), stimulated global eutrophication. However, the relative importance of P and sulfur (S) in initiating, sustaining, and terminating OAEs is still unclear. Elevated P could come from weathering or enhanced regeneration of P associated with S cycling under anoxic conditions. During anoxia, P regeneration can be driven by the reductive dissolution of P-bound iron-oxides linked to pyrite (FeS₂) formation. P released to surface waters further fuels eutrophication. We investigate the role of enhanced P delivery versus recycling associated with FeS₂ burial during the Toarcian OAE (~183 Ma).

We present paired P and S sequential extraction data from Ya Ha Tinda Ranch in Alberta, Canada from across the Pliensbachian-Toarcian (PL-TO) boundary and Toarcian OAE (T-OAE). Iron-P concentrations were highest preceding the PL-TO boundary and decreased until the PL-TO boundary. Local minima in authigenic-P, detrital-P, and organic P at the PL-TO boundary coincided with the lowest $\delta^{34}\text{S}$ values of chromium reducible sulfide (CRS; predominantly FeS₂) at -15‰. Maximum concentrations of authigenic-P, detrital-P, and organic-P coincided with the beginning of the T-OAE negative carbon isotope excursion (NCIE), a return to higher $\delta^{34}\text{S}_{\text{CRS}}$ values of -7‰ across the NCIE, and an increase in CRS (FeS₂) concentrations. We conclude that, while bottom waters were anoxic and sulfidic during much of the Pliensbachian and Toarcian¹, the formation of FeS₂ during the NCIE was associated with less sedimentary P retention. The positive $\delta^{34}\text{S}_{\text{CRS}}$ excursion across the NCIE was linked with increasing amounts of highly reactive Fe^I, which promoted FeS₂ burial. During the recovery, FeS₂ concentrations decreased but remained elevated relative to starting values while authigenic-P, detrital-P, and organic-P remained low. These results imply that the continued P consumption prevented its deposition in the sediment. Enhanced P recycling may have played a role in sustaining low oxygen conditions through the NCIE and return to higher carbon isotope values.

[1] Them II et al. (2018), *PNAS* 115, 6596-6601.