



Sulphur isotopes indicate increased pyrite burial at the onset of OAE 1a in the Tethyan realm

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Oceanic Anoxic Events (OAEs) are examples of geologically short episodes ($<1\text{Ma}$) of severe palaeoenvironmental disturbance likely triggered by massive inputs of isotopically light CO_2 into the ocean-atmosphere system. Increased concentrations of CO_2 fostered global warming and possibly ocean acidification. Enhanced rates of continental weathering and acceleration of the hydrological cycle delivered high amounts of nutrients to coastal areas, resulting in increased marine productivity. As a result, huge amounts of organic material were buried in epicontinental and oceanic basins under oxygen-deficient conditions, leading to the widespread deposition of marine black shales, which is the hallmark of OAEs.

Quantifying the global extent of ocean anoxia and/or euxinia (anoxic and sulphidic waters) is fundamental for understanding the dynamics of the global carbon cycle during OAEs. Sulphur-isotope ratios in the oceans are governed by weathering rates of sulphur-bearing minerals on the continents and hydrothermal fluxes, delivering sulphur of similar isotopic values, and by the burial of gypsum and pyrite. Gypsum precipitation affects principally the concentration of sulphur in seawater with only a small positive fractionation. In contrast, the formation of pyrite involves microbial sulphate reduction, favouring the lighter sulphur isotope ^{32}S and typically causing a large isotopic fractionation.

Overarching parallel positive excursions of carbon and sulphur isotopes are recorded from two of the three major Mesozoic OAEs – during the early Toarcian, albeit with an associated negative shift ($\sim 183\text{Ma}$), and the Cenomanian–Turonian (OAE2, $\sim 94\text{Ma}$) – and have been interpreted as the response to increased pyrite burial in marine sediments under euxinic conditions (Gill et al., 2011; Owens et al., 2013). The Early Aptian OAE 1a or Selli event ($\sim 120\text{Ma}$) is the third major Mesozoic OAE, and is characterized by a relatively abrupt stepwise decline in $\delta^{13}\text{C}$ to a minimum followed by a pronounced long-lasting positive excursion. OAE 1a was preceded by a large negative swing in seawater $\delta^{34}\text{S}$ (Paytan et al., 2004), which has been related to a large-scale deposition of evaporites (decreasing the oceanic sulphate reservoir) during the opening of the South Atlantic Ocean (Wortmann & Chernyavsky, 2007) and/or to increased volcanic degassing (DeBond et al., 2012). However, high-resolution records for sulphur-isotope changes have been produced only for the Pacific Ocean.

We present isotopic data obtained from carbonate-associated sulphate (CAS) from Lower Aptian shallow-water platform carbonates of the central Tethyan region. In the studied sections, $\delta^{34}\text{S}_{\text{cas}}$ shows a positive shift coeval with the carbon-isotope positive excursion associated with the OAE 1a. After the event, sulphur isotope values drop back to pre-event values. As with the early Toarcian and Cenomanian–Turonian OAEs, the positive $\delta^{34}\text{S}_{\text{cas}}$ excursion during OAE 1a is interpreted to reflect enhanced pyrite burial in marine sediments under euxinic conditions; however, evidence for enhanced volcanic inputs or large-scale evaporite deposition is not observed. These results imply that during OAE 1a oxygen-deficient waters spread over large areas, locally attaining euxinic conditions.

References:

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