

The story of sulphur in seawater

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The abundance of S containing compound and their isotopic composition ($\delta^{34}\text{S}$), in the ocean, can shed light on Earth oxygenation with implications to the evolution of life and the abundance and cycling of C, N, P and many metals. In order to understand the coupling between these cycles throughout Earth's history, $\delta^{34}\text{S}$ of seawater sulphate ($\delta^{34}\text{S}_{\text{sw}}$) was measured as early as the 1960s (1) with continuous refinement of the seawater curve (2). Early work utilized evaporite deposits (gypsum and anhydrite) to reconstruct $\delta^{34}\text{S}_{\text{sw}}$ but due to the sporadic occurrence of these deposits in the geological record and their susceptibility to dissolution and post burial diagenesis, the temporal resolution and the errors associated with the data were quite large. In 1998 a high-resolution $\delta^{34}\text{S}_{\text{sw}}$ curve using marine barite was published (3). The curve displayed an increase of about 5‰ over a period of ~7 million years starting around 53 Ma, other rapid excursions were later recorded also at the PETM (4). These are unexpected and surprising result considering the high concentration and long residence time of sulphate in seawater (~20 million years). Such shifts require substantial changes in the S cycle. Making assumptions about various processes, the increase in $\delta^{34}\text{S}_{\text{sw}}$ in the early Eocene was originally attributed to a pronounced decrease in hydrothermal activity combined with a large increase in the rate of pyrite formation; but it was acknowledged that the system is under-constrained and multiple solutions are possible. Since then several other interpretations were put forth (5-8) and other ideas are brewing. We will present the various interpretations and their limitations and illuminate the needs to constrain these interpretations.

- (1) Holser et al, *Chem. Geol.* **1**, 93 (1966).
- (2) Claypool, et al *Chem. Geol.* **28**, 199 (1980).
- (3) Paytan, et al., *Science* **282**, 1459 (1998).
- (4) Yao, et al., *Science* **361**, 804 (2018).
- (5) Kurtz, et al., *Paleoceanography* **18**, 1090 (2003).
- (6) Ogawa et al., *EPSL* **285**, 190 (2009);
- (7) Wortmann, & Paytan, *Science* **337**, 334 (2012).
- (8) Rennie et al., *Nat. Geoscience* **11**, 761 (2018).