

Seawater Sulfate and Climate

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Global changes in climate and atmospheric chemistry are intimately related to the sulfur (S) sedimentary cycle. Seawater sulfate is an important reservoir of S; therefore knowledge of the isotopic composition of sulfate over time is important for understanding numerous geochemical cycles on Earth. Sulfur is commonly present in seawater and marine sediments in one of two states: in its oxidized state as sulfate and sulfate minerals and in its reduced form as H₂S and sulfide minerals. The isotopic composition of S in sulfate in seawater ($\delta^{34}\text{S}_{\text{sulfate}}$) is a function of the relative partitioning of S between the oxidized and reduced reservoirs through time, providing an indicator of change in the geological, geochemical, and biological environments. Most importantly, the amount of reduced sulfur buried in the sedimentary record along with the burial of reduced carbon directly affects the concentration of free oxygen in the atmosphere.

Scientists used information collected from DSDP cores to reconstruct a continuous high-resolution seawater sulfur isotope curve for the past 65 million years (Figure 1). This constructed curve provides evidence that the S isotopic composition of seawater sulfate has fluctuated significantly over time. The S isotopic composition decreased from 21‰ to 19‰ between 21 and 18 Ma, increased abruptly from 19‰ to 21‰ between 18 and 15 Ma, and remained nearly constant at 21‰ from 15 Ma to the present. In the past 65 Ma, it decreased by 2‰. The low values of $\delta^{34}\text{S}$ between 55 and 65 Ma indicate that either pyrite deposition rates were lower or that there was increased input of isotopically light S to the oceans during this time interval. The minimum at about 50 Ma, the Paleocene-Eocene boundary, coincides with an important benthic foraminiferal global extinction, large negative short-term C isotopic excursion, a maximum in deep ocean temperature (2–3 °C), and intense volcanism. The largest shift in the S isotope ratio during the Cenozoic was in the early to mid-Eocene from 21‰ to 19‰ over a period of less than 5 million years, indicating that large changes in the external forcing mechanisms, such as tectonic uplift and weathering, volcanism, or oceanic vertical mixing and productivity, influenced the fluxes and isotopic composition of S input and burial.

A comparison between seawater sulfate and marine carbonates carbon isotope records reveals no clear systematic coupling between the S and C cycles over a few to tens of million years, indicating that changes in the burial rate of pyrite sulfur and organic carbon did not balance over short time intervals in the Cenozoic. The results indicate that the S cycle is much more complicated than previously thought, and more work is underway to unravel the intricacies of this system.

Figure 1: The Cenozoic seawater sulfur isotope curve

