## Seawater, Sulfate, and Climate

Adina Paytan, Stanford University; Miriam Kastner, Scripps Institute of Oceanography; Douglas Campbell and Mark H. Thiemens, University of California San Diego; USA

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 H<sub>3</sub>S and sulfide minerals. The isotopic composition of S in sulfate in seawater  $(\delta^{34}S_{sulfate})$  is a function of the relative partitioning of 5 between the oxidized and reduced reservoirs through time, providing an indicator of change in geological, geochemical and biological the 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 19 to 17‰ between 65 and 55 million years ago (Ma), increased abruptly from 17 to 22‰ between 55 and 45 Ma, from 35 to ~2 Ma remained nearly constant, and in the past 2 Ma decreased by 0.8‰. The low values of  $\delta^{34}$ S between 65 and 55 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 55 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 (~18°C), and intense volcanism. The largest shift in the S isotope ratio during the Cenozoic was in the early to mid-Eocene from 55 to 47 Ma. The pronounced shift from 17 to 22‰ over a period of less than 10 million years indicates 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 then previously thought, and more work is underway to unravel the intricacies of this system.

## Figure 1: The Cenozoic seawater sulfur isotope curve

