The triple oxygen isotope composition of marine sulfate

DAVID T. JOHNSTON[1], BENJAMIN COWIE[1] AND ALEXANDER BRADLEY[2]

[1]Harvard University, Cambridge, MA, USA
[2]Washington University St. Louis, MO, USA

Our collective understanding of the modern and geological sulfur cycle benefits from the fact that microorganisms – the agents of nearly all geochemical S cycling – impart large isotope effects. Most commonly, sulfur isotopes in sulfate and sulfide (both aqueous and in mineral form) are employed to track everything from rates of microbial processes through to the presence/absence of certain metabolic clades in a given environment. In complement to sulfur isotope studies, one under-developed tool to track sulfur recycling comes from the interrogation of oxygen isotope change in sulfate reservoirs (marine, pore water, mineralogical). As an oxidative weathering product, riverine sulfate is posited to carry a memory effect of tropospheric O_2, which importantly, has a unique $^{17}O/^{16}O$ composition reflective of a balance between stratospheric and biospheric fluxes. As S-O bonds are broken and formed through inorganic and biogeochemical activity, the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ composition of the related sulfate reservoir evolves. This 'evolution' thus records a relative contribution from the specific isotopic relationships associated with each processes catalyzing the cycling (microorganisms). In total then, the triple oxygen isotopic composition of marine sulfate records (both modern and ancient) stands as a treasure chest of biogeochemical and atmospheric information waiting to be calibrated.

In this work we will present data from a new laser F_2 fluorination line at Harvard. In addition to presenting details of more precise measurement capacities (and analytical challenges overcome), we present data from a series of environmental sulfate records. These serve to provide an early interrogation of the mass dependent systematics of different microbial processes (which may posses unique mass laws), the sensitivity of seawater sulfate to changes in tropospheric contributions, and the magnitude of variance preserved within geological records.