

## Lessons to learn from MIF-S in Precambrian sedimentary rocks

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The growing record of multiple sulfur isotope data for various forms of sulfur (monosulfide, pyrite, barite, carbonate-associated sulfate) in Precambrian sedimentary rocks from different continents form the basis for our understanding of the early global sulfur cycle as well as the temporal evolution of the atmosphere-ocean system. The overall picture reveals distinct temporal variations in the magnitude of mass-independent sulfur isotope fractionation. Sizeable  $\Delta^{33}\text{S}$  values characterize rocks of Paleoproterozoic age. Mesoarchean sediments display attenuated  $\Delta^{33}\text{S}$  values, followed by high-magnitude  $\Delta^{33}\text{S}$  values for Neoproterozoic and earliest Paleoproterozoic sediments. In addition, distinct temporal variations exist for  $\Delta^{36}\text{S} / \Delta^{33}\text{S}$ . Observed variations in magnitude of the MIF-S signal, based on sulfur extracted from whole rocks, point to distinct changes in the atmospheric composition affecting UV transparency and, as a consequence, the photochemistry that results in mass-independent sulfur isotope fractionation.

Both, isotope signals representing bulk material as well as data obtained at high spatial resolution comprise additional information. Most importantly, the variable relationships between  $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  could point to different metabolic pathways in the early microbial sulfur cycling.

The sedimentary record of mass-independent sulfur isotope fractionation terminates in the early Paleoproterozoic (~2.4 Ga) at the onset of an aerobic world. A detailed multi-isotope study of the respective sedimentary succession on the Kaapvaal Craton, South Africa, provides the temporal and causal framework for this change to a global sulfur cycle that is then driven by oxidative weathering on the continents delivering sulfate to the ocean and microbial sulfur cycling.

## <sup>27</sup>Al NMR studies of the impact of tank waste leachates on Hanford sediment samples

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Using a combination of analytical spectroscopy and wet chemistry techniques, we are investigating the coupling between mineral weathering from caustic waste release and contaminant fate/transport in waste-impacted sediments from the Hanford DOE site. We have examined a range of related samples including montmorillonite, homogeneous precipitates, and Hanford sediments, each reacted with or formed from a simulated tank waste leachate (STWL) containing varying concentrations of Sr and/or Cs. Batch and column studies have been performed, with reaction times varying from 1 d to 1.5 yrs.

In this work, <sup>27</sup>Al magic-angle spinning (MAS) and spectral deconvolutions provide kinetic data allowing us to compare and contrast results from homogenous precipitates, model clay systems, and more complex Hanford sediment samples reacted under similar conditions. Neophase formation is governed by the dissolution of parent clay/sediment and free Si in solution, allowing for the formation of new tetrahedrally-coordinated Al species. More recalcitrant phases form with longer reaction times, as studied from samples washed with acidic ammonium oxalate solutions. Four new phases form containing tetrahedrally-coordinated Al which vary in amount based upon weathering time, contaminant present, or (in the case of homogenous studies) amount of silica present in solution.