

## Terrestrial $\Delta^{33}\text{S}$ and the S cycle during the Archean: Evidence from paleosols

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Determination of multiple sulfur isotopes in Archean paleosols and diamictites shows the widespread presence of mass-independently fractionated S in the regolith developed on the pre-2.5 Ga Earth. All values of  $\Delta^{33}\text{S}$  are negative, indicating that the Archean surface environments incorporated atmospheric S as  $\text{SO}_4^{2-}$ , which carried a negative  $\Delta^{33}\text{S}$  signal. This S was subsequently converted to sulfide by sulfate reduction, most likely bacterial with terrestrial organic matter as a reductant. Pyrite with similar S isotope systematics has been reported from flood-plain deposits. Grains from these two sources were recycled into detrital pyrites now found in sandstones and conglomerates deposited before the rise of atmospheric oxygen. We suggest that atmospherically-generated S<sub>8</sub> was not similarly contained on the continents, rather was lost to the oceans, creating a continental S reservoir with dominantly negative  $\Delta^{33}\text{S}$  values and a predominantly positive S reservoir in marine sediments.

## High Energy Synchrotron X-ray Geochemical Probes

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High energy synchrotron facilities produce x-radiation with high brightness making them extremely powerful tools for a wide variety of spatially-resolved geochemical research. The primary techniques, X-ray fluorescence (XRF) analysis, X-ray absorption fine structure (XAFS) spectroscopy, X-ray diffraction (XRD) and computed tomography (CT), are used to determine properties of earth, environmental and planetary materials including chemical and mineralogical compositions, crystallographic and other physical structures, oxidation states and fluid flow characteristics.

These X-ray probes are common instruments at virtually every synchrotron facility, are highly complementary in their capabilities and are typically heavily oversubscribed. Analyses at various spatial scales are required for this research necessitating the availability of a suite of instruments each optimized for analyses at different scales.

Focused X-ray beams can be produced using techniques that rely on collimation, refraction, diffraction, or reflection. The most common devices found in synchrotron X-ray probes are those based on diffraction or reflection. Flood-field modes are also utilized where high spatial resolution is achieved via the detection components. "Fly-scanning" approaches have greatly reduced mapping times.

Research using these X-ray probes has led to important insights into the geochemistry of toxic metals and metalloids in contaminated sediments and tailings, the efficiencies of contaminant remediation strategies, how bio-accumulation processes affect the distribution of trace toxic metal species and manufactured nanoparticles in soils and organisms, flow properties of porous media and valence states of multivalent elements in igneous materials, for example.

This presentation will describe currently operating instruments and recent experiments at some US synchrotron facilities, primarily at the Advanced Photon Source (APS, Argonne National Laboratory, IL USA), as well as new, advanced capabilities soon to be available at the National Synchrotron Light Source (NSLS-II, Brookhaven National Laboratory, NY USA).