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Understanding the impact of a modern euxinic spring on sediment using bulk sediment and smectite clay-preserved proxies.

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Modern euxinic environments are useful proxies for early Earth. We investigated the morphological and chemical proxies preserved in sediments impacted by a modern euxinic spring, an early Earth proxy, as compared to adjacent unimpacted sediments. We studied two sets of samples: euxinic-spring-impacted creek bank sediment (ICS) and unimpacted creek bank sediment (UCS) at the surface, and euxinic-spring-impacted soil (ISL) and unimpacted soil (USL) samples at 2.2 m depth. We used X-ray diffraction (XRD) to analyze the mineralogy of the bulk sediment and isolated clay fraction. We further examined clay nanoparticles using Scanning Transmission Electron Microscopy (STEM) with Energy-Dispersive X-ray spectroscopy (EDX) to study clay morphology and chemistry. The bulk mineralogy of the impacted sediments includes pyrite and barite in addition to plagioclase, quartz, calcite, and K-feldspar, which were also present in the unimpacted sediment. However, dolomite was observed in all but ICS samples, while gypsum and ankerite were only present in ISL. However, XRD results of clay-oriented mounts show both the impacted and the unimpacted clay fractions are comprised of smectite, chlorite, kaolinite, illite, smectite/chlorite mixed layer clays.

We chose to focus additional analyses on smectite clay nanoparticles because of their known potential for redox reactivity; TEM images of these smectites reveal platy- and cornflake-textured smectites in all samples. However, EDX results reveal differences between the smectites in the impacted and unimpacted samples; unimpacted smectites have Si, Al, Fe, Mg, whereas impacted smectites also contain S, Ba, and Sr. The unimpacted smectites contain Ca and K as interlayer cations while Ca, K, and Na, with traces of Ba, are seen in the impacted smectites. Furthermore, STEM-EDX shows evidence of nanoscale barite and pyrite precipitation on the impacted smectites. These nanoprecipitates are also observed within the euxinic spring. Ultimately, this study demonstrates that (1) sulfide and sulfate minerals can co-exist in modern euxinic sediments, whether in contact with the atmosphere or not, and (2) smectite nanoparticles primarily respond to euxinic conditions by immobilizing cations via adsorption or cation exchange that reflect the chemistry of euxinic water rather than significantly changing their octahedral sheet cation composition.