

## **Impact of reducing conditions on the stability of organic matter and organic-uranium complexes**

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It is well recognized that organic matter persists in environments where the oxygen levels are low, such as alluvial aquifers. However, the mechanisms responsible for carbon preservation in anoxic conditions are unclear and a source of model uncertainty. Further, anoxic, organic-rich sediments are important concentrators of contaminants, such as uranium in its tetravalent state (U(IV)), but little is known about the binding mechanisms of U(IV) in these geochemical environments.

The SLAC-SFA team has been investigating the mechanisms behind C preservation and U(IV) accumulation in anoxic alluvial aquifer sediments from the Upper Colorado River Basin. Utilizing a shift in water soluble carbon chemistry (determined by FT-ICR-MS) between anoxic sediments, where sulfides produced by microbial respiration was confirmed by sulfur XANES spectroscopy, and oxic sediments (no detectable sulfides), we were able to demonstrate the relevance of thermodynamic limitations for preserving carbon in anoxic sediments. The results reveal a clear difference in carbon chemistry consistent with theoretically calculated thermodynamic thresholds and provide unprecedented field-based evidence for thermodynamic preservation of carbon in anoxic conditions. This is important because it illuminates a mechanism previously unrepresented in carbon cycling models; thermodynamic limitations on organic carbon decomposition operate differently than better-recognized kinetic and spatial constraints and need to be represented accordingly. Moreover, carbon exported from anoxic environments has the potential to drive nutrient, contaminant, and carbon cycles in downstream aquatic ecosystems

Additionally our team used a combination of XAS, NanoSIMS, and STXM measurements to demonstrate that complexes of U(IV) adsorb on organic carbon and organic carbon-coated clays in organic-rich natural substrate under field-relevant conditions. Previous research has assumed that U(IV) speciation is dictated by the mode of reduction (*i.e.*, whether reduction is mediated by microbes or by inorganic reductants), but our work showed that precipitation of U(IV) minerals, such as uraninite (UO<sub>2</sub>), can be inhibited simply by decreasing the total concentration of U, while maintaining the same concentration of sorbent. Uranium is less stable and more easily remobilized when bound to surfaces of organic matter and mineral as compared to being incorporated with mineral precipitates. This new finding implies that U(IV) is much more reactive and able to participate in repeated biogeochemical cycling than previously thought to be the case.