

Uranium speciation and heterogeneity in marine phosphorites: insight into the uranium pale-redox proxy

FRANCES M. MEYER¹, ANTHONY CHAPPAZ²,
KRISTINA KVASHNINA³, ELENA F. BAZARKINA⁴,
MADELINE S MARSHALL⁵, JOSHUA M GARBER¹ AND
KIMBERLY V. LAU⁶

¹Pennsylvania State University

²Central Michigan University

³Helmholtz–Zentrum Dresden–Rossendorf

⁴Helmholtz–Zentrum Dresden–Rossendorf e. V., Institute of Resource Ecology

⁵Albion College

⁶The Pennsylvania State University

Presenting Author: fmm5327@psu.edu

Uranium (U) speciation controls its reactivity and mobility in natural systems and is strongly modulated by redox conditions. Uranium enrichment and isotopic composition have emerged as a promising proxy to reconstruct Earth's oxygenation. However, interpretation of U concentrations and isotope ratios is based on poorly constrained assumptions of U burial pathways. The mechanisms of U sequestration, which we hypothesize would be reflected in U speciation, remain unclear. Furthermore, the presence of U(V) in marine sediment—which was thought to be unstable compared to U(IV) and U(VI)—indicates a gap in our understanding of U burial, complicating assumptions about U cycling.¹

To investigate the processes controlling U burial in marine sediment, we characterized U speciation in phosphorites using HERFD-XANES and spatially resolved energy maps at the M₄ edge. A fossil-rich sample comprising phosphatic coated grains from the Permian Phosphoria Rock Complex was analyzed at the European Synchrotron Research Facility. The energy maps (n=2) of U(IV), U(V), and U(VI) demonstrate spatial and chemical heterogeneities and complex correlations between U oxidation states. The collected XANES spectra (n=10) show that the relative proportions of each U oxidation state vary throughout the sample.

The results from HERFD-XANES at the U M₄ edge were combined with XANES from the L₃ edge and complemented by μ -XRF, SEM, and Raman analyses. XANES results at the U L₃ edge reflect a mixture of all three oxidation states within the sample, despite uncertainties in identifying U(V) and U(VI) at the L₃ edge. The results from the characterization techniques indicate that the distribution of U species may vary with organic carbon content, iron, and phosphorus. Therefore, the U distribution in phosphorites does not solely track the redox state of the ocean during deposition, but rather a complex array of syn- and post-depositional processes. Taken together, this new insight complicates the simple, redox-based model of U removal from the ocean and questions the current use of U isotope ratios for paleo-reconstruction purposes.