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Characterizing uranium speciation in marine phosphorites to advance the paleo-redox proxy

FRANCES MEYER[1], ANTHONY CHAPPAZ[2], MADELINE S MARSHALL[3], LEANNE HANCOCK[4] AND KIMBERLY V. LAU[5]

[1]Pennsylvania State University
[2]Central Michigan University
[3]Albion College
[4]Michigan Department of Environment, Great Lakes, and Energy
[5]The Pennsylvania State University

Presenting Author: fmm5327@psu.edu

The amount of oxygen in the ocean has exerted a major control on the development of complex life throughout Earth's history, making it important to understand the timing and frequency of oxygenation changes [1,2]. Because past oxygen contents cannot be directly measured, paleo-redox proxies are used to track changes in oxygen content through time. Records of uranium (U) concentrations and isotopes are invaluable for reconstructing long-term and transient changes in the redox state of oceans [3]. The redox-controlled solubility and isotope fractionation of U make it an applicable proxy for revealing these changes. However, interpreting U concentrations and U isotopes from marine sedimentary rocks as a paleo-redox proxy assumes that burial and isotope fractionation are associated with the reduction of U(VI) to U(IV). Without knowing the actual oxidation states or phase associations of U in marine sedimentary rocks, interpretations of the U isotope proxy remain uncertain. We address this by characterizing U speciation within marine sedimentary samples that are expected to be anoxic.

We used X-ray Absorption Fine Structure spectroscopy at the L3 edge to study U speciation in marine phosphorites from the Monterey Formation (Miocene) and the Phosphoria Rock Complex (Permian). The X-ray Absorption Near Edge Spectroscopy results from six powdered samples provide important context for whole-rock shale U concentration and U isotope analyses reported in paleo-redox studies. Linear combination fitting results indicate a mixture of U(IV), U(VI), and surprisingly, U(V) for both formations. Extended X-ray Absorption Fine Structure data from thin sections provide spatially resolved U speciation and were used to determine characteristics of the solid phases that incorporate different U oxidation states. Taken together, these new insights draw a more complicated picture where multiple U redox pathways occur simultaneously in these settings. The U oxidation states present in marine sedimentary rocks, including the apparent persistence of U(V), could impact the interpretation of the U isotope signature.

[1] Lyons, Reinhard and Planavsky (2014), Nature 506, 307-315.

[2] Lau et al. (2016), Proceedings of the National Academy of Sciences 113, 2360–2365.

[3] Weyer et al. (2008), Geochimica et Cosmochimica Acta 72, 345–359.