Biogenic Non-crystalline Uranium Identified as the Major Component of Uranium Roll-fronts

Uranium (U), the radioactive element that fuels nuclear power plants and occurs naturally in the Earth's crust, is typically mined from large sandstone deposits deep underground. The uranium in these deposits, which are called roll fronts, has long been thought to form over millions of years via chemical reactions of sulfur and other non-biological compounds to form crystalline uraninite. The reduction mechanism for U(VI) in roll-front deposits was thought to be abiotic electron transfer by redox active minerals (pyrite and mackinawite), aqueous sulfide and/or other reactive sulfur species[1–6].

This widely accepted textbook geology is being challenged by scientists in a new study published in *Nature Communications*. Their study offers evidence for a new origin story for the uranium trapped underground in roll-front deposits. Synchrotron radiation-based spectroscopy and isotope fingerprinting were used, among other methods in order to fully probe the potential presence of biogenic non-crystalline U(IV) in an unmined ore zone located 200 m below ground surface in Wyoming, USA. Bulk U L_{III}-edge (17166 eV) extended x-ray absorption fine structure (EXAFS) spectroscopy was performed at Beam Lines 4-1 and 11-2 at SSRL to determine the solid state speciation of U. The data in this region yields information on the oxidation state and local chemical coordination environment of U (coordination number, identity of ligand atom, and distance between U and ligand atom) in the sediment sample. Theoretical calculations of these base structures was used to model the U EXAFS spectrum by comparing data from known U containing model compounds (U-C, U-O, U-P) in the first and second coordination shells. Characterization of U species by EXAFS revealed that the majority (~ 58-89%) of U is bound as U(IV) to C-containing organic functional groups or inorganic carbonate, while uraninite and U(VI) represent only minor components. The uranium deposit exhibited mostly ^{238}U-enriched isotope signatures, consistent with largely biotic reduction of U(VI) to U(IV). Combining the findings, EXAFS spectroscopy and the isotopic measurements strongly support biotic reduction of U(VI) as the dominant reduction pathway for the generation of non-crystalline U(IV) within roll-front deposits.

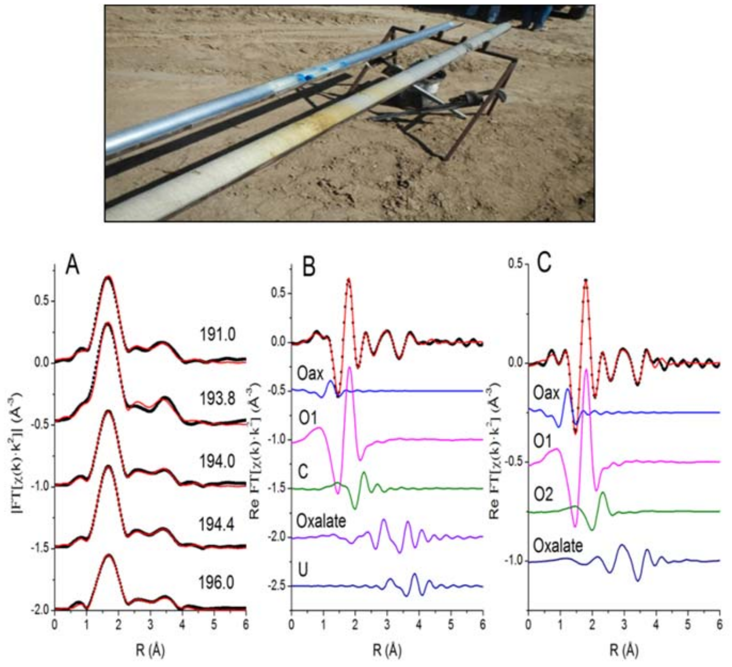

Figure. *Top*: core drilled from 200 m-bgs. *Bottom*: U L_{III}-edge EXAFS spectra (symbols) and models (lines). (A) Magnitude of Fourier transform spectra are offset for clarity for following depths (from top to bottom in m-bgs): 191.0, 193.8, 194.0, 194.4 and 196.0. (B and C) Real part of Fourier transform of the sediments from depths 191.0 m (B) and 196 m (C). The components of the model are shown offset beneath the total model (i.e., O_{ax}, O1, C, Oxalate, U, and O2). Contributions from O_{ax} : axial oxygen atoms from uranyl (U^{VI}); O1, O2: oxygen atoms bound to $U^{(VI)}$ and $U^{(IV)}$ at a longer distance than U-O_{ax} C: carbon atoms from bidentate carbon group; Oxalate: oxalate-like ligand group; U: U neighbors in uraninite are shown in B.

This finding implies that biogenic processes are more important to U ore genesis than previously understood. The predominance of a relatively labile form of U(IV) also provides an opportunity for a more economical and environmentally benign mining process, as well as the design of more effective post-mining restoration strategies and human health-risk assessment. Results from this study may introduce a paradigm shift in the way we think about ore genesis and mining – from implications for human health to restoration practices. The data was published in *Nature Communications,* 8:15538 (June 2017).

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