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Uranium (VI) Incorporation in Paleosol Calcite: Evidence for Sequestration of U on Geologic Time Scales

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Introduction

The transport, mobility and complexation of actinides, including uranium (U), are of great interest for the remediation of high-level nuclear wastes. Past studies have advanced the understanding of the behavior of U in near surface environments using a variety of analytical techniques including ion exchange [1], adsorption [2,3] and co-precipitation [4,5]. These studies shed significant light upon the speciation and transport of U in soils, however they have been performed under laboratory conditions that may not be representative of processes on geologic timescales. Additionally, these studies focus on relationships between two components of natural systems (i.e. U and soil minerals or U and organic material), however in natural environments these overlap.

Current attention has focused on the trace amounts of U (low ppb level to 100s of ppm) recognized in carbonate minerals. The primary interest of U and carbonates has concentrated on the use of the uranium-lead (U-Pb) radionuclide decay scheme for the dating of the sedimentary rock record. Geologic time boundaries, currently based on fossil records and volcanic ash age data, can be even further constrained by dating sedimentary materials with the U-Pb system. Due to the concerns involving human exposure to nuclear wastes, the focus now includes evaluating the crystal chemistry behind the incorporation of U into carbonates.

A sample of a dated caliche paleosol (ancient soil) that was developed on host carbonate of Permian age was chosen for study of U incorporation in natural calcites. The sample was selected because the U-Pb age is very precise, 298±1 Ma, and concordant [6]. This establishes that U has not been mobilized in this paleosol for almost 300 million years. Due to this stable history, the sample should provide significant insight for determining a mechanism for the incorporation of U in calcite in a soil environment on geologic timescales. The paleosol is from a core from the Central Basin Platform of the Permian Basin of West Texas and is from around 2700 meters depth. Geologic relationships demonstrate that the Permian section has not been exposed since burial shortly after its deposition.
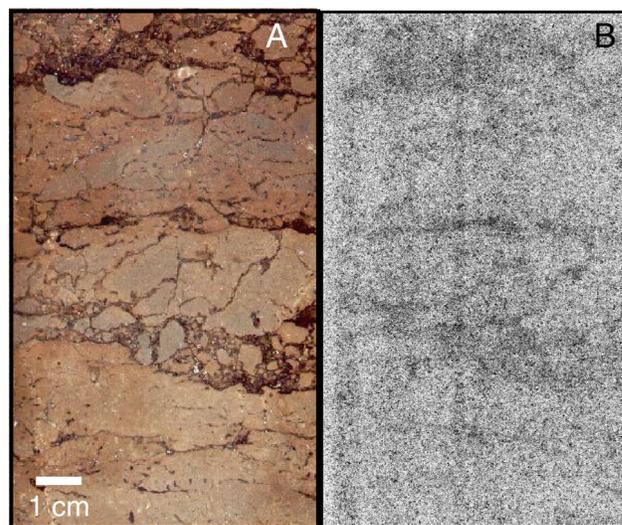
Figure 1. *A) Photomicrograph of polished slab of an* in situ *brecciated dolostone. The dark brown calcite formed around roots that broke up the host rock. B) Phosphor image of the polished slab in A that was left on the imaging plate for 4 weeks. Radioactivity exposes the phosphor plate and provides a hand specimen scale map of the U distribution. It is clear that the U is enriched in the brown organic rich calcite.*

This paleosol is an *in-situ* breccia containing horizontal root casts that break up the host dolomite (Figure 1A). Petrographically, the root casts are composed of dark brown organic rich needle fiber calcite and are lined by pyrite [7]. Fission track data reveal the U concentrations are elevated in the calcified roots, clearly suggesting an association with organic matter. Phosphor imaging techniques reveal the same correlation between U and organic material on a hand sample scale (Figure 1B). Isotope dilution (ID) measurements of 40-70 mg aliquots demonstrate U concentrations of 5-8 ppm for this sample.

Results and Discussion

In order to evaluate U concentrations on a much smaller scale, we utilized the NSLS beamline X26A's unique x-ray fluorescence microprobe capabilities with a detection limit for U of about 1 ppm. In addition, we used simultaneous micro x-ray diffraction (XRD) with a spatial resolution of ~ 10 μm, to characterize mineral phases. Finally, x-ray absorption near edge spectroscopy (XANES) was used to determine the oxidation states of U in the sample.

Preliminary micro-XRD results show three mineral components, high Mg calcite, dolomite and quartz, in addition to the pyrite observed petrographically. The dolomite, most likely, is in the host rock. The presence of high Mg calcite is unexpected due to the low Mg/Ca ratio in most meteoric fluids and to previous suggestions that high Mg calcite is unstable [8] and observed to be susceptible to dissolution by meteoric waters. However, carbonate cements forming in organic rich horizontal root environments have been found to contain up to 4.5 mole percent Mg^{2+} [9]. Additionally, because of its role in photosynthesis, algal material has been shown to have increased Mg^{2+} concentrations [10], suggesting a similar relationship may exist with plants. Further evaluation is necessary in order to understand this occurrence and its possible relationship to U concentrations and speciation in this paleosol.

X-ray fluorescence (XRF) compositional maps were produced for this sample and reveal a heterogeneous distribution of U (Figure 2). Elemental abundances were quantified by spot energy dispersive XRF analysis, quantifying a range in U concentrations from 2-20 ppm in the calcite. Because the aliquots used in the U-Pb system study ranged from 40-70 mg, the XRF determined concentrations are within the expected range based on isotope dilution, which would clearly represent mixing of the finer scale observed by XRF.

Of primary interest are the initial XANES analyses, which illustrate that the calcite with highest U abundances shows an absorption edge shift to higher binding energy consistent with U (VI) (Figure 3). Based on the presence of organics and pyrite, however, this paleosol clearly formed in a reducing environment. While reduction of U at redox fronts is commonly cited as the mechanism for U enrichment in ores [11] and in marine sediments [12], results from wetland studies [13,14] demonstrate that U is at least initially complexed as the uranyl ion with organic functional groups such as carboxylate. Additionally, this observation conflicts with previous studies of natural calcite [15], revealing a substitution of U (IV) for Ca^{2+} in the calcite structure. It is
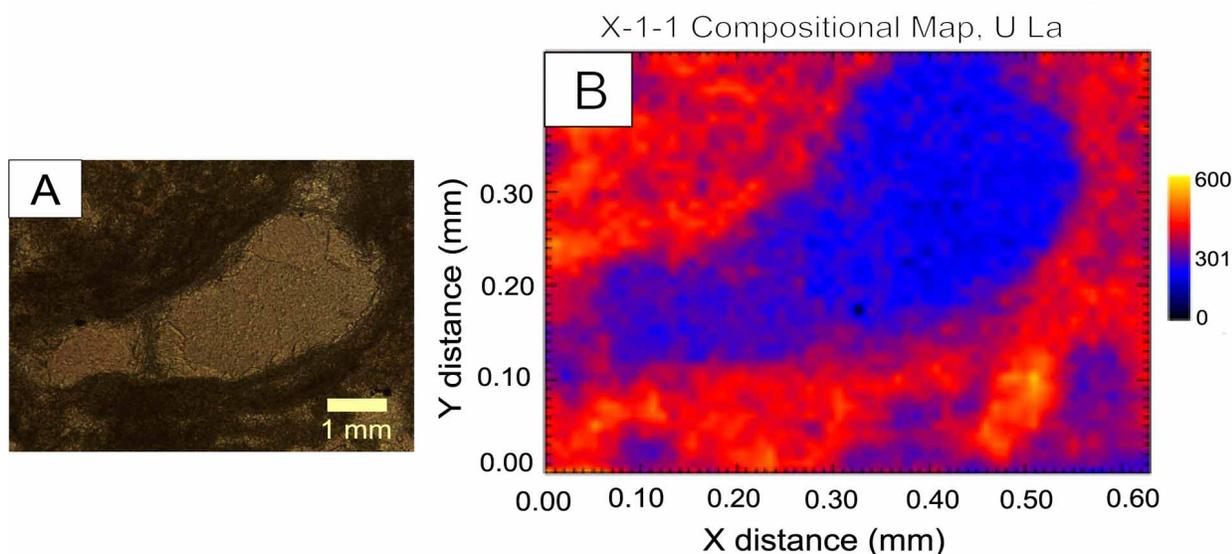
Figure 2. *A) Photomicrograph showing root cast in dated caliche paleosol. B) XRF map showing uranium concentrations for same root cast. The color bar denotes intensity in arbitrary units. Uranium concentrations in this caliche are elevated in brown organic rich calcite*

consistent with observations made on synthetic calcite [4], however, the results of that study imply using calcite to sequester U (VI) over geologic timescales is unfavorable. The inability to compare this sample with previous observations suggests multiple mechanisms exist for the incorporation of U in natural calcites and necessitates the exploration of the U-carbonate-soil organic material system.

Our model for the enrichment of U is similar to models for uranium ore deposits, in that U travels as the oxidized species and is fixed by organic material. However, the results of this study demonstrate that U is incorporated in its oxidized state, implying the reduction of U may not be necessary for incorporation, as assumed in other models. Our hypothesis is that the U (VI) has become bound with organic functional groups such as carboxylate, which the ubiquitous humic and fulvic acids can contain. This U-organic complex is quite stable and may require destruction of the organic compound for the reduction of U to occur. The complex may be incorporated in the calcite structure or may exist as a surface sorbed species. Calcite growth inhibition in the presence of organic material is of concern, however it has been shown that hydrophobic acids, such as humic acids, are more effective growth inhibitors than fulvic acids[16]. Mitterer and Cunningham [17] suggest the carboxyl head group substitutes for the carbonate ion site in the calcite structure. XAFS studies have been used successfully to evaluate the bonding of U-humic acid complexes [18]. Although natural organic matter is highly complex, based on numerous studies of the association of organic matter and U [1,13,18] it is clear that U will exist with active functional groups. Determining the coordination environment of the U in the paleosol calcite is necessary to refine this model.

The results presented from a paleocaliche with uncomplicated U-Pb systematics and U in the oxidized state are in contrast to the established thinking that incorporation of U (VI) is unstable in calcite. Our novel results draw attention to the need for further investigation into the relationship between U and organic material and its role in the sequestration of U (VI) in calcite. Previous attempts to evaluate the behavior of U in near surface processes have focused on the interactions between U and calcite, U and organic material and calcite and organic material. However, in natural environments these constituents overlap, necessitating an evaluation of the entire U-calcite-organic material system.
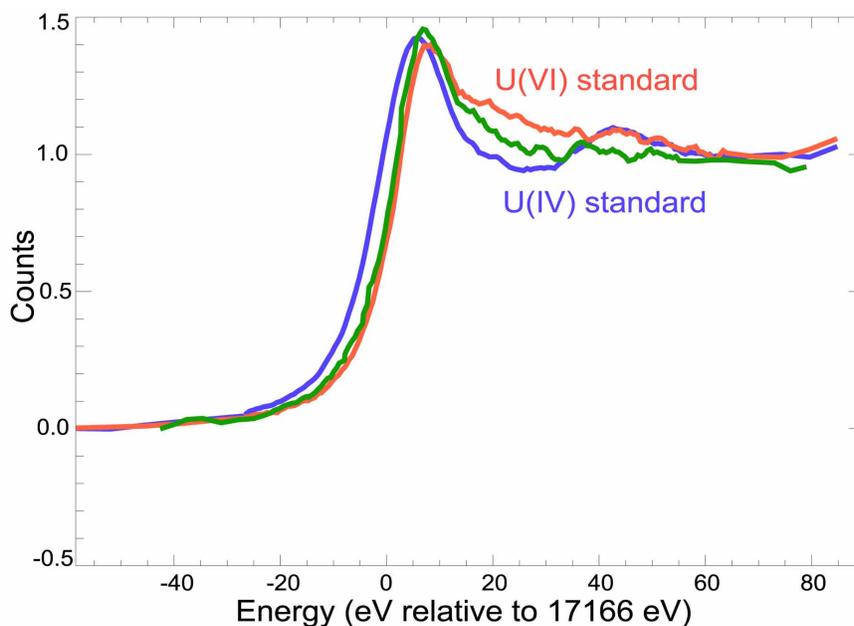
Figure 3. *XANES data for caliche paleosol. Sample spectra shown in green. The spectra for a U (VI) standard are shown in red and U (IV) standard spectra are shown in blue. Sample spectra show a shift in energy consistent with U $^{6+}$ species.*

References

[1] Lenhart, J. J. e. a. Uranium (VI) complexation with citric, humic and fulvic acids. *Radiochimica Acta* 88, 345-353 (1998).

[2] Sylwester, E.R., Hudson, E.A. & Allen, P.G. The structure of uranium (VI) sorption complexes on silica, alumina and montmorillonite. *Geochimica et Cosmochimica Acta* 64, 2431-2438 (2000).

[3] Lenhart, J.J. & Honeyman, B.D. Uranium (VI) sorption of hematite in the presence of humic acid. *Geochimica et Cosmochimica Acta* 63, 2891-2901 (1999).

[4] Reeder, R.J., et al. Uranyl Incorporation into Calcite and Aragonite: XAFS and Luminescence Studies. *Environmental Science and Technology* 34, 638-644 (2000).

[5] Meece, D.E. & Benninger, L.K. The coprecipitation of Pu and other radionuclides with CaCO3. *Geochimica et Cosmochimica Acta* 57, 1447-1458 (1993).

[6] Rasbury, E.T., et al. Dating the time of sedimentation using U-Pb ages for paleosol calcite. *Geochimica et Cosmochimica Acta* 61, 1525-1529 (1997).

[7] Rasbury, E.T., et al. Relationship of uranium to petrography of caliche paleosols with application to precisely dating the time of sedimentation. *Journal of Sedimentary Research* 70, 604-618 (2000).

[8] Reeder, R., et. al. *Carbonates: Mineralogy and Chemistry* (ed. Ribbee, P.H.) (Mineralogical Society of America, 1983).

[9] Mount, J.F. & Cohen, A.S. Petrology and Geochemistry of Rhizoliths from Plio-Pleistocene Fluvial and Marginal Lacustrine Deposits. East Lake Turkana, Kenya. *Journal of Sedimentary Petrology* 54, 263-275 (1984).

[10] Desborough, G.A. A biogenic-chemical stratified lake model for the origin of oil shale of the Green River Formation: An alternative to the playa-lake model. *Bulletin of the Geological Society of America* 89, 961-971 (1978).

[11] Spirakis, C.S. The roles of organic matter in the formation of uranium deposits in sedimentary rocks. *Ore Geology Reviews* 11, 53-69 (1996).

[12] Klinkhammer, G.P. & Palmer, M.R. Uranium in the Oceans: Where it goes and why. *Geochimica et Cosmochimica Acta* 55, 1799-1806 (1991).

[13] Idiz, E.F., et. al. Interaction between organic matter and trace metals in a uranium rich bog, Kern county, California, U.S.A. *Applied Geochemistry* 1, 573-590 (1986).

[14] Owen, D.E. & Otton, J.K. Mountain wetlands: efficient uranium filters-potential impacts. *Ecological Engineering* 5, 77-93 (1995).

[15] Sturchio, N.C., et al. Tetravalent Uranium in Calcite. *Science* 281, 971-973 (1998).

[16] Hoch, A.R., Reddy, M.M. & Aiken, G.R. Calcite crystal growth inhibition by humic substances with emphasis on hydrophobic acids from the Florida Everglades. *Geochimica et Cosmochimica Acta* 64, 61-72 (2000).

[17] Mitterer, R.M. & Cunningham, R. *The interaction of natural organic matter with grain surfaces: Implications for calcium carbonate precipitation* (eds. Schneiderman, N. & Harris, P.M.) (SEPM, 1985).

[18] Denecke, M. A. Determination of structural parameters of uranyl ions complexed with organic acids using EXAFS. *Journal of Alloys and Compounds* 271-273, 123-127 (1998).