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Uranium Incorporation Into Pedogenic Carbonates

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Introduction: Recent U-Pb studies of ca. 300 Ma caliche paleosols from rapidly deposited sections have yielded precise and concordant U-Pb ages (1). These results demonstrate that neither U nor its daughter products have been mobilized from the calcite (CaCO_3) over geologic time scales. This observation suggests great potential for storing radioactive wastes. In contrast, studies of U in synthetic calcite (2) have suggested that the incorporation of the dominant aqueous species, $\text{UO}_2(\text{CO}_3)_3^{4-}$, is unstable in the calcite structure and thus should not be expected to sequester U on the time scales of interest for radioactive waste disposal. One significant difference between natural samples and synthetic samples is the presence of organic compounds. The complexation of U with humates has been analyzed using extended x-ray adsorption fine structure (EXAFS) (3). Humic acids are abundant in soils and thus the research presented here is aimed at determining the relationship between organic matter, U and calcite in paleosols. We examined an in situ breccia with dark brown organic rich calcitized roots to evaluate U concentrations, speciation and to identify mineralogic and elemental correlations. Petrographically, we observe pyrite lining these organic rich rhizoliths. Additionally, bright orange cathodo-luminescence of the root lining calcite demonstrates the incorporation of Mn. Together, these observations show that conditions were reducing at the time of soil formation. The sample is from a Unocal-JNOC drill core of a cyclic marine to terrestrial shelf section in West Texas. This paleosol sample is from a depth of approximately 2500 m in the core.

Methods and Materials: The Bruker SMART 1K CCD system was used for collecting microbeam x-ray diffraction (XRD) data. Energy dispersive x-ray fluorescence (XRF) and x-ray near edge absorption spectroscopy (XANES) data were collected using a Si(Li) detector. All analyses were done using a focused monochromatic beam tuned just above the U L3 absorption edge. The beam was focused to ca. 10 μm in diameter using two, 100 mm long, bent silica mirrors arranged in a Kirkpatrick-Baez geometry.

Results: Preliminary XRD results indicate root cast mineralogy dominated by three mineral components, high Mg calcite, dolomite and quartz in addition to the pyrite observed petrographically. The presence of high Mg calcite is unexpected since previous studies have suggested it is 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+} (4). Further evaluation is necessary in order to understand this occurrence and relationship to U concentrations and speciation in this paleosol.

Element compositional maps were created to evaluate the distribution of U and other trace elements in the sample. From these maps, areas were selected for XRF in order to determine element concentrations. XRF results show that the distribution of U and other trace elements, including Cu, is heterogeneous. More enriched concentrations of U (23 ppm average) and Cu (460 ppm average) correlating with darker areas, are suggestive of more organic material, whereas lower concentrations of U (< 7 ppm) and Cu (30-70 ppm) correlate with lighter areas. The occurrence of U and Cu together has also been seen in studies of U ore deposits. Due to ionic radii size constraints, both Cu^{2+} and U^{6+} should not preferentially occupy the larger Ca $2+$ site in carbonates. This relationship seen at different scales may provide information regarding the long-term immobilization of U.

U XANES show that for calcite with the highest U abundance (~20 ppm), the absorption edge is shifted towards the higher energies consistent with U (VI). These data are inconsistent with other XAS studies of natural calcite (5), and suggest multiple mechanisms for the incorporation of U into carbonates.

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References:

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