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A URANIUM ISOTOPIC PERSPECTIVE ON THE FORMATION OF ROLL-FRONT MINERAL DEPOSITS AND IMPLICATIONS FOR POST MINING REMEDIATION

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'INTRODUCTION'

Roll front deposits are an important global source of economic uranium ore, commonly mined using in situ leach (ISL) methods. The simplified conceptual model for roll front formation calls for the reductive precipitation of U(VI) to U(IV)s as oxygen-rich groundwater interacts with subsurface reductants such as iron minerals, sulfide and anaerobic microbes, forming reduced U minerals such as uraninite and coffinite. While this model captures the broad mechanisms of roll front formation it does not directly address why roll fronts form in only some reducing sediments, the timescale of formation and whether some roll fronts are actively accumulating U and/or migrating. These questions are of geologic interest but more importantly affect the economic and environmental decisions related to ISL mining.

In the USA, the primary concern with ISL mining is the fate of remnant aqueous U(VI) in the mined formation after the cessation of mining and active remediation (e.g. reverse osmosis). In many existing mines at least some portions of the aquifer have U(VI) concentrations in excess of the pre-mining aquifer concentrations and it is unknown how far downgradient this U(VI) will migrate before it is reduced to U(IV) and precipitated. This so-called natural attenuation of residual aqueous U is an important component of designing the lifecycle strategy for ISL mines. There are very few direct constraints on the kinetics of U sorption and reduction reactions that can be directly applied to roll fronts, however, some guidance on this topic comes from recent studies of U remediation across contamination sites in the US Dept of Energy complex [1-4]. There are, however, significant differences in the hydrology and groundwater chemistry (e.g. organic carbon activity) in typical roll front deposits compared to the (primarily) vadose zone studies.

Recent observations from groundwater and minerals in roll front deposits show a remarkable variation in the isotopic ratio of 238U/235U[5-8]. The observations of U isotopes in groundwater combined with the theory that fractionation of the 238U/235U is largely due to reduction of U(VI) to U(IV) should make it possible to quantify the extent of U reduction in the subsurface both before and after mining activities. Modeling the extent of U reduction has been complicated by (1) deviations in the extent of isotopic fractionation from theoretical models and (2) heterogeneities in the isotopic composition of ore minerals. It remains unclear what processes affect the magnitude of isotope fractionation and give rise to heterogeneous mineral compositions. One suggestion is that biotic and biotic U reduction will yield different isotopic effects and that mixtures of these two mechanisms could explain the variations[9, 10]

The purpose of this contribution is to investigate if a 2-dimensional spatial analysis of U and U isotope distributions in a roll front can resolve the aforementioned problems with interpreting the U data from associated groundwater. We demonstrate that the spatial distribution of U, and the U isotope ratios are not random but a result of reactive transport that can be approximated to a pipe flow model and that this information can be used to place constraints on the formation and migration timescales of the roll front.

Geologic and Hydrogeologic settings: The Smith Ranch-Highlands uranium mine is located 50 miles northeast of Casper Wyoming, USA on the southern edge of the Powder River Basin. The U ore is concentrated in fluvial sandstones of the Paleocene Fort Union Formation. Regionally the strata dip to the East at <0.5° and

groundwater flow is mostly in the same direction at 2-3 m/yr [11]. Uranium is concentrated at redox boundaries (roll fronts) that are typically 2-8 meters wide and at depths of 61-366 meters. Uranium typically occurs as uraninite (UO2) and coffinite (U(SiO4)0.9(OH)0.4) coatings on sand grains and is commonly associated with pyrite and carbonaceous matter, the presumed uranium reductants [12-14].

METHODS AND RESULTS

We collected 3 cores through a single roll front in the expected mineralized zone along the depositional axis of the roll front. The cores are spaced approximately 10 meters from one another and are about 6-9 meters in total length. The sediments range from silt and clay-rich horizons to coarse quartz arkose sands. The coarse sediments contain lignite fragments that show some rounding from fluvial transport. Preliminary visual analysis of the core is consistent with a fluvial deltaic type depositional environment. The cores were divided into 0.15-0.3 m sections in the core barrel and packaged in two food grade vacuum bags, evacuated and heat sealed for shipping to the laboratory. Each core hole was logged for gamma radiation, resistivity, and conductivity.

In the lab the cores were scanned with a handheld NaI gamma detector to identify sections of low and high radioactivity. Core sections were opened inside an O2-free anaerobic chamber where an aliquot was preserved inside a glass bottle sealed with a rubber septum and the remainder was stored in gas impermeable Mylar bags. Samples of ˜5 grams were transferred to degassed 15 ml centrifuge tubes and leached successively with a KCl solution (pore water leach), NaHCO3 solution (adsorbed U fraction) and HCl solution to extract the precipitated UO2 fraction without sampling significant U from silicate minerals such as zircon. The acid leachates were then analyzed for U concentrations, 234U/238U and 235U/238U in the Center for Isotope Geochemistry at Lawrence Berkeley National Laboratory.

Results: The cores are numbered 1-3 from upgradient to downgradient for description purposes. The sediments are quartz rich (SiO2 85.1-95 wt%) with large, pink potassium feldspar. Using the ternary chemical classification Na2O-K2O-FeO+MgO all of the core samples plot within the arkose field. Uranium is the only trace element with consistent enrichment above average upper continental crust, with most trace elements between 0.1 and 1 times the upper continental crust.

The concentrations of U in the U mineral leachate fraction vary from approximately 0.5 ppm to 1000 ppm. In each core there is a zone of high U concentration that tail to lower concentrations above and below giving a generally convex concentration profile when compared to depth. The 235U/238U ratios vary by approximately 2‰ amongst the analyzed samples and show a convex relationship compared to the sample depth. The 235U/238U values are slightly enriched in the highest U concentration samples but are depleted in the lower concentration samples. In the axis of the roll front, defined by the highest U concentrations there is a decrease in the maximum 235U/238U ratio in the cores further downgradient.

The 234U/238U are reported relative to secular equilibrium (SE) as activity ratios (AR): 234U/238Usample/234U/238USE. The 234U/238UAR vary from 0.771 to 2.257 but most samples cluster between ˜0.84 and 1.65. In contrast to the 238U/235U and U concentrations the activity ratios show a concave pattern when compared to sample depth with the lowest 234U/238UAR coincident with the highest U concentrations. The highest 234U/238UAR values are generally toward the top and bottom of the cores, however, some of the highest values occur within 0.6 m of the lowest 234U/238UAR in the most upgradient core.

The NaHCO3 leachate is assumed to represent the adsorbed U component. The spatial distribution of 238U/235U (described as ⊠238U) and 234U/238UAR in the adsorbed component are similar to the reduced fraction described above, though the absolute values are distinct. For comparison of the two components we describe Δ238U (⊠238Ureduced-⊠238Uads) and 234U/238UAR (% difference). Samples of the adsorbed component are both enriched and depleted Δ238U compared to the reduced component, however most of adsorbed fractions are depleted in Δ238U compared to the reduced fraction (range of Δ238U -1.63 (-0.6 exclude outlier) to +0.26). All samples have 234U/238U enrichment in the adsorbed fraction varying from 16-271%. Most samples with [U]>10 ppm have 234U/238U enrichments less that 75%, while most samples with [U]<10 ppm have enrichments greater than 75%.

'DISCUSSION AND CONCLUSIONS'

The distributions of U and U isotope ratios in the studied roll front appear to have a systematic distribution, which is distinct from earlier isotopic observations that lacked the resolution to capture this phenomena[5, 7, 9] (but recognized by [15]). In order to understand the distribution of U and U isotope values we constructed a simplified 2 dimensional reactive transport model. The model is constrained by the observed reservoir hydraulic conductivity and the spatial observations of U and U isotopes. First the fluid velocities are set at the maximum value coincident with the high U concentration zone and calculated above and below using a no slip boundary condition at the top and bottom of the domain (i.e. pipe flow model). The model dos not consider hydrodynamic dispersion or chemical diffusion. The U reduction rate is assumed to be a pseudo-zero reaction with at rate that is characterized by the width of the roll front 0.1 μmol L-1 yr-1. The reaction order is reasonable if U reduction is catalyzed by enzymes or by mineral surfaces. The distribution of U and U isotopes is solved:

v dU/dx=-R

Where x is distance (m), v is fluid velocity (m/yr), U uranium concentration in mol L-1 and R is the precipitation rate mol yr-1.

The simulation of uranium reduction over the model domain yields a convex distribution of ⊠238U with the most enriched solids in the center of the domain and more depleted values toward the upper and lower boundaries similar to the observed pattern in the SRH cores. This model is a single-pass analytical solution and does not integrate U addition over the lifetime of the redox boundary, meaning that we cannot directly investigate the concentration profiles.

The model uses a single 238U/235U isotopic fractionation factor and yields U solids that are both enriched and depleted in ⊠238U(s) compared to the starting solution composition. Thus, we can explain enriched and depleted ⊠238U(s) occurring in close proximity to each other solely based on advective transport and a single reduction reaction.

The model does make an additional prediction that the change in ⊠238U(s) with distance should be smallest in the high flow zone and greatest as you approach the low flow zone adjacent to the zero flow boundaries, which we observe in our dataset, though not to the extremes predicted in our model. In one other roll front deposit extreme values of ⊠238U -4‰ in mineralized sands, which would be consistent with similar effects as the model presented above[7].

Preliminary Conclusions: The U isotopic compositions of roll front ores can vary substantially over the meter scale and larger. These variations can be largely explained by advective transport during roll front ore deposition without significant changes in the mechanisms of U mineralization. These findings also suggest that large changes in hydraulic conductivity in the reservoir may affect the ISL mining and remediation efficiencies.

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