Zircon as a Witness to Earth's First 500 Myr: an Experimentalist's View

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The past decade has seen major advances in our understanding of the first 500 million years of Earth history. Cataclysmic events such as the formation of the core, atmosphere and Moon are understood mainly through models and isotopic systematics of large reservoirs (e.g., meteorites, Earth's mantle and/or atmosphere, Moon rocks), but when it comes to details of early-Earth conditions, we must turn to the geologic record. Ancient zircons are the most tenacious record of the early-Earth story. Even though their original host rocks are long gone, Western Australia's Hadean zircons still provide insight into not only the protolith of the magmas in which they grew but also the conditions that prevailed during early crustal magmatism.

The interpretation of chemical and isotopic signatures in natural zircons has been significantly expedited by laboratory experiments that define the high P-T equilibria and kinetic properties of this remarkable mineral. Most basic among these properties is the saturation behavior of zircon in magmas. Knowledge of zircon saturation as a function of melt composition, temperature and pressure provides broad constraints on zircon crystallization scenarios, Hadean or otherwise. In combination with analyses of ancient zircons, other experimentally determined properties shed light on petrogenetic processes and protoliths. The Ti content of zircons provides estimates of magmatic temperatures, and Ce anomalies inform us about oxygen pressures (fugacities) that prevailed during zircon crystallization (and, by inference, in Earth's early crust and mantle). Knowledge of magmatic oxygen fugacities gives us indirect insight into the nature of C-O-H-N-S molecular species in gaseous volcanic emanations. The general picture of early Earth portrayed by the oldest zircons is that the sedimentary cycle was in full swing within 150 Myr of Earth's origin, the oxygen fugacity of the mantle was similar to that of today, and volcanic inputs into the atmosphere were similarly "modern" in molecular character, and neutral—that is, mainly CO_2 and H_2O.

Information is preserved in zircons not only because the crystals themselves have survived, but also because diffusive transport of most ions in zircon is very slow. Oxygen (in H_2O-free environments), U, Th, Pb, Hf, rare earths, Ti, and have been shown to diffuse so slowly that post-crystallization re-setting is unlikely in a zircon that has not been damaged by radioactive decay. On the other hand, O (under H_2O-present conditions), Li, and H may be mobilized in ancient zircons that experience post-crystallization re-heating. Even in the case of Li and O, however, there is evidence that original abundances and/or isotope ratios have been preserved in some cases.

A summary will be provided of experiment-based knowledge of zircon properties (and limitations), followed by a general perspective on early Earth that emerges from "decoding" Hadean zircons.

Diffusion/Deposition/Remobilization of Uranium in Bioreduced Zones

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It is common practice to inject substrates and other reactants to reduce the mobility and/or toxicity of subsurface contaminants through bioreduction and other remediation techniques. These injections result in manipulated zones that are in a state of chemical disequilibrium. For example, bioreduction can significantly reduce the concentration of contaminants (like U) and other inorganics in groundwater but increase the concentration on the solid phase. Due to preferential transport through subsurface heterogeneities, there will be abrupt aqueous concentration gradients between well connected high permeability zones that receive a high concentration of treatment media (low U zone) and adjacent lower permeability zones that do not receive treatment media (high U zone). The objective of this study is to assess the diffusion of U into bioreduced zones from adjacent unreduced zones, deposition of the U in the bioreduced zone and remobilization of U after the bioreduction has stopped.

Laboratory bottle tests, field observations at the U.S. DOE Oak Ridge Integrated Field Research Challenge site during U bioreduction experiments and numerical modelling were employed to meet these objectives. U contaminated soils encapsulated in polyacrylamide hydrogels (Spalding and Brooks, 2005) were used in the lab and the field to determine U release and diffusion rates (Figure 1). A two site kinetic model was used to predict release and diffusion of U from unreduced zones to adjacent reduced zones.

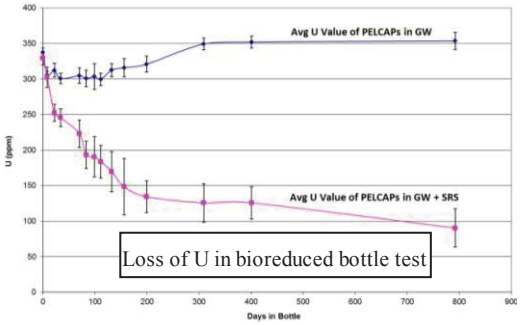

Figure 1: Loss of U from soils encapsolated in hydrogel observed for over 800 days during bioreduction of groundwater.

The results of our study suggest that U will migrate from unreduced zones into reduced zones when bioreduction is active resulting in "extra" U being deposited in high permeability transport pathways. However, if bioreduction conditions are not maintained, an unintended consequence may be an increase in the U flux (relative to pre-bioreduced conditions) as the "extra" U is released as a result of oxygenated groundwater entering the previously reduced zone.

[1] Spalding and Brooks. 2005. *Environ. Sci. Technol.* 39(22):8912-8918