Research Plan

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Modeling Uranium Uptake in Fossilized Teeth and Bones: Potential for Uranium Waste Storage

A. Rationale:

Nuclear meltdowns and waste mishandling have left some of the groundwater supply contaminated with radioactive uranium, and efforts to combat this have resulted in studies about nuclear waste remediation which are relatively short in terms of the geologic time scale (Crowley, 1997). The process by which uranium is taken up and stored in a porous material is integral to the study of nuclear waste remediation. Under certain reducing conditions, uranium, in the form of the polyatomic ion uranyl, UO_2^{2+} can replace calcium ions and become immobilized inside a porous biogenic material (Sharp et al, 2011). In addition, uranium can precipitate inside of these materials if open pore space is available. Uranium itself naturally occurs in minute levels due to the presence of decayed vegetation, which fosters an oxidizing environment key to its mobilization (Banning et al, 2013). Therefore, uranium can become incorporated easily into aquifers via groundwater flow. Furthermore, the element can be present in the environment as a harmful byproduct of nuclear energy production. In high concentrations, uranium poses a threat to the freshwater ecosystem, exposing the flora and fauna to high dosages of damaging radioactive decay (Matthews et al, 2009). To prevent the introduction of chemically unbound uranium to an ecosystem, phosphate materials are often used to sequester the radioactive element (Martinez et al, 2014). The hexavalent uranyl ion, $(UO_2)^{2+}$, can be effectively immobilized by reacting with the calcium phosphate mineral, hydroxyapatite, present in mammal teeth and bones. Uptake laws are used to model the chemical addition of uranium into a remediation system and provide insight into the immobilization of the element over time. Previous uptake laws have described the uptake of uranium in the porous dentine and rigid enamel of mammalian teeth yet have not assessed the uptake rate with regard to a system's isotopic signature (Pike and Hedges, 2001). The potential for hydroxyapatite to be utilized as an effective Permeable Reactive Barrier (PRB) remains a promising and cost-effective alternative to the nuclear waste containers being evaluated by the Yucca Mountain Site Characterization Project (Gdowski, 1997).

B. Research Question and Hypothesis:

Research Question: Can uranium uptake and immobilization be simulated in hydroxyapatite fossils as a predictive model for the behavior of the radioactive waste?

Hypothesis: By taking advantage of preserved geologic samples, a history of U uptake can be determined for a 14-million-year-old *Scaphohippus intermontanus* horse tooth and foot bone. This way, the timeline of radioactive waste immobilization can be predicted. Due to its combined porosity and durability, the dentine from the tooth sample will remediate larger quantities of uranium waste in shorter periods of time than the bone sample.

C) Procedure/Risk and Safety Analysis/Data Analysis:

The experiment will be performed at Stony Brook University under the supervision of Professor E. Troy Rasbury, Professor William Holt, and Ms. Kathleen Wooton.

(i) Procedures:

Preparation of Samples:

- Tooth samples will be placed in Beuhler Epoxicure epoxy
- Epoxy will utilize a 4:1 ratio of resin to hardener

- Used to provide structure for the teeth and to prevent fracturing when cut
- The bone samples may be sturdy enough to cut without epoxy
- All samples will be sliced into thick sections of about 5 mm using a Beuhler IsoMet slow saw
- One side of each of the thick sections will be polished on a glass plate
- Sequence of 120, 320, 400, and 600 grits

(ii) Risk and Safety:

- A senior supervising scientist will be present during all times of experimentation
- Lab safety course will be taken prior to experimentation
- Persona Protective Equipment (PPE) will be worn at all times while in the lab.
- Beuhler IsoMe Slow saw is gravity-fed and personal protective equipment in the form of gloves and protective eyewear will be utilized for the duration of the cutting
- The Agilent 7700 Series LA-ICP-MS laser is fully contained within the machine. The LA-ICP-MS will be used according to manufacturer's recommendations.
- The U and Pb are naturally occurring in the samples deemed to be free of potential risk
- Epoxy is standard and over the counter, posing no risk
- The data from the National Synchrotron Light Source II will be obtained by a trained professional
- Data Analysis is deemed to be free of potential risk

(iii) Data Analysis:

Laser Ablation Inductively Coupled Plasma Mass Spectrometry:

- LA-ICP-MS data will be recorded to examine smaller sections of the samples with a higher degree of precision

- Twenty-five congruent lines situated side by side on a 2-D plane will be ablated to form elemental maps of the sections of dentine and enamel for tooth sample and to map cortical and spongy bone in bone sample
    - The lines will be approximately 8500 μm long, covering the aforementioned sections in a small amount of space
    - They will be ablated 50 μm apart from each other, using a 20 μm diameter laser beam at 10 μm/s speed of laser travel
- The laser measures isotopes and calculates isotopic ratios for Pb-206, Pb-207, Pb-208, Th-232, U-238
    - These ratios will then be used to calculate isotopic ages for the different sections of the sample and included in the uptake model.

Tender Energy Spectroscopy:

- The National Synchrotron Light Source II (NSLS II) will be in the tender energy range, 1 to 5 keV, to create a map and determine the speciation of select elements in the tooth sample
    - Chlorine, phosphorus, and uranium will be analyzed using an 8 μm beam of electrons, which spans 10 μm pixels in the resulting images.

Modeling in MATLAB code:

- A code will be designed to read in data collected from individual spots and the full maps previously measured using the LA-ICP-MS
- It will calculate the best-fitting τ value for the set of data, indicating the timescale in which the majority of the uranium was taken up in each sample

D. References:

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NO ADDENDUMS EXIST