Effect of Hafnium on Glass Structure and Dissolution

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Reactions that occur at the solid-water interface control the composition of the worlds fresh water, soil development and nutrient distribution, the cycling of elements in the Earth's Critical Zone, and to predict the impact from the disposal of vitrified nuclear waste [1]. Recently, multi-scale or hybrid models, which capitalize on advancements in the understanding of solid-water interfacial reactions, have been used to better describe the macroscopic interactions occuring in the systems [2]. However, knowledge gaps in the fundamental understanding of solid-water reactions impede the ability to accurately describe microscopic processes (e.g., sorption, surface layer formation, etc.) that represent the underlying phenomena controlling macroscopic reaction kinetics.

An important step in improving our ability to accurately forecast radionuclide release from vitrified waste is to establish a link between the glass atomic-level structure and macroscopic dissolution behavior. This study extends the previous work by Pierce et al. [3], by evaluating the effect the high-valence cation hafnium has on the structure and chemical durability of alkali aluminoborosilicate glass.

Results from flow-through experiments show a ~100× decrease in the dissolution rate with increasing Hf content from 0 to 20 mol% HfO_2. The results also reveal a divergence in the magnitude between the average steady state rates measured in dilute and near-saturated conditions. Monte Carlo simulations indicate that the divergence in glass dissolution behavior results from the formation of a low coordination Si sites when Si from the saturated solution adsorbs to Hf on the glass surface. The residence time of the low coordination Si site is longer at the glass surface and increases the density of anchor sites from which altered layers with higher Si densities can form than in the absence of Hf. These results illustrate the importance of understanding solid-water/solid-fluid interactions by linking macroscopic reaction kinetics to nanometer scale interfacial processes.

[1] Brown and Calas (2012), Geo. Perspec., **1**. [2] Steefel and Maher (2009), Rev. Min. & Geo. **70,** pp485-532. [3] Pierce et al. (2010), GCA, **74**, 2634-2654.

Back to the future: high-sensitivity noble gas mass spectrometers with modern electronics.

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Spectrometers designed 30 years ago, operated in a single-collector mode, remain capable of routinely measuring argon isotopic ratios that may vary over five orders of magnitude, with precisions better than 0.2% for gas species in quantities of ~ 10^{-16} mol. Aging electronics are the Achilles heel of these systems. A focus of our activities is to develop a new generation of novel electronic device upgrades for the control of typical noble gas mass spectrometers (e.g., the MAP-215 and similar instruments). Over the past 30 years, most analog circuits have been redesigned to use MOS (Metal Oxide Semiconductor) technologies that consume less power, are smaller, and allow more circuitry to improve the performance of a given device. Such devices can incorporate circuitry to protect against external or internal transients. For example, a newly designed emission regulator is able to sustain leakage (as caused by the slow deposition of filament metal on the insulating components of the source) between the source, half-plates, filament and repeller without damage. Considering electromagnet and filament control, stability to within 1 to 2 parts per million can be achieved. The use of 24-bit analog to digital converters coupled with more powerful, responsive power supplies will result in significantly reduced electromagnet settling time. The thermal stability of these devices is enhanced by using state of the art, low power, enclosed circuitry with convective cooling. Multiple sensor inputs are incorporated to allow monitoring and logging of environmental conditions such as temperatures and humidity. All critical voltages and currents are controlled, and monitored over an Ethernet interface. This control eliminates noise from potentiometers and other moving electromechanical components, and permits full logging of parameters useful in automatic tuning algorithms. This level of control also will permit expedient changes and tuning of source parameters for analysis of different isotope groups (He, Ar, etc.). It is possible to completely control all of these electronics remotely through a standard web browser. Test data generated in this effort are presented in this forum for analytical standards and geologic samples of varying age and context.

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