

Thermodynamic stability of U60 nanoclusters based on solubility measurements

SHANNON L. FLYNN*, JENNIFER E. S. SZYMANOWSKI, PETER C. BURNS, AND JEREMY B. FEIN

Dept. Civil Eng. and Geological Sci., University of Notre Dame, Notre Dame, IN 46556, USA (Correspondence: sflynn4@nd.edu)

U60 nanoclusters are uranyl peroxide based spherical phases that are approximately 2 nm in diameter, with a stoichiometry of $K_{18}Li_{42}[(UO_2)(O_2)OH]_{60}$. Although U60 nanoclusters remain intact in alkaline solutions for at least a year, their thermodynamic stability has not been determined. Of particular interest is whether the nanoclusters behave thermodynamically as a solid phase or as an aqueous species. In this study, we measured the dissolution of U60 nanoclusters under several pH conditions in order to determine their thermodynamic stability. We used the experimental results, in conjunction with aqueous speciation modelling, to calculate an ion activity product (IAP) for each condition studied using two approaches: 1) assuming unit activity for the U60 'solid', and 2) treating the U60 as an 'aqueous' ion.

U60 crystals were made in a mother solution of uranyl nitrate, potassium chloride, hydrogen peroxide and lithium hydroxide. Crystals were harvested by vacuum filtration and then disaggregated in nanopure water, creating a suspension of U60 nanoclusters of known concentration. Batch U60 dissolution experiments were conducted in Teflon reaction vessels at pH 7.5, 8.0 and 8.5, with approximate nanocluster concentrations of 1.4, 2.8 and 6.0 g/L. Samples were extracted periodically for 14 days. Each sample aliquot was divided into two portions: an unfiltered portion for total K, Li and U analysis, and a portion that was filtered through a 10 k Da molecular weight sieve to determine the aqueous concentrations of K, Li and U in each sample. All metal concentrations were determined using ICP-OES. The presence of U60 nanoclusters was verified using electrospray mass spectroscopy at the beginning and end of each dissolution experiment and no other phases were created during the course of the experiments.

Aqueous concentrations achieved steady-state values within 24 hours in each experiment. IAP values, calculated from the experimental measurements assuming unit activity for the U60 nanoclusters and accounting for the aqueous speciation of K, Li, and U, were found not to vary significantly with pH, but to vary as a function of nanocluster concentration, with the calculated IAP value increasing with increasing nanocluster concentration. The variation in the calculated IAP as a function of nanocluster concentration suggests that the assumption of unit activity for the nanocluster is invalid. Models with non-unit activity for the nanocluster yield significantly less variation in the calculated IAP values as a function of nanocluster concentration. Our results suggest that the U60 nanoclusters behave more like aqueous species than a solid phase, and our calculated stability constant for the U60 nanoclusters can be used to estimate the solubility of the nanoclusters under a range of aqueous conditions. Our results underscore the importance of characterizing the charging behavior of these nanoclusters in order to better constrain their activity coefficients and hence their solubility behavior.

Resilience of bacterial communities in a pristine aquifer despite changes in the availability of sulfate

THEODORE M. FLYNN^{1,2*}, ROBERT A. SANFORD¹, JORGE W. SANTO DOMINGO³, NICHOLAS J. ASHBOLT³, AUDREY D. LEVINE³, AND CRAIG M. BETHKE¹

¹University of Illinois at Urbana-Champaign, Department of Geology Urbana, IL, USA

²Argonne National Laboratory, Bioscience Division, Argonne, IL, USA, tflynn@anl.gov (* presenting author)

³U.S. Environmental Protection Agency, Office of Research and Development, Cincinnati, OH, USA

We test how bacterial communities in a pristine aquifer respond to geochemical changes by incubating initially-sterile sediment traps in groundwater with a relatively high (1.5 mM) or low (0.04 mM) concentration of sulfate for one year, then transferring each trap to the opposite well. We sequenced 16S rRNA genes and created terminal restriction fragment length polymorphism (T-RFLP) profiles of the bacterial community from these switched traps, then used multivariate statistics to compare them with control traps which had remained in the same well for the duration of the experiment. These analyses showed that despite the 12 month incubation in a well with a 40-fold difference in the availability of sulfate, the bacterial communities attached to the switched traps retained a characteristic structure more similar to the well in which each trap was initially incubated than to the control community where they were subsequently placed. Although the relative abundance of many populations on the switched traps remained unchanged by this change in the availability of sulfate, the relative abundance of certain phyla associated with sulfate reduction (*Desulfobacter* and *Desulfobulbus*) was found to increase or decrease along with the corresponding change in the availability of sulfate. Other functional groups whose abundance has also been linked to the amount of sulfate in groundwater, however, such as the iron reducers *Geobacter* and *Desulfuromonas*, appeared unaffected by the switch between high and low sulfate wells. These results indicate that many bacterial populations present in an aquifer community do not simply represent the taxa are most favored by current geochemical conditions. Rather, the biogeographical and geological history of the area play a significant role in determining the composition of the bacterial community. Predicting its response to external perturbations, whether naturally-occurring or anthropogenic, would therefore require a more holistic understanding of the environment being studied than can be provided by a survey of bacterial populations alone.