Actinide sorption and reactivity at the muscovite-aqueous interface

M. SCHMIDT[1, 2,*], S. S. LEE[1], R. E. WILSON[1], K. E. KNOPE[1], P. FENTER[1], L. SODERHOLM[1]

[1]Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL, USA
[2]Current Address: Institute for Nuclear Waste Disposal, Karlsruhe Institute for Technology, Karlsruhe, Germany, moritz.schmidt@kit.edu (* presenting author)

Introduction

We present recent findings regarding the interaction of tri- and tetravalent actinides (Th, Pu) with the charged (001) basal plane of muscovite. *In situ* crystal truncation rod measurements and resonant-anomalous x-ray reflectivity were applied to investigate structures in the near-interface region under varying solution conditions (ionic strength, actinide concentration, chemical speciation of the actinide, background electrolyte).

Results

The results show a broad variety of potential forms of interaction, that strongly depends on the actinides' aqueous chemistry. The strongly hydrated cations do not shed their hydration layers upon sorption, but remain as extended outer sphere complexes [1]. In this sorption state the cations are highly concentrated in the near-interface region, and also highly mobile which allows for subsequent reactions (e.g. polymerization) between sorbed species to occur. In the case of plutonium this interfacial reactivity has been found to dominate the sorption behavior.

The results are expected to provide valuable input to the ongoing discussion about potential nuclear waste repository strategies as well as enrich the molecular level understandifng of the actinides' environmental geochemistry in general.

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Unraveling the chemical space of extreme natural environments and chondritic organic matter

PHILIPPE SCHMITT-KOPPLIN[1*], ZELIMIR GABELICA[2], NANCY HINMANN[3], MICHAEL GONSIOR[4] , WILLIAM COOPER[5], REGIS GOUGEON[6], MOURAD HARIR[1], NORBERT HERTKORN[1]

[1]Helmholtz Zentrum Muenchen, Analytical BioGeoChemistry, Germany schmitt-kopplin@helmholtz-muenchen.de
[2] Université de Haute Alsace, Lab. GSEC, France
[3] Uniersity of Montana, Missoula, USA
[4] University of California, Irvine, USA
[4] Linköping university, Linköping, Sweden
[6] Université de Bourgogne, Institut Jules Guyot, France

Natural organic matter (NOM) occurs in soils, freshwater, marine and hydrothermal environments, in the atmosphere and represents an exceedingly complex mixture of organic compounds that collectively exhibits a nearly continuous range of properties (size-reactivity continuum). The fate NOM in the bio- and geosphere is governed according to the rather fundamental restraints of thermodynamics and kinetics. In these intricate materials, the "classical" signatures of the (geogenic or ultimately biogenic) precursor molecules, like lipids, glycans, proteins and natural products have been attenuated, often beyond recognition, during a succession of biotic and abiotic (e.g. photo- and redox chemistry) reactions. NOM incorporates the hugely disparate characteristics of abiotic and biotic complexity.

Numerous descriptions of organic molecules present in organic chondrites (COM) have improved our understanding of the early interstellar chemistry that operated at or just before the birth of our solar system. However, all molecular analyses were so far targeted toward selected classes of compounds with a particular emphasis on biologically active components in the context of prebiotic chemistry. Here we demonstrate that a non-targeted molecular analysis of the solvent-accessible organic fraction of Murchison extracted under mild conditions allows one to extend its indigenous chemical diversity to tens of thousands of different molecular compositions and likely millions of diverse structures. This molecular complexity, which provides hints on heteroatoms chronological assembly, suggests that the extraterrestrial chemodiversity is high compared to terrestrial relevant biological and biogeochemical-driven chemical space.

(ultra)High resolution analytical approaches will be presented in their application to unravel the chemical nature and organic signatures in biosystems [1], geosystems [2-4] with a focus on extreme environments such as hydrothermal and meteoritic origins [5] with a special focus on sulphur organic compounds.

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[4] Schmitt-Kopplin *et al.* (2011) Biogeosciences Discuss. **8**, 11767-11793.
[5] Schmitt-Kopplin *et al* (2010) *PNAS* **107(7)**, 2763-2768.