

Origin of N isotopic anomalies in meteoritic and cometary organic matter

JÉRÔME ALÉON

CSNSM, CNRS/IN2P3/U. Paris Sud. Bat. 104, 91405 Orsay
Campus, France. (Jerome.Aleon@csnsm.in2p3.fr)

Organic molecules in meteorites and comets display a large range of nitrogen isotopic variations of unclear origin. It is widely assumed that ^{15}N excesses trace an interstellar-like chemistry in a cold dense medium, mostly by analogy with deuterium chemistry [e.g. 1]. However, chemical models face difficulties in achieving the level of ^{15}N enrichment relative to the ambient interstellar/protosolar gas observed in meteorites and the relationship between ^{15}N and D excesses remains obscure [2,3]. Here I present isotopic fractionation calculations coupled with mixing calculations aiming at reproducing the observed distribution of ^{15}N and D excesses in acid insoluble organic matter from carbonaceous and ordinary chondrites, in subgrains nicknamed hotspots and nanoglobules, as well as in interplanetary dust particles, samples from comet Wild 2 returned by the Stardust mission and in HCN from comet Hale-Bopp. I show that the N-H isotopic compositions in these samples can be explained by a mixture of three components : (1) a late isotopic exchange with a ^{15}N -D-rich gas produced by ion-molecule reactions, possibly in the solar protoplanetary disk (PPD), (2) a D-poor, ^{15}N -rich component best preserved in the Isheyevo chondrite of abundance anti-correlated with meteoritic age, indicating a late origin in the solar PPD and (3) a minor D-rich ^{15}N -poor component of likely presolar origin, best preserved in ordinary chondrites. The anti-correlation between ^{15}N excesses and meteoritic age extends to bulk isotopic composition and differentiated objects suggesting a general trend of increasing $^{15}\text{N}/^{14}\text{N}$ ratio in organic molecules as the solar PPD ages and clears.

- [1] Busemann *et al.* (2006) *Science* **312**, 727-730 [2] Rodgers and Charnley (2008) *Mon. Not. R. Astron. Soc.* **385**, L48-L52.
[3] Briani *et al.* (2009) *P. Natl. Acad. Sci.* **106**, 10522-10527.

Spectroscopic characterization of U(IV)-biomass complexes

DANIEL S. ALESSI¹, JUAN S. LEZAMA-PACHECO²,
JOANNE E. STUBBS³, MARCUS JANOUSCH⁴,
PER PERSSON⁵, JOHN R. BARGAR² AND
RIZLAN BERNIER-LATMANI¹

¹Ecole Polytechnique Fédérale de Lausanne, EPFL,
Switzerland, (daniel.alessi@epfl.ch)

²Stanford Synchrotron Radiation Lightsource, Menlo Park, CA
94025, USA

³Consortium for Advanced Radiation Sources, University of
Chicago, Chicago, IL 60637, USA

⁴Swiss Light Source, Paul Scherrer Institute, Switzerland

⁵Department of Chemistry, Umeå University, Sweden

Uranium contamination in the subsurface is an enduring problem throughout Europe and North America. Current strategies for the remediation of uranium aim at transforming the soluble and mobile oxidized form of uranium, U(VI), to the reduced and relatively immobile form, U(IV). Until recently, reduction of U(VI) to U(IV) was assumed to produce solely the sparingly soluble mineral uraninite, $\text{UO}_2(\text{s})$. However, recent research reveals that other species of U(IV), referred to here as 'monomeric U(IV),' can form as the product of microbial U(VI) reduction. Because monomeric U(IV) lacks the crystalline structure of uraninite, it is likely to be more labile and susceptible to reoxidation. For this reason, geochemical models that assume $\text{UO}_2(\text{s})$ as the sole product of U(VI) reduction may not capture the true system behavior.

Here we use infrared spectroscopy (IR), uranium L_{III} -edge X-ray absorption spectroscopy (XAS), and phosphorus K-edge XAS analyses to determine the binding environment of monomeric U(IV) associated with *Shewanella oneidensis* MR-1 bacterial cells. Several systems were tested as a function of pH, including: cells without uranium, cells with adsorbed U(VI), cells that produced monomeric U(IV) and cells that produced uraninite as a product of U(VI) reduction. Uranium XAS analyses confirmed the reduction of U(VI) to U(IV) in U(IV)-containing systems, and the presence of either monomeric U(IV) or $\text{UO}_2(\text{s})$ was confirmed by extended X-ray absorption fine structure (EXAFS). IR analyses revealed a strong coordination of U(IV) with phosphate groups in the monomeric U(IV) systems -coordination not seen in the other systems. The P EXAFS results provide further evidence of U(IV)-phosphate coordination in monomeric U(IV) when compared to an abiotic U(IV)-phosphate reference. The results of this study provide valuable insights into the binding environment of the monomeric U(IV) species associated with microbial biomass and reaffirm the conjecture that phosphate coordination is critical in the formation of the species.