

Atomistic approaches to determine redox reaction mechanisms of U, Np, and Pu on mineral surfaces

U. BECKER, L. SHULLER, D. RENOCK AND R. EWING

University of Michigan, Department of Geological Sciences,
2534 CC Little, Ann Arbor, MI 48109

The rich redox chemistries of U, Np, and Pu control the chemical and physical properties of nuclear materials at different stages in the nuclear fuel cycle from extraction to disposal. The redox chemistry of the actinides can be predicted based on the Eh-pH conditions; however, adsorption to mineral surfaces and redox reactions on the surface are impacted by the physicochemical properties of the mineral surface itself.

In recent studies, our research groups as well as others have been challenging the traditional way redox processes are being treated in the near-surface environment. One example that has been studied is the complicated interplay between uranyl complexes, sulfide/oxide surfaces, and organic and inorganic reductants. Our findings indicate that, despite many decades of research, the key controls of surface-mediated mechanisms and, hence, the rates of environmentally-important redox processes are still poorly understood. There are a number of reasons for this: 1) these processes almost always involve a complex series of elementary reactions, each involving the transfer of one electron at a time, 2) it can be unwieldy to resolve the influence of individual environmental parameters (pH, pe, pO₂, concentration of other oxidants and reductants, other ions in solution, temperature, etc.) in rate experiments, 3) it can be challenging to differentiate rate constants for heterogeneous (surface) processes and homogeneous (solution) processes in order to assess the catalytic effects of the surface itself, and 4) rate-limiting processes such as spin transitions have been widely ignored so far. Our calculations address fundamental questions with regard to many different redox systems: Does the mineral surface directly participate in the redox event or indirectly participate by acting as a heterogeneous catalyst or an electron shuttling device for the transport of charge (and/or spin) between co-adsorbates.

Methane formation in abandoned coal mines: Role of acetogens and acetoclastic *Methanosarcinales*

S. BECKMANN^{1*}, T. LÜDERS², M. KRÜGER³,
F. VON NETZER², B. ENGELEN¹ AND H. CYPIONKA¹

¹ICBM, Univ. of Oldenburg, Oldenburg D-26129, Germany

(*correspondence: s.beckmann@icbm.de)

²IGOE, Helmholtz Zentrum Munich, D-85764, Germany

³BGR, Geomicrobiology, Hannover D-30655, Germany

Mine gas has come into the focus of the power industry and is being used increasingly for heat and power production. Worldwide, about 7% of the annual methane emissions originate from coal mining. In abandoned coal mines, stable carbon and hydrogen isotopic signatures of methane indicate a mixed thermogenic and biogenic origin. While thermogenic methane is a remainder of geological processes, biogenic formation is still going on [1]. Besides hard coal, possible sources for methane are large amounts of mine timber left behind after the end of mining.

In two abandoned coal mines in Germany, methanogenic archaea are responsible for the production of substantial amounts of methane [2]. The mines are characterised by low O₂ concentrations at high humidity and fungal mats mainly on the mine timber. We analysed active methanogens as well as the active bacteria involved in the trophic network by stable isotope probing (DNA-SIP). Therefore, the ¹³C-labeled precursors of methane (acetate and H₂+CO₂) were fed to liquid cultures from hard coal and mine timber. Directed by the methane production kinetics, samples for DNA-SIP coupled to subsequent quantitative PCR and DGGE analyses were taken from long term incubations over 6 months. Surprisingly, the formation of ¹³C-methane was linked to acetoclastic methanogenesis in both, the ¹³C-acetate and H₂+¹³CO₂-amended cultures of coal and timber. H₂+¹³CO₂ was mainly used by acetogens related to *Pelobacter acetylenicus* and *Clostridium* species. Active methanogens, closely affiliated to *Methanosarcina barkeri*, utilized the readily available acetate rather than the thermodynamically more favourable hydrogen. Thus, the methanogenic microbial community appears highly adapted to the environment where acetate is a much more prominent intermediate than H₂.

[1] Thielemann *et al.* (2004) *Organic Geochemistry* **35**, 1537-1549. [1] Krüger *et al.* (2008) *Geomicrobiology Journal* **25**, 315-321. [2] Beckmann *et al.* (2011) *Geomicrobiology Journal* **28**(4). [3] Beckmann *et al.* (2011) *Applied and Environmental Microbiology* doi:10.1128/AEM.02818-10.