

Hydrogeologic controls on microbial methanogenesis in shales and coalbeds in the Illinois Basin

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Economic accumulations of biogenic gas in the deep subsurface have recently been recognized as an unconventional semi-renewable energy source. Methane is generated as microbes reduce carbon dioxide and ferment organic acids (primarily acetate) sourced from organic-rich substrates, such as the Upper Devonian New Albany Shale (~1500m deep) and Pennsylvanian coal beds (~160m deep) in the Illinois Basin. The occurrence of biogenic methane in different geologic units of variable age, depth and depositional environments provide the unique opportunity to investigate hydrologic controls on methanogenesis. We hypothesize that although CO₂ reduction is dominant in both the shales and coals, acetate fermentation is favored in shallow coal zones near recharge areas where rapid infiltration of modern groundwaters transports nutrients and maintains low salinity concentrations. This hypothesis is investigated using recent groundwater sampling results for solute chemistry, water and gas stable isotopes, microbial studies, and carbon-14. Carbon isotope values of CO₂ and CH₄ show that CO₂ reduction is the dominant methanogenic pathway in coals and shales, though in select locations of low chloride concentrations (up to 3.5 mM) within shallow (~120m) coalbeds, acetate fermentation is apparent. However, deuterium isotope values of CH₄ and H₂O show exclusively CO₂ reduction. The density of microbial cells (8.69E03 to 3.26E06 cells/mL of formation water) suggests that both substrates are supporting comparable amounts of microbial activity, however subsequent molecular biology analyses may enable the characterization of the shale and coalbed microbial communities to differentiate between dominant metabolic processes. Carbon-14 ages indicate that younger groundwaters have lower salinity concentrations and correspond to higher amounts of organic substrate degradation, suggesting a link between groundwater residence times (or velocities) and methanogenesis.

Mechanisms of U(VI) retention on montmorillonite and hectorite

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Introduction

Al- and Mg-smectites can retain significant amounts of U(VI) in soils, sediments, or glass weathered layers, and this sorption property can control the fate of this element in nuclear waste repositories. Possible retention mechanisms vary as a function of solution physico-chemical conditions, but also of the sorbate crystallochemistry. This study shows how distinct mechanisms can be observed for U(VI) sorption on montmorillonite and hectorite under similar conditions.

Materials and methods

Suspensions of purified clay minerals (2 g/L hectorite or montmorillonite) were reacted in 0.5 M NaCl at pH 7.17 (hectorite) and 6.61 (montmorillonite) with 10 and 15 μM U(VI), respectively. Self-supporting films of reacted clay minerals were obtained by draining suspension aliquots on cellulose nitrate filters. Uranium L₃-edge Polarized EXAFS (P-EXAFS) spectra of the self-supporting films were collected in fluorescence mode on the FAME beamline (ESRF, France). P-EXAFS data were reduced, and analyzed using standard procedures.

Results and interpretation

Angular dependence of EXAFS spectra was observed for U(VI)-sorbed hectorite, but not montmorillonite. Sorbed U(VI) retained the uranyl conformation for both sorbates, with O_{yl} at 1.79 and 1.82 Å on montmorillonite and hectorite, respectively. The equatorial O_{eq} shell was split in two subshells at 2.29 and 2.47 Å for montmorillonite, and 2.35 and 2.53 Å for hectorite, ruling out fully hydrated UO₂²⁺(aq). On montmorillonite, U(VI) was surrounded by ~0.5 Al/Si at 3.30 Å. This shell and the negligible angular dependence point to the formation of edge surface complexes, in line with previous studies [1, 2]. In contrast, for U(VI) on hectorite, only ~0.2 Mg/Si near 3.2 Å could be modelled, and no EXAFS contribution was observed beyond 3.6 Å. This, and the significant spectral anisotropy suggest that U(VI) either sorbs to hectorite tetrahedral sheets, or forms poorly ordered planar oligomers bound to the hectorite surface (basal planes or edge sites).

[1] J.G. Catalano and G.E. Brown. *Geochim. Cosmochim. Acta* **69**, 2995-3005 (2005). [2] C. Hennig, T. Reich, *et al. Radiochim. Acta* **90**, 653-657 (2002).