

Nanoscale study of the mineralogical and geochemical evolution of black shales with increasing maturity

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Gaseous hydrocarbon generation processes occur within gas shales as a response to increases in thermal maturation. While efforts have been directed at unravelling the resource potential of these unconventional systems [1], their spatial variability in chemistry and structure is still poorly understood at the sub-micrometer scale. For instance, intra-particle nanoporosity has been documented within overmature gas shale samples but has not yet been attributed to any specific organic macromolecule [2]. Here, we have characterized samples of the Lower Toarcian Posidonia Shale from northern Germany at varying stages of thermal maturation using a combination of compositional organic geochemistry and spectromicroscopy techniques, including synchrotron-based scanning transmission X-ray microscopy (STXM). We document geochemical and mineralogical heterogeneities down to the nanometer scale within the investigated samples at all levels of thermal maturity [3,4].

In particular, authigenic albite crystals containing nanometric halite inclusions have been documented within the investigated mature and overmature samples. The presence of such tracers of palaeobrine-carbonate interactions supports a maturation scenario for the Lower Toarcian Posidonia Shale intimately related to ascending brine fluids. In addition, various types of asphaltene- and NSO-rich bitumen have been detected within the same samples, very likely genetically derived from thermally degraded organic precursors. Furthermore, the organic macromolecules displaying intra-particle nanoporosity have been identified as pyrobitumen residues, such nanoporosity likely resulting from the formation of gaseous hydrocarbons. By providing *in situ* insights into the fate of bitumen and pyrobitumen as a response to the thermal evolution of the macromolecular structure of kerogen, the results reported here constitute an important step towards better constraining hydrocarbon generation processes during natural gas shale maturation.

[1] Jarvie *et al.* (2007), *AAPG* **91**, 475-499. [2] Loucks *et al.* (2009), *J. Sediment. Res.* **79**, 848-861. [3] Bernard *et al.* (2010), *Chemie der Erde - Geochemistry* **70(S3)**, 119-133. [4] Bernard *et al.*, *Marine and Petroleum Geology*, in review.

Does the electron transfer process determine the product of U(VI) reduction?

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The bioremediation of uranium-contaminated sites is based on the amendment of an electron donor to stimulate microbial activity. Typically, Fe(III) and U(VI) serve as electron acceptors for microorganisms with the former supporting microbial growth. However, this biostimulation process may generate competing mechanisms of uranium bioreduction. While direct enzymatic reduction of U(VI) by microbes is a possible route of immobilization of U(IV), Fe(II) produced by the reduction of Fe(III) also is thermodynamically capable of abiotically reducing U(VI).

Here we investigate the question of whether different U(IV) products are expected from these various U(VI) reduction processes. Specifically, we consider the reduction of U(VI) via direct enzymatic reduction by both Gram-positive and Gram-negative bacteria, via abiotic reduction by Fe(II)-bearing minerals as well as through a potential combination of these direct and indirect processes in sediment columns.

The results indicate that geochemical conditions dictate the product of U(VI) reduction. For example, the same microorganism produced a monomeric sorbed U(IV) complex in the presence of particular solutes but nanoparticles of the mineral uraninite in their absence. A phosphate-reacted magnetite (Fe₃O₄) suspension produced a similar monomeric U(IV) product while unreacted magnetite produced uraninite. Finally, in studying U(VI) reduction in sediments, both laboratory and field-run columns yielded non-uraninite U(IV), suggesting that *in situ* geochemical conditions favor monomeric U(IV) formation.

This work shows that, while the kinetics of U(VI) reduction have been shown to depend on the reduction mechanism, the end-product of the reduction is largely determined by the geochemical conditions under which the reduction—biotic or abiotic—takes place.