Deciphering the transformation of nitrogen in sedimentary rocks during natural and artificial maturation

C.J. ILLING[1,2] AND C. OSTERTAG-HENNING[1]*

[1]Bundesanstalt für Geowissenschaften und Rohstoffe,
Stilleweg 2, D-30655 Hannover, Germany
(*correspondence: Christian.Ostertag-Henning@bgr.de)
[2]present address: Westfälische Wilhelms-Universität - Institut für Geologie und Paläontologie, Corenstr. 24, D-48149 Münster, Germany (c.illing@uni-muenster.de)

A sequential extraction method for different nitrogen (N) forms in sedimentary rock samples was established. The method differentiates between exchangeable NH_4^+, N in the bitumen, HCl-hydrolysable N (amino-N in kerogen and N in clay minerals), kerogen bound N and N fixed in feldspars and other stable minerals. Using this method a natural maturity series of marine shales (Posidonia Shale, Hils Syncline, NW Germany), covering the maturity range immature to early gas window and a series of Carboniferous coals of different maturities from the early oil window into the gas window (Ruhr area, W Germany) was investigated.

For the Posidonia Shale sample set a significant decrease of the total nitrogen content from 5500 to 3500 ppm is evident during maturation. This loss of nitrogen is accompanied by a transformation of nitrogen between the different N pools in the sedimentary rock: The amount of exchangeable NH_4^+ increases up to the peak oil stage, the amount of bitumen-bound nitrogen is very low and slightly descreasing with maturity, the hydrolysable N is increasing with maturity with a plateau from the peak oil stage on, and the kerogen N is significantly decreasing – most rapidly in the early oil window. The overall transformation and expulsion of N was modelled.

Based on these results, two major processes are identified and quantified: (1) release of nitrogen from the kerogen as either organic N compounds or ammonium, which might be adsorbed and later on fixed into the (clay) mineral matrix. (2) a release of ammonium at higher maturities or under changed fluid compositions out of the mineral matrix during metamorphism.

Artificial maturation experiments, conducted in sealed gold capsules, on those sample sets verify the interpretation based on the natural maturation series.

Incorporation of uranium by oxides and phyllosilicates: Effects on redox and retention

EUGENE S. ILTON*, SEBASTIEN N. KERISIT
AND ANDREW R. FELMY

Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99352, USA
(*correspondence: eugene.ilton@pnl.gov)

U (VI) transport in the environment can be attenuated by a variety of mechanisms including precipitation, adsorption, occlusion and structural incorporation in minerals, and reduction to sparingly soluble U (IV). In this talk, we will present results of experiments and molecular simulations that indicate the importance of structural incorporation on the redox and retention behavior of U. Examples will include both reductive and redox inert oxides, and micas. For example, it will be shown that the diffusion of U (VI) into the interlayer region of ferrous micas results in reduction and enhanced resistence to subsequent oxidation. Further, both the type and concentration of alkali cation in solution can strongly affect the extent of reduction as well as the proportion of U (VI), U (V), and U (IV). In the case of magnetite, incorporation of U into secondary phases appears to inhibit reduction of U (VI) to U (IV), with stabilization of U (V) occurring instead. Such observations may be limited to conditions where the initial pH is low with consequent dissolution and precipitation of Fe and U phases as pH increases. We will also present preliminary molecular modeling results on potential coordination environments for U (IV), U (V), and U (VI) in such secondary phases, and relate the data to issues concerning the relative stability of the different oxidation states.

Funding provided by DoE-OBES Geosciences.