

Precipitation Kinetics of Uranium by Sedimentary Organic Matter under Diagenetic and Hydrothermal Conditions

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Abstract

The reduction kinetics of uranyl cations to uraninite in aqueous solution by two lignites with different maturities were experimentally determined under diagenetic or hydrothermal conditions (180°–200°C). Both the uranyl reduction and lignite dehydrogenation reactions observed confirm previous mechanistic hypotheses (Nakashima et al., 1984, 1987; Nakashima, 1992a, b). Reduction is a first-order reaction with respect to uranyl cation and organic substrate. For both of the reactions studied, reduction and dehydrogenation, the activation energies measured in experiments using two different lignites were within experimental error. These values are 115 ± 15 kJ/mol for uranyl reduction, and 59 ± 13 kJ/mol for lignite dehydrogenation. Estimates of the half-lives of U in aqueous solutions have been completed based on the kinetic parameters by assuming that the rate-determining step is uranyl reduction to uraninite. The results suggest a rough time-scale range of U deposition rates with large uncertainties on the pre-exponential factor. The half-life of U precipitation is estimated to be on the order of 3 h to 1 yr under modest thermal conditions (200°–100°C), 340 yr for radioactive waste repositories (50°C), and 104 to 105 yr at the Earth's surface (25°–4°C).