



Isotopic and Experimental Constraints on Subsurface U Transport and Fate

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U- and Th- series nuclides have provided essential tools for studying weathering and subsurface element transport processes. The radionuclides U, Th, Ra, Rn, and Pb have a range of half-lives and contrasting chemical behaviours, and the isotopic decay systematics that connect the different isotopes can be used to quantify the rates of trace element transport and the extents of interaction with the aquifer rocks. This can often be linked to rates of soil formation, chemical and mechanical weathering of watersheds, and potentially, subsurface water flow rates. However, this requires a comprehensive understanding of the mechanisms controlling the behaviour of each element.

Data from the unconfined Mojave River Basin aquifer, with a reasonably well-defined flow pattern and ground-water ages of up to 40,000 years illustrates the response of the U/Th series nuclides to extended water- rock interaction. Measurements of 222Rn find relatively uniform rates of Rn recoil ejection by decay of parent 226Ra throughout the aquifer. If the ratio of recoil rates $222\text{Rn}/234\text{Th}=1$, then the rate of release of 234Th, which rapidly decays to 234U, can be obtained. This therefore defines the input of 234U, which is expected to increase with groundwater age, regardless of the extent of reversible adsorption. Although 234U is also released by weathering, the amount of recoil-derived 'excess' 234U is obtained directly from 234U/238U ratios. Measured excess 234U concentrations are actually relatively constant and up to 104 times lower than calculated. The simplest explanations are that one of the basic assumptions widely used to interpret U behavior is invalid, and either the release of 222Rn is by mechanisms that do not apply to other nuclides and so the 234Th recoil rate is up to 104 times less, or U is irreversibly removed even from oxic groundwaters.

To address the first possibility, we have made the first direct laboratory measurements of recoil of both 222Rn and 234Th from mineral separates and bulk Mojave aquifer materials. Radon concentrations in solutions in contact with samples within sealed containers were used to determine 222Rn recoil rates. Determining the concentration of recoiled 234Th required both keeping Th in solution (using EDTA solutions), and limiting leaching of U and Th (by freezing the solution). Consistent relative recoil rates of 222Rn/234Th of 6-8 were found, which are maxima due to likely adsorptive Th losses. Nonetheless, it is clear that measured 222Rn concentrations can be used to determine the rates of U release. In the Mojave, these values indicate that 234Th recoil in the Mojave aquifer will still generate 103 higher 234U concentrations than observed, requiring irreversible U removal.

A possibility for removal of U from oxic groundwater is the reduction of soluble U(VI) to relatively insoluble U(IV) by reduced Fe in clay minerals. A series of experiments were conducted with four different standard clay minerals (smectite SWy-2, nontronite NAu-1, Fe-rich chlorite CCa-2 and illite IMt-1) to study U adsorption and desorption under oxygen-free and CO₂-free conditions and under a range of solution pH of 4.0 - 7. A general trend of increased adsorption at higher pH values was observed. Clays with a smectite structure (SWy-2 and NAu-1) showed different U adsorption and desorption behaviour depending on whether the structural Fe in the clay mineral was reduced or oxidized prior to U adsorption. 95-100% of total U was adsorbed onto reduced clay particles within several hours whereas only 20-80% (depending on pH) of total U was adsorbed onto oxidized clay particles over 30 days. Desorption experiments were conducted by adjusting the solution pH to 2.6. About 90% of adsorbed U was released into solution within a few hours from oxidized clay particles (SWy-2 and NAu-1)

whereas almost 100% of U remained adsorbed onto reduced smectite SWy-2 and 90-65% remained adsorbed onto reduced nontronite NAu-1 even after 7-8 days at low pH. This provides strong evidence that the structural Fe(II) of clay minerals acts as an efficient reductant for adsorbed U(VI) reducing it to immobile and non-exchangeable U(IV).

Overall, these results indicate that although U is highly soluble in oxic environments, interactions with Fe-bearing clays can substantially limit its mobility. Combined measurements of Rn and U isotopes can still be used to quantify the rates of U removal in the subsurface, although widely used transport models must be modified to incorporate this removal mechanism.