Iron dissolution kinetics in mineral dust under more realistic aerosol conditions: Re-considering pH scale

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Iron (Fe) is a micronutrient that mediates the primary productivity in the global ocean. A significant source of such Fe in the surface ocean is from dust. It is therefore important to quantify the flux of bioavailable Fe from dust, which is strongly dependent on Fe solubility. Fe in dust is mostly insoluble, but such Fe may become soluble after reacting with acidic species during transport. In the last 20 years, many laboratory studies have been conducted to measure the dissolution kinetics of Fe in dust at pH from 1 to 5. It is now known that clouds may actually decrease Fe solubility because of its higher pH, e.g., >4. In contrast, aerosol water can be more acidic but more complicated in composition. However, most of the previous lab studies were conducted under much simplified conditions compared to those in aerosol water. These results, when applied, could lead to large bias in global models. In this work, I measured Fe dissolution kinetics in dust under conditions closer to aerosol water.

The results showed that at the same [H^+] concentration at (1 g dust L^{-1} solution), (i) $(NH_4)_2SO_4$ at 1 mol L^{-1} slows down Fe dissolution; and (ii) NH_4Cl at 1 mol L^{-1} accelerates the Fe dissolution in dust. Based on these results, I propose to use an effective pH scale for simulating Fe dissolution kinetics in aged dust in models. This pH scale considers the activity of H^+ ion and [HSO_4^+], both of which can be predicted by the AIM thermodynamic model (http://www.aim.env.uea.ac.uk/aim/aim.php).

In addition, oxalate (0.03 M $Na_2C_2O_4$) significantly accelerates the dissolution of Fe in dust (1 g dust L^{-1} solution, 0.1 N H_2SO_4 or 0.01 N H_2SO_4, and 1 M $(NH_4)_2SO_4$).

Changes in $^{238}U/^{235}U$ associated with reductive immobilization of uranium in groundwater

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The prevalence of groundwater contamination associated with uranium (U) mining and milling activities has driven the need for the development of effective and economically feasible remediation strategies. U is mobile in its oxidized state, U(VI), but immobile and much less toxic in its reduced state, U(IV). Thus, U(VI) reduction to U(IV) is proposed as a remediation strategy for U contaminated groundwaters. The former U mill site in Rifle, Colorado (USA) hosts experiments that investigate the rates and mechanisms of targeted U immobilization techniques. Our research focuses on the development of $^{238}U/^{235}U$ (discussed as $\delta^{238}U$) as a tool for evaluating immobilization in the subsurface.

U concentrations and $^{238}U/^{235}U$ values have been monitored over the course of three field experiments at the Rifle, CO field site in 2010–11, 2011–12 and 2012–13. These experiments examined changes in U concentrations and $^{238}U/^{235}U$ values associated with biostimulation, desorption and re-oxidation. Large variations accompany acetate-induced biostimulation under both iron reducing and sulfate reducing conditions. In both casees, ^{238}U is preferentialy reduced to U(IV), leaving the remaining groundwater U(VI) relatively isotopically light ($\Delta^{238}U = -1.3$ and -1.9‰, respectively). Changes in $^{238}U/^{235}U$ accompany changes in the U concentration (dropping from ~150–200 ppb U prior to the acetate injection to ~10 ppb U). During the post-injection phase, as concentrations rebounded, absence of $^{238}U/^{235}U$ greater than pre-injection values implies the primary source of U is advection of U(VI), rather than re-oxidation of U(IV). Bicarbonate-induced desorption, which led to a doubling in the U concentration, has been demonstrated to result in no significant U isotopic fractionation [1].

Our research demonstrates the potential for $^{238}U/^{235}U$ to detect U reductive immobilization in the subsurface and to distinguish between removal by this process and relatively temporary processes such as sorption. U isotopes join the growing number of heavy stable isotopes with demonstrated potential for use in environmental monitoring.

[1] Shiel *et al.* (2013) *Environ. Sci. Technol.* **47**, 2535–2541.

DOI:10.1180/minmag.2013.077.5.19