

## Uranium isotope fractionation associated with biostimulation experiments at the Old Rifle mill site

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Microbial and geochemical factors controlling subsurface U mobility are evaluated in the U contaminated aquifer at the former U mill site in Rifle, CO USA. Biotic reduction of U(VI) is induced by the injection of acetate (electron donor) into the contaminated aquifer and is used to immobilize U as U(IV). Experimental plots consist of monitoring wells both upgradient and downgradient of an injection gallery. The 2010–11 experiment (Plot C) was designed to isolate the impacts of reduction and sorption processes. Previous work has shown large shifts in  $^{238}\text{U}/^{235}\text{U}$  (hereafter discussed as  $\delta^{238}\text{U}$ ) accompany U(VI) bioreduction ( $\Delta^{238}\text{U} = 1.05\%$ ) [1]. We provide the results of a more detailed study to increase confidence in the use of  $\delta^{238}\text{U}$  as an indicator of U(VI) reduction and seek to apply this method to bioremediation experiments in which groundwaters are treated with acetate only or both acetate and bicarbonate (desorbs U from aquifer solids). In addition, this data set gives us, for the first time,  $\delta^{238}\text{U}$  measurements during rebound of U(VI) concentrations as reduction wanes. This is particularly important as the long-term success of this remediation technique depends on the stability of sequestered U(IV).

We present groundwater U(VI) concentration and  $\delta^{238}\text{U}$  results for two wells downgradient of the injection gallery; one of the wells (CD-01) was amended with acetate and the other (CD-14) with both acetate and bicarbonate. Preinjection values for the two wells are identical to those upgradient, within the uncertainties. For CD-01, the acetate injection upgradient led to a dramatic drop in [U(VI)] (from 165 to 10.6 ppb) and  $\delta^{238}\text{U}$  (from 0.03 to -1.32‰), resulting from the preferential removal of  $^{238}\text{U}$  as reduced U(IV). An excursion to greater  $\delta^{238}\text{U}$  values during the period when [U(VI)] was at a minimum may be related to a contribution of relatively heavy U from nano-colloidal U(IV) in the filtered groundwater. After the amendment ceased, the groundwater [U(VI)] and  $\delta^{238}\text{U}$  returned to approximately preinjection values. Lack of an increase of  $\delta^{238}\text{U}$  above preinjection values is consistent with advection of U(VI) from upgradient, rather than reoxidation of U(IV), as the primary source.

For CD-14, a large increase in the [U(VI)] was induced by the bicarbonate injection (up to 415 ppb), while no change was observed in  $\delta^{238}\text{U}$ . This is in agreement with previous Rifle field experiments that revealed the absence of significant U isotope fractionation with adsorption-desorption of U(VI) [2]. The acetate injection led to a dramatic decrease in the [U(VI)] and  $\delta^{238}\text{U}$  values (to 15 ppb and -1.19‰). The recovery of [U(VI)] and  $\delta^{238}\text{U}$  is much slower for CD-14. Despite the return of [U(VI)] to preinjection values by the end of the field season, sustained U isotope fractionation (-0.43‰) is observed.

[1] Bopp *et al.* (2010) *Environ. Sci. Technol.* **44**, 5927–5933. [2] Laubach *et al.* (2010) *GSA Abstracts with Programs* **42**, 231.

## Dissolved rhenium and molybdenum in rivers

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Various workers have reported dissolved concentrations of Re and Mo in rivers and have generally concluded that sulfide weathering is the dominant source of these elements. This is based both on the well-known association of these elements with Black Shales as well as correlation with fluvial sulfate. We have examined the dissolved concentrations of Re and Mo in the Yukon River Basin in Alaska, the Loch Vale watershed, the lower Mississippi River, and the East Pearl River (Miss.). We find that fluvial sulfate correlates nearly 1:1 with estimates of non-carbonate calcium, suggesting that the fluvial Re- and Mo-sulfate correlations are not necessarily conclusive of a sulfide source. We also observe significant seasonal variability of Mo and sometimes Re in some rivers, suggestive of seasonal redox effects on element mobilization and transport.