Highly Depleted Gypsum Veins at the Rifle Site Attributed To Multiple Episodes Of Redox Cycling

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The Department of Energy's Old Rifle site is a former uranium mill site situated along a floodplain of the Colorado River in western Colorado. The aquifer underlying the site consists of 6-7 m of Quaternary alluvium overlying the Tertiary Wasatch Formation. Sulfate concentrations in Old Rifle groundwater are elevated (8-10 mM), with unusually low sulfur isotope ratios ($\delta^{34}S$ values from -6‰ to -10‰). Further, higher groundwater uranium concentrations in shallow groundwater at the Old Rifle site are correlated with the higher groundwater sulfate concentrations and lower $\delta^{34}S$ values. To determine the source of the sulfate and its relationship to uranium mobility, we have analyzed the $\delta^{34}S$ values of sulfate minerals found in rock outcrops around the site.

The source of the low $\delta^{34}S$ sulfate in groundwater appears to be gypsum veins within the Wasatch Formation, which outcrops the north and west of the Old Rifle floodplain. Veins of gypsum sampled from outcrops of the upper Wasatch have $\delta^{34}S$ values lower than any previously reported in the literature (as low as -56‰). These veins are located in high permeability shear zones and are associated with secondary Fe-hydroxide minerals including visible iron staining. Fossilized plant material found in several of the shear zones is believed to have created localized reducing zones leading to precipitation of Fe-sulfide minerals from groundwater sulfate. Biologic reduction of sulfate produces a large negative shift in the $\delta^{34}S$ value of the resultant sulfide. After the reducing potential of the organic matter was exhausted, the system converted to oxidizing conditions producing low $\delta^{34}S$ sulfate and Fe oxides from the sulfides, leading to the formation of the gypsum veins. Low $\delta^{34}S$ secondary hydrous Na and Mg sulfate minerals precipitating at active groundwater seeps from outcrops of the Wasatch indicate that this is an on-going process.

Modern analogues of these naturally reduced zones have been found in the Old Rifle groundwater. These reduced zones are characterized by lignitic organic carbon containing abundant framboidal pyrites with $\delta^{34}S$ values as low as -70‰ (Ravi Kukkadapu, Personal Communication). Associated with these pyrites are greatly elevated concentrations of uranium (Qafoku et al., 2009). Oxidation of these reduced zones would lead to mobilization of reduced metals, including uranium, which may explain the high background concentrations of metals in the Rifle groundwater outside of the tailings-impacted area.

[1] Qafoku et al. (2009) Environmental Science & Technology 43, 8528-8534.