Extensive denitrification in the subsurface of the Oak Ridge Site, Tennessee

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The operation of a waste disposal facility on the Oak Ridge Reservation in East Tennessee has resulted in extensive subsurface contamination. Groundwater is highly contaminated near the source with U (>60 ppm), Tc (>40,000 pCi/L), nitrate (up to 40,000 ppm), and acidity (pH range of 3 to 7). Due to high groundwater nitrate concentrations at this site, nitrate is often the most abundant electron acceptor available for microbial growth in the subsurface, and denitrifying bacteria have been shown to predominate over the microbial communities. Significant quantities of gases (CO_2, CO, H_2 and CH_4) indicative of microbial activity were also detected in groundwater, including high concentrations of N_2O (up to 4% of gases) and excess N_2.

The dissolved nitrates are intimately linked to the fate of uranimum contamination via redox cycles. To quantify the relative roles of dilution, assimilatory uptake, and denitrification as mechanisms of nitrate attenuationan, an integrated hydrobiogeochemical study was conducted. The fate of nitrate and denitrification products (N_2O and N_2) were investigated by means of mass-balance and stable isotope techniques. The degree of denitrification is up to 13% or greater, and systematic variations in $\delta^{15}N$ were observed (NO_3>N_2O>excess N_2) with decreasing concentrations of dissolved nitrates. Large negative isotope fractionations were calculated during denitrification: -30's and -40's of ‰ for $\delta^{15}N$ and $\delta^{18}O$, respectively. Large isotopic variations of the intermediate N_2O, including site-specific $\delta^{15}N$ fractionation, also provide insights into extensive denitrification processes of dissolved nitrate in groundwater at the site.

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Isotopic fractionation of cadmium into calcite

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Isotopic analyses of dissolved Cd (cadmium) in surface seawater have recently shown great potential as a new proxy for disentangling phytoplankton Cd (and by inference 'nutrient') utilization from abiotic processes, such as ocean mixing. Extending this information into the past requires the signal to be captured and faithfully preserved in a suitable sedimentary archive. However, the importance of environmental factors and the controls they may have on Cd isotopic fractionation into such archives, particularly calcite, remain poorly understood.

To this end, we performed controlled inorganic $CaCO_3$ precipitation experiments in artificial seawater solutions to understand such environmental controls. We precipitated calcite under different growth rates, temperatures, salinities, and ambient [Mg^{2+}], measuring isotopic compositions using double spike MC-ICPMS.

We find that the isotopic fractionation factor for Cd into calcite, $\alpha_{Cc\text{-}Cd}$, in artificial seawater solutions is always less than unity (i.e. light isotopes of Cd preferred in the reaction product) and appears to be insensitive to the majority of environmental factors studied. The magnitude of the fractionation factor shows no response to temperature or Mg concentration; or growth rate across the ranges studied.

However, no isotopic offset was recorded between the growth solution and carbonate when precipitated from de-ionized water, in contrast to those precipitated from artificial seawater solutions. This and other observations lead us to conclude that the cause of isotopic fractionation is related to kinetic isotope effects during the largely unidirectional incorporation of Cd at the mineral surface. This process is modulated by increased ion blocking of surface sites as salinity – and therefore the concentration of impurity ions – increases.

With the isotopic constraints from our experiments, we evaluate the role of $CaCO_3$ productivity in surface waters in the modern oceanic Cd budget, comparing with phytoplankton physiological Cd utilization. We conclude that carbonates are unlikely to play a significant role in setting the Cd isotope composition of seawater, although they are likely to be a minor sedimentary sink (and thus temporal archive) because of the low solubility of $CaCO_3$-bound Cd.