Chemosorbents for natural and artificial radionuclides detection by *in situ* gamma counting in natural waters

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Improving monitoring of anthropogenic radionuclides produced during nuclear fission is essential for safeguarding water after inadvertent or purposeful introduction of radionuclides into natural water bodies. Both traditional (e.g., MnO_2, FeO, Me-Cyanoferrates, Cation/Anion exchangers) and novel chemosorbents for a diverse range of fission product elements including Co, Zr, Ru, Ag, Te, Sb, Ba, Cs, Ce, and Eu, were tested in synthetic and natural waters and compared in this study. Novel nano-resins included self-assembled monolayers on meso-porous supports (SAMMS). The functionalized nano-surfaces of these resins greatly increase the effective surface area allowing for a variety of functional groups that can be targeted for specific analytes. Six different SAMMS functional groups were investigated. Batch experiments determined distribution coefficients and column experiments determined the extraction efficiency from the different waters and flow conditions. MnO_2 was the best overall traditional resin, in both batch and column experiments, and was the only resin tested with good extraction of Ba. Cyanoferrates were best for Cs, and SAMMS-HOPO, SAMMS-Diphos best for Ce and Eu, and thiol-functionalized SAMMS best for Ag. These test results suggest effective and rapid concentration of radionuclides from a few liters of fresh, brackish and coastal ocean waters into about 1-2 cm^3 of mixed resin, to be gamma counted in-situ.

Fe, S, and C isotopes record great microbial diversity in the Neoarchean

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The largest excursion of δ^{56}Fe values yet measured in sedimentary rocks occurs in whole-rocks and minerals of 2.9 to 2.4 Ga age. The negative δ^{56}Fe values of these Fe-rich rocks cannot be explained by abiologic processes such as extensive oxide precipitation, but instead require processes that can produce large quantites of low-δ^{56}Fe iron, and bacterial iron reduction (BIR) is the most likely mechanism. New C isotope data for organic C and carbonate C in black shales of Neoarchean age that have been previously analyzed for Fe isotope compositions provide strong support for heterotrophic respiration pathways. $\delta^{13}C_{carb}$ values as low as -25 ‰ for carbonate in Fe-rich black shales that have negative δ^{56}Fe values provide additional support for the importance of BIR in driving Fe cycling in the Neoarchean. The highly negative $\delta^{13}C_{carb}$ values rule out carbonate formation from seawater, but instead require microbial organic carbon oxidation in the sediment column beneath the sediment-seawater interface prior to lithification.

In contrast, some high-Fe, low-δ^{56}Fe shales in carbonate units deposited in restricted marine settings have near-zero $\delta^{13}C_{carb}$ values, indicating equilibrium with seawater. The negative δ^{56}Fe values in these Fe-rich rocks cannot be explained by extensive abiologic oxide preciptation, but instead likely reflect accumulation of $Fe(II)_{aq}$ by BIR on adjacent continental shelves, consistent with the Fe isotope basin shuttle model of Severmann *et al.* (2008, *Geology*); in the Neoarchean, however, the trap for low-δ^{56}Fe $Fe(II)_{aq}$ produced by BIR reduction may have been carbonates rather than sulfide, to the degree that bacterial sulfate reduction was low, which would have restricted dissolved sulfide contents.

New S isotope data on the same samples confirm that bacterial sulfate reduction was limited in some environments. The restricted range in δ^{34}S values for these samples, in contrast with the wide range in δ^{56}Fe values, is consistent with global trends for marine sedimentary rocks of Neoarchean age that suggest that BIR was most extensive prior to expansion of bacterial sulfate reduction, as proposed by Johnson *et al.* (2008, *Ann. Rev.*).