

Bioaccumulation of gold by filamentous cyanobacteria at 25-200°C

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The role of filamentous cyanobacteria (*Plectonema boryanum* UTEX 485) on the mobility of gold has been examined under controlled conditions in order to understand the origin of secondary gold deposition, and the effect of complex organic/inorganic reactions on the morphology of gold particles. The cyanobacteria were reacted with aqueous gold-chloride and gold thiosulfate complexes (~5 mM gold) at 25 to 100°C for up to one month, and 200°C for one day. Eh, pH, total gold, and sulfur were measured on the quenched solutions, while the bacteria and precipitated solids were analyzed using a combination of TEM-EDS and XPS.

Addition of gold(III) chloride complex to the cyanobacteria killed the cultures instantly, and also resulted in quantitative precipitation of octahedral crystal plates of gold. The particle size of gold increased with increase in temperature from an approximate diameter of 1.5 µm at 25°C to 10 µm at 100°C. Addition of gold(I) thiosulfate complex to the culture at 25°C resulted in separation of the filaments into their constituent cells after two weeks. Precipitation of gold was associated with membrane vesicles released by the cyanobacteria. At 60 to 200°C, precipitated gold on cell surfaces was in the form of cubic nanoparticles (~25 nm). TEM-EDS indicated Au:S ratios close to 3:1, and XPS showed that the sulfur was present dominantly as reduced species. Within the cells, gold nanoparticles were very fine grained (≤10 nm).

Under abiotic conditions, the gold chloride and gold thiosulfate complexes were stable for one month at 25°C; nanoparticles of gold were precipitated in the blank experiments at 60 to 200°C.

Biogeochemical redox transformations of technetium-99 in Hanford and Oak Ridge sediments

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Technetium-99 (⁹⁹Tc) is a frequent subsurface contaminant at sites of nuclear materials processing, due to its long half-life and its high mobility in oxidized form as pertechnetate [Tc(VII)O₄⁻]. Pertechnetate, however, can be immobilized in soil or sediment via reduction to poorly soluble Tc(IV) oxide, either by direct microbial enzymatic reduction or by indirect reduction by biogenic Fe(II). Both reduction mechanisms have been proposed for immobilizing Tc *in situ* in the subsurface, but for such remedial strategies to be effective long-term, the Tc must be maintained in the reduced form. Because limited data are available on the long-term stability of Tc(IV) in the environment, we examined the oxidation of both biotically and abiotically reduced Tc in subsurface sediments from the U.S. Department of Energy's (DOE's) Hanford and Oak Ridge sites.

Pertechnetate (20 µM) that was added to extensively bioreduced, pasteurized Hanford (Ringold) sediment was completely reduced to TcO₂ in ~24 h. After venting to air, the reduced Tc was oxidized to a soluble form (TcO₄⁻, presumably) after ~100 days. To extensively bioreduced Oak Ridge (FRC) sediments, 1 mM TcO₄⁻ was added and was observed to be completely reduced after 50 days. After ~140 days of venting to air, ~70% of the reduced Tc was oxidized to a soluble form. To compare these results with oxidation of biogenic TcO₂, 20 µM biogenic TcO₂ was added to anaerobic, unreduced Ringold and FRC sediment. Biogenic TcO₂ was more rapidly and thoroughly oxidized in unreduced Ringold than in unreduced FRC sediment, presumably because of a higher concentration of manganese (III, IV) oxides in the former sediment. However, biogenic TcO₂ was more rapidly oxidized by air (i.e., in aerobic buffer) than by either anaerobic Hanford or Ringold sediment.

Our results indicate that while TcO₄⁻ reduced by biogenic Fe(II) is relatively labile with regard to oxidation by O₂ and Mn oxides, there exists a fraction that is resistant to air oxidation in highly reduced sediment. Studies are underway to identify the nature of these refractile fractions and the causes for their relative stability.