Transformations of silver nanoparticles in environmental systems

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The persistence, toxicity, and effects of silver nanoparticles (AgNPs) released to the environment depends on their eventual speciation. Reduced sulfur-silver species are predicted to dominate the eventual species that form. However, in the environment, especially in aerobic conditions, other ligands are more abundant, such as Cl^-, organic thiols, SO_4^{2-}, Br, and I^-. To idenity important transformations from 'weathering' and predict the speciation of silver naoparticles weathered in environmental samples, engineered AgNPs were weathered in various environmental conditions including: wastewater treatment byproducts, aerobic and anaerobic soils, and in simulated wetland mesocosms. Synchrotron-based X-ray absorption spectroscopy was used to speciate AgNPs aged under simulated weathering conditions in the laboratory. Comparisons between the speciation of AgNPs that had been weathered for up to 18 months in a simulated wetland and laboratory weathering can be used to create particles that mimic the observed changes in environmental samples. Protocols to rapidly weather engineered nanomaterails will allow researchers to use NPs with properties representative of the materials that will be in the environment rather than those of the pristine materials. This will enable better predictions of the environmental fate, transport, and effects of engineered nanoparticles.

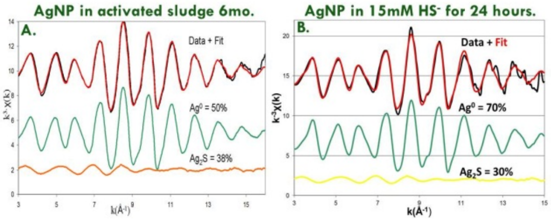

Figure 1: The original AgNPs containing ~90% Ag^0 have been transformed to approximately 50% Ag^0 and 30%Ag_2S after 6 months of ageing in activated sludge, shown in A. B shows the resulting particles from a laboratory ageing process that has produced a particle of somewhat similar composition after only 24 hours of ageing in Na_2S.

The Os isotopic record of organic rich sediments from the Benguela Upwelling System, Namibia

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Several recent studies [1-5] have shown a correlation between osmium isotopic variations in marine sediments and glacial-interglacial cycling. These correlated variations have been used to argue for direct climatic control on weathering intensity and/or on the composition of erosional products. However these rapid fluctuations in the marine Os isotopic records suggest a residence time for Os in seawater (3 to 10 ka) that is much shorter than that inferred from mass balance (~ 25 to 40 ka, [6-8]). Furthermore, potential problems linked to sampling site or sediment type, such as basin isolation, detrital contributions, and low sedimentation rate, could bias many of the existing Os records.

To obtain a reliable, high resolution record of marine Os isotopic variations in Quaternary times, we are analyzing sediments from ODP Leg 175, Site 1084, drilled off the coast of Namibia beneath the Benguela Upwelling System. This is an open ocean site containing rapidly deposited (~ 18 cm/kyr) organic rich sediments, which should be unaffected by the possible problems that may have plagued earlier studies. We currently have results for 9 samples spanning the most recent 35 ka of this record. These samples have extremely high Re and Os concentrations (58-157 ppb and 0.19-0.34 ppb, respectively). Their $^{187}Os/^{188}Os$ ratios are quite constant (1.044 ±0.013, 2σ), and show only a tiny hint of the nearly 7% decrease in $^{187}Os/^{188}Os$ during the last glacial maximum observed in several previous studies. Instead, the uniformity of the Benguela Os record is similar to that reported for an early Pleistocene record from the equatorial Pacific Ocean [9]. The discrepancies between the Os records from different sediment types and localities must be better understood before these records can be used to constrain relationships between climate and weathering.

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