Nature of environmental nanoparticle development at mineral-water interfaces

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The nucleation and growth of metal oxide nanoparticles and films on mineral surfaces can markedly affect aqueous metal contaminant transport and other surface-controlled reactions. Therefore, a holistic understanding of mechanisms and kinetics of nanoparticle development is required to predict more accurate prediction of the fate and transport of various contaminants. However, direct *in situ* observations of nanoparticle development have been challenging because of lack of proper tools.

To improve our understanding of the nature of environmental nanoparticle development, we have designed a time-resolved grazing incidence small angle x-ray scattering (GISAXS) setup for mineral-water interfaces. The size, shape, and distribution of iron oxide nanoparticles on quartz surfaces are monitored in real-time as a function of exposure time, ionic strength, and the presence of steps at the mineral surfaces. The iron oxide nuclei begin to grow close to steps rather than on terraces. The earliest nuclei sizes are 1.8 ± 0.5 nm (lateral radius) and are evenly distributed at the mineral surfaces (12 ± 1 nm interparticle spacing at 10 mM ionic strength at initial time). The interparticle spacing shows a strong dependence on ionic strength. Larger interparticle spacings occur at higher ionic strengths due to a limitation of free aqueous ferric ion availability. As exposure time increases, the nuclei began to coalesce with each other and form larger surface clusters. We also found that the surface steps direct the iron oxide nucleation and affect the kinetics of nucleation and growth of iron oxide nanoparticles. For comparison, we generated simulations of the nanoparticle scattering at quartz substrates and also conducted *ex situ* measurements of samples with atomic force microscopy (AFM).

Complementary with AFM, *in situ* time-resolved GISAXS can provide statistically improved morphological information of the early stage of environmental nanoparticle growth. Detailed information about these early processes are crucial in the design of more accurate geochemical modelling of the fate and transport of contaminants.

Sources of alkaline and tholeiitic volcanic rocks from the CEVP (Vogelsberg, Germany) inferred from Hf, Pb, and Os isotopes

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Alkaline and tholeiitic basalts from the 15 Ma Tertiary Vogelsberg area complex (CEVP; Germany) show large ranges in their initial Sr (^{87}Sr/^{86}Sr: 0.7032-0.7041), Nd (εNd: +5.4 to -1.8) and Pb, Hf and Os isotopic compositions. ^{176}Lu/^{177}Hf ratios of the alkaline basalts are low (0.005-0.008) and suggest derivation from a grt- and amph-bearing source. ^{176}Lu/^{177}Hf ratios of the ol- and qtz-tholeiites are higher (0.008-0.011) suggesting less garnet in the source or elimination of garnet due to higher degrees of melting. Primitive (high-Ni, Cr) nephelinites and basanites have variable Pb and Hf isotope compositions (^{206}Pb/^{204}Pb: 18.85-19.61; εHf +5.0 to +8.9) and highly variable ^{187}Os/^{188}Os isotope values (0.129-0.263) and Os concentrations (14-130 ppt). Although lithospheric mantle generally has low (sub-chondritic) ^{187}Os/^{188}Os, the least radiogenic compositions among Vogelsberg nephelinites/basanites resemble those in lithospheric peridotite xenoliths from the CEVP. Most Vogelsberg ol- and qtz tholeiites have lower Pb and Hf isotope compositions (^{206}Pb/^{204}Pb: 18.61-19.01; εHf : +2.6 to +7.2) but ^{187}Os/^{188}Os is even more variable than in the alkaline lavas (0.150-0.763). Lower Os concentrations in the ol- and qtz-tholeiites (2-32 ppt) compared to the alkaline rocks imply they would be particularly susceptible to crustal contamination. This is supported by model calculations which suggest that radiogenic Os isotope ratios up to 0.763 are possibly the result of < 25% assimilation of felsic lower crust or a partial melt thereof with ^{187}Os/^{188}Os: 0.90 and 25 ppt Os. This study suggests that crustal contamination in “primitive” continental volcanic rocks is more widespread than assumed, but is often not recognized using conventional isotope systems.