

Redox dynamics of mixed metal (Mn, Cr, and Fe) ultrafine particles

PETER S. NICO^{1*}, BENJAMIN M. KUMFER²,
IAN M. KENNEDY² AND CORT ANASTASIO³

¹Earth Sciences Division, Lawrence Berkeley National Laboratory, One Cyclotron Rd., Berkeley, CA 94720, USA (*correspondence: psnico@lbl.gov)

²Department of Mechanical and Aeronautical Engineering, University of California, Davis, CA 95616

³Department of Land, Air & Water Resources, University of California, Davis, CA 95616

Recent epidemiological studies have demonstrated a correlation between exposure to fine particulate matter and an increased incidence of cardiovascular morbidity and mortality. Unfortunately the mechanisms behind this correlation remain largely unknown. Ultrafine particles (smaller than 100 nm) have been reported to be particularly relevant pathologically due to their small size and high reactivity. The primary constituents of ambient ultrafine particles are carbon, organic compounds and metals. The metals, in particular the transition metals, may play a key role in determining the toxicity of ultrafine particles. Of the transition metals, Fe, Cr, and Mn are of particular interest because of their abundance and the fact that their redox chemistry alters their bioavailability and toxicity.

The impact of particle composition on metal oxidation state, and on changes in oxidation state with simulated atmospheric aging, are investigated experimentally in flame-generated nanoparticles containing Mn, Cr, and Fe. The results demonstrate that the initial fraction of Cr(VI) within the particles decreases with increasing total metal concentration in the flame. In contrast, the initial Mn oxidation state was only partly controlled by metal loading, suggesting the importance of other factors. Two reaction pathways, one reductive and one oxidative, were found to be operating simultaneously during simulated atmospheric aging. The oxidative pathway depended upon the presence of simulated sunlight and O₃, whereas the reductive pathway occurred in the presence of simulated sunlight alone. The reductive pathway appears to be rapid but transient, allowing the oxidative pathway to dominate with longer aging times, i.e. greater than ~8 hours. The presence of Mn within the particles enhanced the importance of the oxidative pathway, leading to more net Cr oxidation during aging implying that Mn can mediate oxidation by removal of electrons from other particulate metals.

Investigation of Thallium isotope fractionation during sorption to Mn oxides

SUNE G. NIELSEN¹, CAROLINE L. PEACOCK² AND
ALEX N. HALLIDAY¹

¹Dept. of Earth Science, University of Oxford, Parks Rd, OX1 3PR, UK

²National Oceanography Centre Southampton, University of Southampton, Waterfront Campus, European Way, Southampton SO14 3ZH, UK

Thallium (Tl) is one of the heaviest elements for which variation in natural stable isotope composition has been recorded. To date, the largest isotope fractionation factor reported has a magnitude of about 20 ε²⁰⁵Tl-units (where ε²⁰⁵Tl = 10⁴ × ((²⁰⁵Tl/²⁰³Tl)_{sample} - ²⁰⁵Tl/²⁰³Tl_{NIST 997}) / (²⁰⁵Tl/²⁰³Tl_{NIST 997})) and occurs between seawater and hydrogenetic marine ferromanganese (FeMn) crusts [1]. Recently, it was proposed that Tl isotope variations of this size most likely occur during equilibration of the two valence states of Tl, +1 and +3 [2].

Mn oxide phases are extremely efficient scavengers of dissolved trace-metals. Tl is highly enriched in marine FeMn deposits relative to seawater and empirical studies show positive Tl-Mn correlations [3]. A previous x-ray absorption spectroscopy (XAS) study of Tl sorption by the principle Tl-carrier in Fe-Mn crusts, δ-MnO₂, suggests that Tl is almost exclusively present in this mineral as Tl³⁺, despite the solution used for sorbing Tl onto δ-MnO₂ consisted solely of Tl⁺ [4]. Hence, we hypothesize that Tl isotopes might fractionate as a function of Tl oxidation by different Mn oxide phases.

Here we have performed Tl-sorption experiments at seawater pH with δ-MnO₂ (7Å-vernadite), 10Å-vernadite and todorokite, equilibrated over various time scales. Tl-sorbed Mn oxides were investigated with XAS for Tl oxidation state and Tl crystal-chemistry. Aliquots of the same Tl-sorbed samples were separated for Tl isotope composition determination. Supernatants were also kept for Tl isotope analysis.

Thallium speciation and isotope compositions for the Tl-sorbed Mn Oxides will be presented and discussed in the context of theoretical predictions. Additionally, we will present Tl XAS analyses of a range of natural FeMn crust samples, for which Tl isotope data is already available [1].

[1] Rehkämper *et al.* (2002) *EPSL*. [2] Schauble (2007) *GCA*. [3] Li (1982) *GCA*. [4] Bidoglio *et al.* (1993) *GCA*.