Preliminary results for the interactions between two sparingly soluble solid phases in $Cr(OH)_3(s)$ and birnessite suspension

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Contamination of groundwater by hexavalent chromium of natural origin has been reported elsewhere. Yet the mechanisms for the natural Cr(VI) contamination remain unclear especially under neutral and basic pH conditions.

This study investigated the interactions of two sparingly soluble solid phases between $Cr(OH)_3(s)$ and birnessite. The rates and extents of Cr(VI) release from $Cr(OH)_3(s)$ were examined in the presence of synthetic birnessite, the most common type of manganese oxides in the environment. The suspensions were prepared with 1 g/L each of $Cr(OH)_3(s)$ and/or birnessite in 0.05 M $NaNO_3$ at pH 7, 8, and 9, where the solubility of $Cr(OH)_3(s)$ remains constant at minimum. The values of pH were maintained using 10 mM MOPS (pH 7), TRIS (pH 8), or borate (pH 9) buffers. Dissolved Cr or Mn was not detected at all pHs examined when either solid phase were present alone. By contrast, substantial amounts of dissolved Cr(VI) were released from $Cr(OH)_3(s)$ in the mixed suspensions. The rate and extent of Cr(VI) release increased with increasing pH. Our previous results showed that the oxidative dissolution of $Cr(OH)_3(s)$ by amorphous $MnO_2(s)$ also increased with pH at pH 6 – 8 although the heterogenous redox reactions between aqueous Cr(III) species and $MnO_2(s)$ should be proton-consuming. These previous results were ascribed to anioic sorption behavior of Cr(VI) because the extent of Cr(VI) soption to the the reacting solid phases increased with decreasing pH. However, Cr(VI) sorption to either solid became negligible at $pH \geq 8$, indicating that the larger amount of Cr(VI) released at pH 9 compared to that at pH8 cannot be explained only by sorption. We will present the possible mechanisms for pH dependence of the solid-solid interaction.

Aerosol chemical composition and source characterization during 2008 VOCALS REX

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Chemical composition of aerosol particles ($D_p \leq 1.5$ μm) over the northern Chilean coastal waters was determined on board the US DOE G-1 aircraft during VOCALS experiment between October 16 and November 15, 2008. The chemical species determined included SO_4^{2-}, NO_3^-, NH_4^+, and total organics (Org) using an Aerodyne Aerosol Mass Spectrometer, and SO_4^{2-}, NO_3^-, Cl^-, $CH_3SO_3^-$, NH_4^+, Na^+, Mg^{2+}, Ca^{2+}, and K^+ using a particle-into-liquid sampler-ion chromatography (PILS-IC) technique. The results show that the marine boundary layer (MBL) aerosol mass in the study domain was dominated by non-sea-salt SO_4^{2-} followed by Na^+, Cl^-, Org, NH_4^+, and NO_3^-, in decreasing importance; $CH_3SO_3^-$, Ca^{2+}, and K^+ rarely exceeded the limits of detection of ~0.05 and ~0.15 μg/m^3 for anions and cations, respectively. The SO_4^{2-} aerosols were strongly acidic as the equivalent NH_4^+ to SO_4^{2-} ratio was typically less than ~0.2; this inference of high acidity is consistent with on-line conductivity measurement of aqueous samples collected by the PILS. NaCl particles, presumably of sea-salt origin, showed chloride deficits but retained more than half equivalencies. They are believed to be externally mixed with the sulfate aerosols as the equivalent H_2SO_4 concentrations far exceeded that of Cl^-. Dust particles appeared to play a minor role based on volume differences between that derived from observed mass and calculated using particle size distributions. Because the aerosol SO_4^{2-} concentrations were substantial (>0.5 μg/m^3) exhibiting a strong gradient toward the land, and the ocean-emitted dimethylsulfide and its oxidation product, $CH_3SO_3^-$, were typically very low (i.e., ≤ 40 parts per trillion, and 0.05 μg/m^3, respectively), the SO_4^{2-} aerosols observed in the northern Chilean coastal MBL are believed to be mainly of terrestrial origin. Back trajectory calculations indicate sulfur emissions from power plants and smelters along coastal regions of Peru and Chile are plausible sources of these SO_4^{2-} aerosols.