

Water Vapor Interactions with FeOOH Particle Surfaces

XIAOWEI SONG* AND JEAN-FRANÇOIS BOILY

Department of Chemistry, Umeå University, Sweden *Email: xiaowei.song@chem.umu.se

Iron oxyhydroxide (FeOOH) minerals play important roles in a variety of atmospheric, terrestrial and technological settings. Interactions with water vapor are particularly important given the predominance of water-bearing gases in the environment. In this work, molecular details of water adsorption reactions at FeOOH surfaces were resolved using vibrational spectroscopy, quartz crystal microbalance and molecular dynamics. Acidified and alkalified mineral surfaces were investigated to determine protonation effects on interfacial water loadings and structures. The effects of residual salts on the surfaces were further studied by resolving competitive hydration processes between surface-bound Cl⁻ ions and hydroxyl groups.

This work reveals the initial mechanisms of formation of thin water films on mineral surfaces under atmospheric conditions [1]. We show that thin films of adsorbed water display liquid water-like attributes. The affinity of surface (hydr)oxo groups for water molecules is strongly dependent on their abilities at forming hydrogen bonds. Coordination number and site accessibility/steric constraints are main factors. These groups have moreover stronger affinities for water than chemisorbed water (-OH₂) and Cl-exchanged group (e.g. -Cl, μ -Cl). Finally, we identified a *surface memory effect* showing that original surface protonation states can be retrieved by evacuating surfaces from surface-bound waters. This confirms that the original surfaces were at thermodynamic equilibrium prior water uptake reactions and that all reactions are reversible. This reversibility may further hold in mineral particles undergoing several water condensation-evaporation cycles in nature. This work thus opens a path for understanding water structure as well as condensation reactions on these important mineral particles.

[1] Song X.W., Boly J.-F. (2013), Chem. Phys. Lett. 560, 1-9.

A stable isotope perspective on tracing natural and anthropogenic Hg emissions at the global scale.

JEROEN E. SONKE

Observatoire Midi-Pyrénées, 14 avenue E. Belin 31400 Toulouse, sonke@get.obs-mip.fr

A decade of research on the natural variations in mercury (Hg) stable isotope abundances has shown large variations across biogeochemical reservoirs. These variations result from the gradual separation of heavy/light or even/odd Hg isotopes during the numerous physicochemical processes that shuttle Hg across the Earth's surface. As a result, a Hg isotopic measurement gives rise to four useful isotope fingerprints that may characterize its source, or code for the transformations that Hg has undergone in the past.

Tracing the dominant natural and anthropogenic Hg emissions at the global level is a challenge. The further Hg emissions travel from their source, the more likely it is that oxidation/reduction, sorption or (de-)methylation reactions modify the original source Hg isotope signatures. This presentation illustrates an integrated approach to evaluate Hg isotope tracing at the global scale. Similar to modern and historic Hg emission inventories, a parallel Hg isotope library needs to be built per industrial sector and geographical region. Industrial processes include Hg transformations that may change isotope signatures and need to be understood. Monitoring of the isotopic composition of emitted Hg species and associated Hg deposition at different spatiotemporal scales is necessary. Finally, monitoring of critical receptor environments on continents and oceans and on different time scales (modern, geologic) will tell if globally relevant emission sources can be recognized. All of these tasks are compatible with box and process models of the global Hg cycle, so that Hg isotopic information may in the near future be integrated in global models to help understand Hg cycling.

The approach will be illustrated for coal fired power plant (CFPP) emissions: A coal Hg isotope library, containing ~200 coal samples from historically dominant coal burning regions has been made. A study on two large Chinese coal fired power plants suggests that stack emission Hg isotope signatures are slightly modified from feed coal signatures by emission control technologies. Bi-weekly monitoring of gaseous and particulate Hg isotope signatures in Asian urban-industrial environments is compatible with a dominant CFPP source. Finally, a preliminary attempt to integrate an emission isotope library in a global Hg box model will be compared to historical records of Hg deposition and isotopic variation in peat bogs.