

Modeling isotopic signatures of nebular chlorine condensation

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Recent measurements of $^{37}\text{Cl}/^{35}\text{Cl}$ in bulk chondrites and the silicate Earth suggest a relatively homogenous distribution of chlorine isotopes¹, but significant variation has been found in other planetary samples. In order to assess the potential for stable chlorine isotope ratio measurements to constrain the origin and transport of chlorine in chondritic parent bodies and other planetary precursors, and more broadly in minerals and ices, we calculated equilibrium $^{37}\text{Cl}/^{35}\text{Cl}$ isotope fractionations between gas-phase HCl and the crystalline phases HCl.3H₂O, NaCl (halite), KCl (sylvite) and Na₄Al₃(SiO₄)₃Cl (sodalite) using a combination of experimental vibrational frequencies and electronic structure (DFT) models. Sodalite is estimated to have ~0.7‰ lower $^{37}\text{Cl}/^{35}\text{Cl}$ than HCl at ~950 K, the expected 50% condensation point for silicate-hosted chloride. This fractionation is in the same direction, but somewhat smaller than, the ~1.3‰ $^{37}\text{Cl}/^{35}\text{Cl}$ depletion observed in primitive sodalite inclusions in Allende¹. Calculated halite-sodalite fractionation at 1098 K is also of the same sense but smaller than an experimental calibration (0.02‰ vs. 0.3‰) [1]. In contrast, HCl.3H₂O hydrate is predicted to have 3-6‰ higher $^{37}\text{Cl}/^{35}\text{Cl}$ than coexisting HCl gas in equilibrium at temperatures relevant to low-pressure gas/crystal partitioning (roughly 140-160 K). This enrichment in ice is opposite in sense to what would be expected in a general rapid condensation process — more mobile ^{35}Cl -bearing molecules with weaker H-Cl bonds should react faster and thus ^{35}Cl should be enriched in the rapid condensation product. It is also opposite in sense to predicted and observed equilibrium isotope fractionation between HCl vapor and liquid water [2], but may overlap fractionation associated with disequilibrium evaporation. These results suggest that it may be possible to distinguish between icy [3] and silicate sources of chloride to planets and planetary precursors, so long as chlorine condensation is not quantitatively complete. Acid hydrate-derived high $^{37}\text{Cl}/^{35}\text{Cl}$ signatures, if found, could additionally indicate a post-condensation origin of chlorine-bearing minerals in chondrite minerals, and would be consistent with correlated high chlorine abundances and hydration in CI chondrites.

[1] Sharp *et al.* (2007) *Nature* **446**, 1062–1065. [2] Sharp *et al.* (2010) *GCA* **74**, 264–273, Schauble *et al.* (2003) *GCA* **67**, 3267–3281. [3] Zolotov & Mironenko (2007) *LPSC* #2340.

Modes of interaction between inorganic engineered nanoparticles and biological and abiotic surfaces

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Engineered nanoparticles are subjected to various aging and transformation pathways when they are emitted into the environment. One important pathway is connected to their attachment to biological or inorganic surfaces (e.g. planktonic invertebrates, plant leaves, biofilms or soil and sediment particles).

In this study the attachment of $n\text{Ag}^0$ and $n\text{TiO}_2$ to daphnia, plant leaves and organic as well as to inorganic model surfaces was studied, with the objective to understand the physicochemical interactions, in order to examine a possible link between (eco)toxicological effects and the attachment of the nanoparticles.

Surface-nanoparticle interactions were investigated in ecotoxicological test systems and in laboratory sorption experiments. The model surfaces were chosen to cover a wide range of intermolecular interactions considering van-der Waals interactions as well as proton donor and acceptor interactions. Samples were analysed quantitatively by ICP-MS and qualitatively by microscopic techniques (optical microscopy, environmental scanning electron microscopy and atomic force microscopy including nanomechanical properties).

In ecotoxicological test systems, attachment of nanoparticles to *Daphnia magna* occurred in large nanoparticle clusters and inhibited the molting of individuals. The deposition mechanism is in these systems determined by aggregation processes. In contrast, sorption of individual nanoparticles occurred from stable suspensions. The sorption coefficient was determined by the chemical nature of the model surfaces as well as by the surfaces accessible for the nanoparticles.

The current results show that attachment is determined by an interplay between physicochemical nanoparticle-surface interactions, colloidal stability and physical characteristics.