Supramolecular aggregation of natural organic matter promoted by complexation with Ca^{2+}, Mg^{2+}, and Na^+ ions in aqueous solutions

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The interaction of natural organic matter (NOM) with metal ions, minerals and organic species in soil and water allows NOM to form water-soluble and water-insoluble complexes of widely differing chemical and biological stabilities. Metal–NOM interaction induces strong correlations between the concentration of natural organic matter and the speciation, solubility and toxicity of many metals in the environment. In water purification and desalination, NOM is also implicated in fouling of nanofiltration and reverse osmosis membranes, either as the primary foulant or as a conditioning layer for microbial attachment (“biofouling”).

In this work we compare the effects of various metal ions on NOM aggregation in the aqueous phase, probed by dynamic light scattering (DLS) and large-scale molecular dynamics (MD) computer simulations. This allows a detailed molecular-scale statistical analysis of the structures of metal–NOM aggregates. The DLS measurements show that Ca^{2+} ions present in a Suwannee River NOM (SRNOM) solution lead to the formation of a wide range of supramolecular structures with sizes between 100 and 1,000 nm. In contrast, Mg^{2+} and Na^+ do not affect the aggregation of SRNOM as strongly.

MD simulations confirm these observations and show that NOM can aggregate in aqueous solutions by two different mechanisms. On the one hand, NOM molecules can spontaneously aggregate by hydrogen bonding between their functional groups when only Na^+ and Mg^{2+} are present as background cations. This promotes the formation of spherically-shaped NOM clusters. On the other hand, if Ca^{2+} ions are present in solution, they can more strongly bind two different NOM molecules by co-complexing the carboxylate groups, thus promoting the formation of longer linear and branched aggregate structures. When Ca^{2+} is added to the simulated solution, the aggregation also equilibrates noticeably faster (within 5 ns) and the observed aggregates are more stable than those with Mg^{2+} or Na^+.

Argide interference reduction for Fe isotopic analysis by MC-ICP-MS

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MC-ICP-MS measurement of Fe isotopic ratios ($\delta^{56/54}$, $\delta^{57/54}$, $\delta^{56/57}$) is subject to major polyatomic interferences inherent to the ICP source: ArN^+ (54), ArO^+ (56), $ArOH^+$ (57). Several approaches have been used to minimize the significance of these interferences. [1] A smaller, 10^{10} MΩ, resistor or [2] a 20V range (-10 to 10V) to enable measurement of a large ^{56}Fe signal, and [3] sacrifice of the verification of the mass-dependent fractionation by limiting the measurement to ^{54}Fe and ^{57}Fe have all been used for analysis on a Nu Plasma. These techniques require a higher Fe signal and increase this signal relative to the interferences, and thus require μg Fe samples sizes. Other techniques include [4] specially design cones to reduce argides formation (Neptune), [5] use of a collision cell to eliminate argides (Isoprobe), and high resolution to fully [5] or partially [4] resolve polyatomic interferences.

We aim to measure accurate and precise Fe isotopic ratios in small samples on a Nu Plasma in low resolution to enable monitoring of matrix effects. To do this argide production and transmission need to be reduced but not at the expense of instrument sensitivity for Fe. To date, a number of instument parameters have been investigated: desolvator system (Aridus vs. DSN) and transport of the desolvated sample to the torch; interface vacuum; geometry and orifice size of cones, and their positioning relative to the ion beam; defining slit width; choice of ion beam for tuning.

Our optimal set-up uses the Aridus with low O_2 and N_2 permeability plastic tubing between the desolvator and the torch, reduced interface vacuum, A cones, wide slit and when argide contributions to Fe masses are high, tuning optimized using an argide-free metal ion (e.g. Mn^+). Under these conditions Fe samples can be measured in the low hundreds ng.

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