

## Adsorption of organics and nanoparticles at mineral-water interfaces.

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We present our recent work, developing and applying complementary computational methods to gain atomistic insights into systems comprising mineral-organic-water interfaces. The research scheme involves the use of *ab initio* including van der Waals interactions and experimental data to validate rigid-ion or polarizable potential models which are then applied within energy minimization (EM) and classical molecular dynamics (MD) techniques. This robust approach covers the evolution of systems of different sizes and for different lengths of time allowing the evaluation of structures and dynamic properties.

The focus of our attention is on layered minerals including metal hydroxides, clay minerals and organo-clays interacting in the aqueous environment. The presence of organo-compounds (OCs) and nanoparticles (NPs) which can impact on the environment by entering the food chain, can also disrupt the mineral/water interfaces affecting the physico-chemistry of aqueous systems.

Several examples are discussed including adsorption and transport of OCs on montmorillonite and pyrophyllite and of fullerene on brucite in the presence of water capturing their atomistic features and helping to interpret experiments. The CLAYFF [1] and GAFF [2] or CVFF [3] force fields are applied to the clay surfaces and OCs and NPs respectively. Flexible TIP3P [4] and shell models of water are used in solvated systems. Interatomic potentials are tested against DFT calculations using VASP [5]. EM and MD employ the METADISE [6] and DL\_POLY [7] codes.

Our results indicate that the interplay between the adsorption, which is surface-site as well as counter-ion-site dependent, and the transport of OCs and NPs on soil clay significantly disrupts the structure of the mineral-water interface [8,9] which has previously been shown to extend well above both mineral and nanoparticle surfaces [10]. Finally we find that the energy of adsorption is strongly affected by the inclusion of the van der Waals interactions within the DFT simulations and of the polarizability terms in the potential models within classical techniques.

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## Magnesium isotope fractionation during bacterial mediated carbonate precipitation

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Magnesium is the eight most abundant element in the Earth's crust, and the fourth most abundant species in seawater. As such it is an essential component of life, with pivotal roles in the generation of cellular energy as well as in plant chlorophyll<sup>[1]</sup>. The biogeochemical cycling of Mg is associated with mass dependant fractionation (MDF) of the three stable Mg isotopes, <sup>24</sup>Mg, <sup>25</sup>Mg and <sup>26</sup>Mg<sup>[1]</sup>. The largest MDF of Mg isotopes has been recorded in carbonates, with foraminiferal tests displaying the lowest  $\delta^{25}\text{Mg}$  and  $\delta^{26}\text{Mg}$  compositions<sup>[2]</sup>.

Bacterial carbonate precipitation is known to have occurred in modern and ancient Earth surface environments<sup>[3,4]</sup>, with cyanobacteria having a dominant role in carbonate formation during the Archean. In this study, we aim to better constrain the extent to which Mg isotope fractionation occurs during cellular processes, and to identify when, and how, this signal is transferred to carbonates. To quantify these effects we have performed biologically-induced carbonate precipitation experiments using several bacteria strains. The organisms are grown under defined organic and Ca/Mg ratios in artificial seawater, and under temperature controlled conditions that promote carbonate formation. Carbonate spheres of ~100 microns diameter are produced, which are amenable to SEM, EMP and Mg isotopic analysis by MC-ICP-MS. In order to compare our experimental data to natural samples we will present Mg isotope data for modern and ancient stromatolites, which are laminated carbonates produced by micro-organisms. Our new data will shed light on tracing bacterial signals in the geological record.

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