

Computational modelling of water and amino acid adsorption at corundum structured oxide surfaces

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The interactions between biomolecules and inorganic surfaces play an important role in many natural environments and hence it is essential to understand the nature of the chemical interaction between the biomolecule and the surface, the resulting biomolecule conformation and the influence of other surface species notably water. This can be achieved by using atomistic simulation techniques and we have focused on the corundum structured oxide α -Cr₂O₃ and compared with the structural analogues of α -Fe₂O₃ and α -Al₂O₃.

We have used a combination of simulation techniques to investigate the surfaces and surface adsorption. These include potential-model based techniques using the static lattice code METADISE [1] for generating the initial structures of the surfaces and the molecular dynamics code: DL_POLY [2] on incorporation of water. The interatomic potentials were then tested with DFT using VASP [3].

The results from both interatomic potentials and DFT show that the {10.2} and {00.1} surfaces are the most stable and energetically prefer dissociative adsorption. The adsorption energies are in reasonable accord, for example DFT predicts -0.75 eV on the {10.0} surface compared to -0.84 eV. The DFT studies on the different forms (neutral, anionic and cationic) of glycine (Gly) 1, lysine (Lys) and glutamic acid (Glu) have been used to test and develop the potential models. The results show that the neutral amino acid molecules become anionic on adsorption at low coverage on anhydrous Al₂O₃ and Cr₂O₃. An oxido-amino acid complex is formed with the creation of an ionic-covalent bond M-O(C). Finally, the results show that hydroxylation of the surfaces clearly modify amino acid adsorption.

[1] Watson *et al.* (1996), *J. Chem. Soc. Farad. Trans.*, **92**, 433-438. [2] Smith and Forester (1996) *J. Mol Graph* **14**, 136-141 [3] Kresse & Furthmuller (1996), *Phys. Rev. B*, **54**, 11169-11186.

Magnesium isotope fractionation in a hardwood forest of Southern Québec, Canada

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Magnesium (Mg) is an essential macronutrient for plants, acting as the coordinating cation for chlorophyll as well as serving other important metabolic functions. Recent laboratory studies have demonstrated mass dependent fractionation of Mg within plants [1,2], while there is only one confirmation of plant fractionation in the field to date [3]. Our study builds on previous work through an investigation of Mg isotope fractionation in a forested ecosystem. Broader questions motivating this work include the potential impact of forest Mg cycling on the signature of the continental weathering flux of Mg delivered to the oceans by river flow.

Mg isotope fractionation is being examined in a forested first order catchment in southern Québec, Canada, dominated by sugar maple (*Acer saccharum*) and characterized by soils developed from granite, mangerite and anorthosite. Thus far, we observe fractionation coupled with the uptake of Mg into maple trees from the soil pool as well as significant internal plant fractionation. Preliminary $\delta^{26}\text{Mg}$ ($^{26}\text{Mg}/^{24}\text{Mg}$) values for the study plot exhibit an overall fractionation range of 1.15‰ (23% of reported terrestrial variation). Most interesting is considerable fractionation associated with the degradation of chlorophyll during leaf senescence. We believe translocation of light chlorophyll-bound Mg back into the tree accounts for this finding, driving whole leaf $\delta^{26}\text{Mg}$ to higher values prior to litter fall. Measured $\delta^{26}\text{Mg}$ values of senescent leaves and litter range from $-0.88 \pm 0.10\text{‰}$ to $-1.32 \pm 0.09\text{‰}$. Analyses of soil water and stream water samples during low and high flow indicate that Mg isotope values in the stream may be influenced by fractionation during plant uptake; however, a lithology driven (particularly silicate weathering [4]) control is still under investigation. With this presentation, we will review the progress made to date on factors influencing Mg isotope fractionation in a forested catchment.

[1] Black *et al.* (2008) *Environ. Sci. Technol.* **42**, 7831-7836. [2] Bolou-Bi *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 2523-2537. [3] Tipper *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 3883-3896. [4] Tipper *et al.* (2006) *EPSL* **250**, 241-253.