Molecular dynamics simulations of the electrical double layer on smectite clay surfaces

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We report new molecular dynamics (MD) simulation results elucidating the structure of the electrical double layer (EDL) on smectite surfaces contacting mixed $NaCl$-$CaCl_2$ electrolyte solutions in the range of concentrations relevant to pore waters in ocean sediments and in geologic repositories for CO_2 or high-level radioactive waste (0.34 to 1.83 $mol_c\ dm^{-3}$). Our simulations used methodologies known to correctly describe the structure and diffusion coefficients of water and solutes in smectite interlayer nanopores [1]. Our results confirm the existence of three distinct ion adsorption planes (0-, β-, and d-planes), often assumed in EDL models [2,3], but with two important qualifications: (1) the location of the β-, and d-planes are independent of ionic strength or ion type and (2) "indifferent electrolyte" ions can occupy all three planes. Charge inversion occurred in the diffuse ion swarm because of the affinity of the clay surface for $CaCl^+$ ion pairs. Therefore, at concentrations $\geq 0.34\ mol_c\ dm^{-3}$, properties arising from long-range electrostatics at interfaces (electrophoresis, electro-osmosis, co-ion exclusion, colloidal aggregation) will not be correctly predicted by most EDL models. Co-ion exclusion, typically neglected by surface speciation models, balanced a large part of the clay mineral structural charge in the more concentrated solutions. Water molecules and ions diffused relatively rapidly even in the first statistical water monolayer, contradicting reports of rigid "ice-like" structure for water on clay mineral surfaces.

[1] Bourg & Sposito (2010) *Environ. Sci. Technol.* **44**, 2085.
[2] Sverjensky (2006) *Geochim. Cosmochim. Acta* **70**, 2427.
[3] Goldberg *et al.* (2007) *Vadose Zone J.* **6**, 407.

Quantifying weathering and erosion rates using cosmogenic nuclides.

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Quantifying chemical weathering and physical erosion rates, whose sum corresponds to denudation rates, is of great importance across a wide range of environmental science disciplines Until recently, this has nevertheless been difficult over millenial timescales. Accumulating within mineral grains exposed to cosmic ray secondary particles in the uppermost few meters of the Earth's surface, *in situ*-produced cosmogenic have provided opportunities to quantify on such timescales not only the mineral grains exposure duration near the surface, but also the rates of the processes bringing them to the surface and removing them from above it.

Corresponding to their build-up in the suitable mineral over thousands of years, the cosmogenic nulide concentrations measured in rocks, sediments or soils are relatively insensitive to short-term fluctuations and thus allow quantifying natural, long-term weathering and erosion rates. More, they permit to evidence landscapes that are not at natural steady state because affected by natural hazards (landslides) or by anthropogenic activities. Cosmogenic nuclides thus provide reliable methods to measure long-term average denudation rates in a wide range of settings and to point out any perturbations that may have disturbed them.

Through the presentation of pertinent case studies from notably Brasil, Taïwan and Africa, the following general types of denudation-related problems will be addressed: (i) denudation rates from rock surface samples; (ii) denudation rates from vertically mixed continental sediments; (iii) spatially averaged denudation rates.