

Recognizing the environmental significance of ternary surface complexes 30 years after their “discovery”

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Schindler and Bourg first described the existence of ternary surface complexes (TSC) in 1978 to justify some unexplainable metal behavior at the solid-liquid interface in the presence of organic ligands [1, 2]. This “discovery” was the result of a discussion with Sigel (Basel Univ.) at the 1977 Fall Meeting of the Swiss Chemical Society in Bern about analogy with ternary dissolved complexes. At just about the same time, Davis and Leckie reported similar conclusions in the presence of an inorganic ligand [3]. Although this concept has since been used repeatedly, this has most often been for very theoretical cases or for applied situations with simple surfaces and simple water chemistry (i.e., no natural organic matter).

The general relevance of TSC to the partitioning of heavy metals between aqueous and sediment phases in natural waters is discussed here. Organic matter (OM), because of its ubiquitous presence and complexing ability, can significantly influence the solubility of some heavy metals. It might maintain them in solution at high pH (dissolved complexation) but, because of the formation of TSC, it can also significantly decrease their solubility, especially at low pH (the case of podzols -sandy soils, rich in OM). This is demonstrated here for the adsorptive behavior of 3 heavy metals of increasing reactivity (Zn, Cd, Cu) in the presence of natural (fulvic acid) or model (salicylate) organic matter.

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Isotopic fractionation by diffusion in liquid water and clay nanopores

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Aquifers, clay caprocks, marine sediments and other low-permeability, clay-rich porous media play important roles in the integrity of freshwater aquifers, the viability of brine aquifers, depleted hydrocarbon reservoirs, and deep-sea sediments as CO₂ sequestration and hazardous liquid waste disposal sites, the contribution of diagenetic burial to global biogeochemical cycles, and the formation of gas hydrate clathrates. At the field scale, the hydrogeology and biogeochemistry of such media is commonly investigated by comparing measured pore water chemical and isotopic compositions with the predictions of geochemical hydrogeology models [1, 2]. However, very few data are available on the isotopic mass-dependence of solute diffusion coefficients in liquid water, an important parameter of such models [3], and no data are available, to our knowledge, on the isotopic mass-dependence of solute diffusion coefficients in water-filled nanopores or near mineral surfaces. In our previous research, we used molecular dynamics (MD) simulations to determine the isotopic mass-dependence of the diffusion coefficients of lithium, magnesium, chloride [4] and noble gases (He, Ne, Ar, Xe) in liquid water [5]. Our simulation results were consistent with available experimental data [3] and allowed us to reconsider the hydrologic and geochemical modeling in several previous studies [5, 6]. Here, we present additional MD simulation results on the isotopic fractionation of calcium, alkali metals (Na⁺, K⁺, Cs⁺), and methane (with C or H isotopic substitution) by diffusion in liquid water, as well as results on the isotopic fractionation of Ar, Li⁺ and Ca²⁺ by diffusion in smectite interlayer nanopores. Our findings are consistent with experimental results on the ratio $D(^{13}\text{CH}_4)/D(^{12}\text{CH}_4)$ in water-saturated coarse-grained rocks [7] and with very recent experimental data on the fractionation of potassium and calcium isotopes by diffusion in liquid water [8].

[1] Fantle & DePaolo (2007) *GCA* **71**, 2524-2546. [2] Donahue *et al.* (2008) *GCA* **72**, 2287-2297. [3] Richter *et al.* (2006) *GCA* **70**, 277-289. [4] Bourg & Sposito (2007) *GCA* **71**, 5583-5589. [5] Bourg & Sposito (2008) *GCA* **72**, 2237-2247. [6] Bourg (2008) *GCA* **72**, 5852-5854. [7] Schloemer & Krooss (2004) *Geofluids* **4**, 81-108. [8] Bourg *et al.* (2009) *Phys. Rev. Lett.* (in review).