

Interactions of organic matter with minerals – Ultimate stabilization in soils?

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All organic matter (OM) in soil derives from primary production, i.e. from leaves and roots. The initial decomposition of these primary sources depends largely on their chemical properties with recalcitrant aromatic constituents being more resistant. Since intrinsically labile compounds also accumulate in soils, we have to address the factors that add to the observed stabilization of compounds spanning a wide range of intrinsic stabilities.

Adsorption of OM to pure mineral surfaces and its (co-) precipitation with amorphous Fe and Al phases and metals mostly result in preferential enrichment of lignin-derived aromatic compounds. This fractionation along with the formation of strong innersphere complexes between mineral surfaces and OM may be the key process in the stabilization against microbial decay. Weak mineral–organic bindings are favored at a small availability of sorption sites where other solution constituents like phosphate effectively compete with OM. In this case, N-rich, less aromatic and less complex OM accumulates selectively, resulting in minor stabilization of bound OM [1].

Factors supporting the stabilization of sorbed OM in soil include (i) the surface area and reactivity of minerals, (ii) the inherent stability of OM, and (iii) strong bonds decreasing its desorption as a precondition for microbial utilization [2]. The stability of sorbed OM seems to be largest in the mineral subsoil because of the availability of bare and reactive minerals irrespective of the intrinsically labile character of OM. Despite small $\Delta^{14}\text{C}$ values of subsoil OM, the accumulation of microbial residues and a continuous production of dissolved OM indicate ongoing C turnover also in such ‘high-stability environments’. This is supported by the results of incubation experiments. Therefore, interactions of OM with minerals do not result in ultimate stabilization and the usefulness of ^{14}C as a universal measure of C stabilization might be questioned.

[1] Schneider *et al.* (2010) *GCA*, in press. [2] Mikutta *et al.* (2009) *GCA* **73**, 2034–2060.

Molecular mechanisms of the librational motions of water in the interlayers of hydrocalumite

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Hydrous interlayers of layered double hydroxides (LDHs, anionic clays) can contain H₂O molecules and a wide variety of anions which often occupy well-defined structural positions and coordinations. Hydrocalumite, also known as Friedel’s salt, [Ca₂Al(OH)₆]Cl·2H₂O, has a well-ordered Ca, Al distribution in the hydroxide layer and a particularly high degree of H₂O, Cl ordering in the interlayer. Thus, it represents an excellent model system for detailed molecular-level studies of the structure and dynamics of nano-confined water in minerals.

We used molecular dynamics (MD) simulations and quasielastic neutron scattering (QENS) to investigate the dynamics and mechanisms of H₂O librational and reorientational motions in the hydrocalumite interlayers at temperatures above and below the previously discovered order-disorder interlayer phase transition. The experimental and MD modeling results are consistent in capturing the important details of the dynamics of nano-confined water and the effects of the orientational ordering of the interlayer H₂O molecules. Unexpectedly, the MD simulations also reveal that the dominant mechanism of H₂O reorientation is not the rotation in the plane of the molecule, but a ‘flipping’ motion in which one hydrogen bond to a neighboring interlayer Cl⁻ ion remains intact, while another H-bond changes its coordination between two other neighboring Cl⁻ ions.

The combination of QENS and MD approaches provides new otherwise unobtainable information, significantly adds to our current understanding of the H₂O structure and dynamics in LDH phases, and can now be extended to probe the dynamics of nano-confined and interfacial water in more disordered phases (LDH, clays, cement, etc.), for which much less initial structural information is available.