

The compared reactivity of different organic matters and clay in the whole soil and at the microscale: Unraveling the reactivities by combining chemical analysis and physical fractionation

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Organic carbon is one of the most reactive, often the most reactive component of common soils. Despite this, describing inside a complex soil matrix the reactivities of the different habits of organic matter (bioclasts, bacteria, degraded solid and dissolved organic matter) and the relative contribution to reactivity of mineral compounds is still a challenging task. The study focus on the reactivity determination of metals, protons, and generally complexing compound. A procedure is presented based on 'soft' granulometric fractionation separating coarse soil aggregates (>250 and 250-63 μ m), silty (63-20 μ m) and fine (20-2 and <2 μ m) soil fractions. The whole-fraction reactivity toward protons and Cu(II) (taken as example of complexing trace elemental cations) is compared to the fraction-specific total organic carbon (T_{OC}) and aqua regalis extracted Al (E_{Al}) content. T_{OC} varies in the soil fractions dependent on 20 years lasting organic amendments in the studied silty-loam soil. E_{Al} content represents the acid, and consequently the relative water accessible clay content in each fraction. Combining linearly these reactivities descriptors allows accessing to the reactivity contribution of different soil organic matters, soil clay and a residual phase. The comparison with referenced reactivity knowledge shows that this method allows accessing representative reactivities of studied components. With this method the soil aggregates are preserved. They are known to represent specific microbial habitats. This opens interesting perspectives relative to the study of biogeochemical site effects in the complex soil matrix.

Thermodynamic Constraints on Stability of Ceramics under Extreme Conditions – Phase Change and Amorphization from Chemical Effects of Radioactive Decay

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In addition to radiation damage, ceramics in a nuclear reactor or waste form undergo chemical changes as a result of fission and radioactive decay. Because ceramics are typically ionic solids with stringent requirements to maintain appropriate cation size and charge balance on various sublattices, and such transmutations change both the size and charge of ionic species, one can expect phase change, exsolution, and/or vitrification arising from these chemical changes as well as from radiation damage. Two examples are discussed: the incorporation of rare earth fission products in UO₂ and the effect of the decay of Sr to Y to Zr and of Cs to Ba in titanate waste forms incorporating these short-lived fission products. In the former case, rare earths are accommodated by creation of oxygen vacancies, which change ionic and thermal conductivity and, in many cases, stabilize the fluorite phase. In the latter, using perovskite, pollucite, and fersnoite as examples, a general trend of destabilization is seen, with exsolution of new phases and extensive vitrification arising from the violation of charge balanced substitution within the initial structures. Such behavior has the potential to diminish waste form durability