

CRYSTAL CHEMISTRY OF CLAYS AND ASSOCIATED OXIDES :  
CONSTRAINTS FOR ELEMENT TRANSFER AND MINERAL  
FORMATION PROCESSES AT THE EARTH'S SURFACE.

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Important progresses have been recently accomplished in the detailed structural knowledge of poorly organized clay minerals and associated Fe-Mn oxides. This arises as well from the development of adapted spectroscopic methods as from the correlation of crystal chemistry with geochemical, petrological and field data. On the other hand, mineral surfaces, which are of primary importance in all water-rock interactions, need to be investigated with appropriate spectroscopic tools, in order to determine the trapping sites of trace elements at the surface of Fe-Mn oxides which are efficient scavengers of heavy elements during weathering and alteration. New informations may be derived from the relation between crystal chemical parameters and element transfer during weathering and alteration and with soil formation conditions. These data may also be used for assessing the contamination arising from heavy metals and from radionuclides in the low temperature environments.

Spectroscopic tools are choice methods for investigating crystal chemistry of trace and minor components in minerals. Furthermore, on account on their independence on crystalline state of the material, they can be used for investigating the formation fluids as well as the intermediate products which exist prior mineral crystallization. Spectroscopic methods have been chosen according to the complementary picture they give about mineral crystal chemistry. Synchrotron radiation X-ray Absorption Spectroscopy (XAS), gives information local structure around the various cations building low temperature minerals (clay minerals, iron and manganese oxides) and precursors (solutions, gels). Electron Paramagnetic Resonance (EPR) is a sensitive method (ppm level) which allows to investigate as well the sites occupied by trace elements in clay minerals such as kaolinite as

radiation defects. The examples presented include kaolinite crystal chemistry investigated with EPR, iron oxide formation from aqueous solutions and gels and sorption sites of minor elements on Fe-Mn oxides.

Kaolinites present various paramagnetic centers which are either transition element ions or radiation-induced defects. The information content of EPR spectra of kaolinite concerns mostly the formation conditions of these crystals, as these paramagnetic centers are stable and are memorized in the kaolinite lattice.  $\text{Fe}^{3+}$  or  $\text{Mn}^{2+}$  occur as substituted ions in two distinct sites and as adsorbed outer sphere complexes, respectively. The actual picture is complicated by the presence of iron oxide coatings which cannot always be removed by deferrating treatments and by the perturbation from intimately associated phases as mica. On the other hand, the influence of energetic external radiation on the creation of defect centers has been firmly established experimentally and a quantification of the total accumulated dose investigated in order to use kaolinite as a naturally-occurring dosimeter. Field evidence has also been used to prove the relation with uranium-bearing minerals and the discrepancies observed are interpreted in terms of mobility of short lifetime radioactive elements posterior to kaolinite crystallization. These data, together with geochemical informations as stable isotope geochemistry and with crystallographic data such as in-plane and stacking disorder, allow to decipher among the various generations of kaolinites, a mineral which has otherwise a monotonous chemistry. We thus have now a new tool to think about the genetic relations which exist between the generations of kaolinites constituting weathering profiles and alteration products.

The formation of iron oxides has been investigated using XAS, from the starting ferric ion-containing solution to the final crystalline hematite. The evolution of the local structure around iron is interpreted in terms of the polymerization of isolated octahedra by sharing edges and corners. High polymers lead to ferric gels which may be characterized by a local structure similar to goethite or lepidocrocite. When ageing at 92°C, a specific structure is observed with face-sharing octahedra. This stage represents an intermediate step in the hematite formation from gels, by considering that hematite lattice is obtained by a trioctahedral reorganization of vacancies. Hematite is obtained from the ferric gel by a solid-solid transformation and this transformation may be hindered by impurities such as silica. Indeed similar structures are found in naturally occurring poorly crystalline iron oxides such as Fe-vernadites and feroxyite. Similar studies have also been undertaken on Al-Si amorphous soil components such as allophane and imogolite in order to get data on aluminum surrounding. Finally, Fe-Mn oxides are efficient sorbents and XAS may be used to determine the sites involved in the sorption process, the kind of complexes involved (inner-sphere vs. outer sphere) and the relation with the mineral lattice. The example

of uranium sorption on amorphous iron oxides is presented. Uranium occurs as inner-sphere uranyl complexes bound to the iron octahedra by edge-sharing. One specific structural characteristic concerns the similarity of the corner length in  $\text{FeO}_6$  octahedra and in equatorial oxygens around uranyl groups which favours the fit between both sites. XAS has thus shown the diversity of the "amorphous" iron oxides, which cannot be put in evidence by conventional diffraction-based methods. It also establishes the close relation between microscopic properties (namely local structures) and macroscopic behaviour (phase stability). In short, XAS gives us the key to understand the structural mechanisms governing mineral formation and element trapping at mineral solutions interface.

Spectroscopic data obtained on kaolinites and associated Fe oxides may be used as constraints on the dynamics of soil formation and evolution and of element transfer during alteration. Important applications concern the history of laterites, the behaviour of some heavy metals in low temperature environments and the assessment of radionuclide migration in natural analogs of nuclear waste storage in volcanic tuffs.