Structural defects in layered structures: Their determination and their impact on reactivity

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Clay minerals are layered structures that suffer from various and frequent crystallization faults, including point defects (e.g. layer vacancies and/or isomorphic cationic and anionic substitutions) and stacking defects (e.g. interstratification, well-defined or random stacking faults) that complicate the study of their structure, compared to most of other minerals. Determination of their crystal-structure is even further complicated by the small size of these minerals that possibly result from a "poisoning effect" induced by the presence of foreign cations in their layers.

The determination of the actual crystal structure of clay minerals, in particular the nature and density of structural defects, is however of paramount importance to understand and model clay minerals reactivity[1]. X-ray diffraction patterns of clay minerals often only exhibit 00*l* reflections and a few asymmetrical *hk* bands, while the *hkl* reflections are absent owing to the systematic occurrence of random stacking faults[2] (i.e. turbostratism; random translations in the layer plane and/or random rotation about the normal). To overcome this problem, a mathematical formalism was developed that allows the calculation of X-ray diffraction patterns from structures affected by various density and nature of structural defects, including turbostratism[3]. This development led to a better understanding of the structure from many clay minerals, including layer structure (e.g. nontronite[4]) and, using a complementary analysis of 00*l* reflections, of interlayer water and cations organization [5, 6].

It is however obvious that not only clays suffers from the here above mentioned crystallization defects. Rather, nanocrystalline (i.e. particles smaller than 100 nm) and defective lamellar structures affected by turbostratism are ubiquitous in natural and man-made environments. One can for example cite manganese[7] and iron oxides[8] or nanocrystalline calcium silicate hydrates[9] (C-S-H). The former two are reported to control the fate of many trace elements in the environment, including metals and actinides (in the case of vernadite, a manganese oxide) or oxyanions (in the case of fougèrite, an iron hydroxide). These minerals also often exhibit redox properties (e.g. Mn^{3+}/Mn^{4+} or Fe^{2+}/Fe^{3+}) that enables for the degradation of organic compounds[10] [11]. Contrastingly, C-S-H is not found in natural environments, but is the main hydration product from various types of cement, including ordinary Portland cement, controls main cement chemical and physical properties[12, 13], and exerts a strong control on trace elements mobility. All these minerals and phases have close structural similarities with clays, as already noticed decades ago[14], and thus methods used for the analysis of clay mineral structure are transposable to these phases. As for clays, a sound understanding of the crystal structure from these minerals and phases is a fundamental basis for many applications. First, the nature of point defects determines the type of elements that can be sorbed (typically, in the case of oxides, isomorphic substitutions create a limited layer charge deficit and favour the sorption of alkali and alkali-Earth elements as hydrated outer-sphere complexes, whereas layer vacancies favour the sorption of multivalent elements as inner-sphere complexes) and, second, the density of these defects dictate the overall reactivity.

The present work will review recent applications of the specific method used to model X-ray diffraction patterns from nanocrystalline and defective lamellar structures, and will demonstrate that modelling can be used to retrieve accurate structural information, such as crystallite sizes and interlayer and layer structure, including nature and density of structural defects (Figure 1). The consistency between this method and other spectroscopic (e.g.

synchrotron X-ray absorption spectrometry) or microscopic (e.g. transmission electron microscopy) techniques will be illustrated on nanocrystalline manganese (vernadite) and iron (fougèrite) oxides and nanocrystalline calcium silicate hydrates (C-S-H).
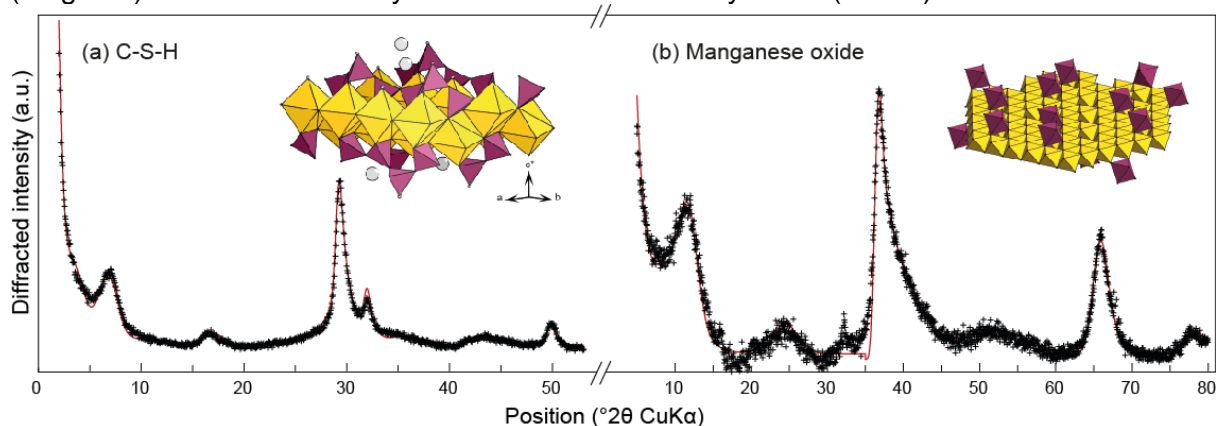

Figure 1. Exemple of refined X-ray diffraction patterns from two nanocrystalline and turbostratic structures: C-S-H[8] (a) and a biogenic manganese oxide[15] (b). In both patterns, crosses are the experimental points and solid lines the calculated patterns. The two insets at the top right of each pattern are sketches of refined layer structures. In C-S-H, layers are built of Ca polyhedra (yellow) with ribbons of wollastonite-like Si tetrahedra (purple) running at the surface. In the manganese oxide, layers are built of Mn octahedra (yellow) and layer vacancies capped by interlayer Mn sorbed as inner-sphere complexes (purple). In both cases, typical crystallite size is 10 nm in the layer plane and 3 to 5 nm perpendicular.

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