Cation vacancies and lattice strain in nano-sized ferrihydrite reveal clues to surface structure

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The large reactive surface area exhibited by the natural nanomineral ferrihydrite makes this phase an important component in many natural aqueous geochemical systems. Recent structural studies using total x-ray scattering methods have revealed new details regarding the complex structural aspects of its interior atoms. Complementary physicochemical and magnetic data have provided further insight into the nature of disorder, in particular, the presence of substantial cation vacancies. Collectively, these results confirm the basic crystal structure of 2-line ferrihydrite and predict a composition of $Fe_{8.2}O_{8.5}(OH)_{7.4}$.

In contrast to the bulk, the structural and compositional aspects of the surfaces of ferrihydrite remain largely unexplored. Although challenging to determine directly, clues regarding links between surface and bulk structures are emerging. For example, size-dependent strain in ferrihydrite, evidenced by anisotropic changes in lattice dimensions, could reflect the restructuring of surface atoms to coordination geometries that differ substantially from those of the interior. The increase in size-dependent strain with decreasing particle size may also be linked to composition and the presence of Fe (III) vacancies totalling ~18% occurring in specific octahedral and tetrahedral iron sites. Surface restructuring and the occurrence of surface defects are expected to be of importance in understanding the reactivity, stability, and transformation of environmental ferrihydrite.

Sol-gel and isotropic/nematic transitions in aqueous suspensions of swelling clay minerals: A structural and rheological study on size-selected particles

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The phase behavior of swelling clay minerals that are strongly anisotropic bidimensional colloids has been studied for nearly one century as these natural materials control various environmental processes and are extensively used in industry. The occurrence of an isotropic/nematic transition in clay suspensions has been debated since Langmuir's pioneering work who reported a macroscopic phase separation in hectorite suspensions. Such a behavior was subsequently rationalized by Onsager on the basis of a competition between orientational entropy and the packing entropy governed by the excluded volume. However, in most clay minerals studied so far, a sol-gel transition is systematically observed, that hinders the I/N transition. Furthermore, the structure and formation mechanisms leading to the gel remain rather ill-defined. By working on various natural clays, nontronites and beidellite, we recently evidenced true I/N transitions occurring at lower concentrations than that of the sol-gel transition. In this talk, we will analyze the influence of particle anisotropy on the phase diagrams. We will focus on the evolution of both the sol/gel and I/N transitions by combining optical observations, SAXS experiments and rheological measurements. We will show that the system is purely repulsive at low ionic strength and that the I/N transition can be rationalized on the basis of Onsager's approach. Though the structure of the gel remains somehow elusive, we will show that some of its rheological features can be understood through an approach based on effective volume fraction and orientational effects.

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