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102 - Crystallite size effects on the structure and physicochemical properties of ferrihydrite

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Abstract: The structure and physicochemical properties of the nano-sized (from 1.6 to 4.4 nm) ferrihydrite samples were systematically investigated by integrating X-ray diffraction (XRD), X-ray pair distribution function (PDF), X-ray absorption spectroscopic (XAS), magnetic analyses and Thermogravimetric (TG). The XRD data of all samples are fitted well with the Michel structure model and their PDF are similar, indicating that the long-range ordered structure does not vary with crystallite size. XAS analysis shows that the ferrihydrite samples also have similar local atomic structure with almost the same Fe-O and Fe-Fe interatomic distances but increasing numbers of neighboring Fe atoms as size increases. Magnetic data indicates that ferrihydrite samples are antiferromagnetic with a ferromagnetic-like moment at the lower temperature (100 K and 10 K), but paramagnetic at room temperature. In addition, magnetization decreases with increasing size, and the smallest sample 2LFh_1 has much higher coercivities (B_c) and magnetization value than the other samples, implying that the surface structure may predominate the changes in magnetism with size for the disordered ferrihydrites. Smaller-sized ferrihydrite has less magnetic hyperfine splitting and a lower unblocking temperature (T_B). Both the amount of physically adsorbed water and micropore volume of ferrihydrite decrease, while the molar ratios of structural OH/Fe and mesopore size increase with increasing size. These varied physicochemical properties as a function of crystallite sizes should be considered in assessing environmental behaviors of ferrihydrite in soils or other environmental systems.