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Coordination study of rare earth elements on Fe oxyhydroxide and Mn dioxides: Part II. Correspondence of structural change to irregular variations of partitioning coefficients and tetrad effect variations appearing in interatomic distances

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ABSTRACT

Experimental distribution coefficients of rare earth elements (REEs) between Fe oxyhydroxides (FeOOH) and Mn dioxide (δ-MnO_2) and solutions [K_D(REE)] exhibit anomalous variations: preferential uptake of light REEs by Mn dioxide, a step-like trend in K_D(REE) in the Er-Tm-Yb-Lu region, and fractionation of K_D(Y) from K_D(Ho). Extended X-ray absorption fine structure (EXAFS) spectroscopy was applied to determine coordination states of Er, Tm, Yb, Lu, and Y adsorbed onto FeOOH and δ-MnO_2 to assess structural changes around the REE site. The structures obtained, combined with previously determined structures of light REEs-sorbed Fe and Mn samples, corresponded to variations found in K_D(REE). The structural parameters in the first coordination sphere suggest that La, Pr, and Nd adsorbed onto δ-MnO_2 have a distorted tenfold-coordination sphere and differ greatly from La-, Pr-, Nd-, and Sm-sorbed FeOOH, which have a mixture of eightfold- and ninefold-coordination spheres. In contrast, heavy REEs including Y adsorbed onto Fe and Mn samples' local structures have an eightfold-coordination sphere. The preferential uptakes of light REEs by δ-MnO_2 are explained by the structural change. The irregular variations of heavy REEs and Y fractionation from Ho in K_D(REE) do not, however, correspond to any change found in the coordination sphere. During characterization of the first coordination sphere, the W-type tetrad effect appears in the series variation of interatomic distances of REE^{3+}_{aq} and REE-sorbed FeOOH and δ-MnO_2. The occurrence of a tetrad effect indicates that the interatomic distances relate not only to the electrostatic field but also to a quantum field.

Keywords: X-ray absorption spectra, rare earth elements, iron oxyhydroxide, manganese dioxide, structural change, tetrad effect, Y fractionation from Ho