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SORPTION MECHANISMS OF LANTHANUM ON OXIDE MINERALS

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Abstract—The retention of hazardous species, including many of the lanthanides, on soils and sediments is vital for maintaining environmental quality. In this study, high-resolution transmission electron microscopy (HRTEM) was used to identify surface precipitates of La and their degree of atomic ordering on oxides of Mn (birnessite), Fe (goethite) and Ti (rutile) over a pH range of 3 to 8. At pH > 5.5, the aqueous concentration of La was fully depleted by all three metal-oxides. On birnessite, surface precipitation of La-hydroxide occurred at pH ≥ 5 and appears to be the dominant sorption mechanism on this mineral. Surface precipitation was not observed on rutile or goethite until much higher pH values, 6.5 for rutile and 8.0 for goethite. Precipitation is thus correlated with the points of zero charge (PZC) of the minerals, 6.3 for rutile and 7.8 for goethite, and in each case was observed only at pH values above the PZC. Although La sorption was extensive on all of the minerals at the higher pHs, the depletion of La from solution by rutile and goethite at pH values well below the PZC indicates that the sorption mechanism differs from that on birnessite. While surface precipitation was found to be the dominant sorption mechanism of La on birnessite, surface complexation of monomeric or small multinuclear species appears to predominate in La retention on rutile and goethite at most commonly encountered pH values.

Key Words—Electron microscopy, Lanthanum, Metal-oxides, Sorption.

INTRODUCTION

Continuing increases in environmental contamination impart great importance to understanding reactions of hazardous species with clay minerals in soils and sediments. Radionuclides and their derivatives, such as many of the lanthanides, are of particular concern due to the longevity and extreme toxicity of many of these species. Reactions that remove such contaminants from the mobile aqueous phase in surface environments diminish their risk. However, the strength of retention and potential for re-mobilization must be known in order to properly assess the risk imposed by the retained species. Accordingly, the sorption mechanism of a contaminant on soil materials must be determined to ascertain the stability of the sorbate.

Although oxides, oxyhydroxides and hydroxides often comprise only a small fraction of the solids in soils or sediments, their reactivity, propensity for forming structural coatings, and high surface areas make them very influential in the sorption of hazardous species. Ion retention on hydrous oxides can be accomplished through various processes which include absorption, adsorption (an isolated surface complex), surface polymerization, surface precipitation (a 3-dimension growth pattern of a multinuclear surface phase) or precipitation of discrete particles. The term sorption is used here to denote retention without implications as to the mechanism. The potential for remobilization of a sorbate will depend upon the sorption mechanism and ultimately its chemical composition, structure and surface morphology (Hochella 1990). The composition and structure will dictate the bond strength of the sorbate while the surface morphology determines the fraction of the sorbate exposed to the interfacial fluid. The morphology is only important for multinuclear surface species. For a sorbate with a uniform composition at less than monolayer coverage, a clustered precipitate may be more stable than a distributed one because the former will have a lower exposed surface area. However, at coverages greater than monolayer coverage the converse is true: a clustered precipitate will have a greater exposed surface area and thus be more reactive. Therefore, it is necessary to determine the sorption mechanism of a sorbate in order to assess its retention strength.

Traditionally, macroscopic methods have been used to determine sorption mechanisms and the surface structures of sorbed species. Although meaningful and important information on sorption phenomena has been obtained with these approaches (Hayes and Leckie 1986), they do not directly provide molecular level information. Therefore, for further understanding on a microscopic level one must employ techniques that directly yield sub-nanometer information on surface reactions. Recent advances in such techniques have greatly enhanced the ability to discern sorption mechanisms in colloidal systems.

In this study, the sorption of La on various metal-oxides common to soils and sediments was investigated. Our objective was to employ an atomic-scale experimental technique, high-resolution transmission electron microscopy (HRTEM), as well as more traditional bulk analysis, to glean information on the sorption processes of the lanthanide elements, using La as a model. Knowledge of lanthanide retention in the environment is important because it limits the mo-

Table 1. Selected properties of the birnessite, goethite, rutile minerals studied.

Mineral	Surface area (m²/g)¹	PZC²	Reference
Birnessite	223	2.7	Fendorf and Zasoski (1992)
Goethite	52	7.8	Atkinson et al. (1968)
Rutile	44	6.3	Fendorf et al. (1992)

[1] EGME.

[2] Determined by potentiometric titrations and electrophoretic mobilities.

bility and bioavailability of these elements produced in significant amounts during the fission of uranium and plutonium reactor fuels, for example, ^{144}Ce, ^{147}Pm, ^{152}Eu, and ^{154}Eu (Brookings 1984; Rard 1988). The HRTEM technique was employed to discern surface structural modifications of oxides after reacting with La, and to determine the nature and spatial distribution of such modifications when present. The results derived from these analyses provide the detailed information necessary to assess the retention strength of La sorbed on metal-oxides.

MATERIALS AND METHODS

Batch Sorption Studies

Batch studies were performed to determine the quantity of La sorbed on birnessite (δ-MnO$_2$), goethite (α-FeOOH) and rutile (TiO$_2$). These oxides were chosen because they are common in many soils and sediments and possess a range of chemical/physical properties, thereby allowing the effects of surface properties on the sorption mechanism of La to be investigated. Selected properties of the specific materials synthesized are listed in Table 1. The surface area of these minerals were determined by the ethylene glycol monoethyl ether (EGME) method (Heilman et al. 1965). The PZC's were determined by potentiometric titrations using 0.01 N HNO$_3$ and NaOH and electrolyte strengths of 0.1, 0.01 and 0.001 M NaNO$_3$, and by measurement of their electrophoretic mobilities as a function of pH in 0.1 M NaNO$_3$ (Akeson et al. 1989).

For the batch experiments, suspensions of 167 m^2 L^{-1} hydrous oxide were made by dispensing the material into 30 mL of 0.1 M NaNO$_3$. The oxides were then allowed to hydrate for 24 h. Reactions were initiated by adding La as a nitrate salt to the systems; a La concentration of 1000 μM was used. The reactions were performed over the pH range of 3 to 8. A 20 mM La(NO$_3$)$_3$ stock solution was used to obtain the desired La concentration, and HNO$_3$ and NaOH were used to adjust the solution pH, which was maintained constant during the reaction period.

Following initiation, the reacting systems were placed on a rotary shaker for 72 h at 25°C. After this reaction period the suspensions were separated by filtering through a 0.22 μm pore membrane. The effluent solutions were analyzed for total La with a Beckman 50U Spectrophotometer at 353 nm. The filtrate was then rinsed with 20 mL of distilled, deionized water in preparation for TEM analysis.

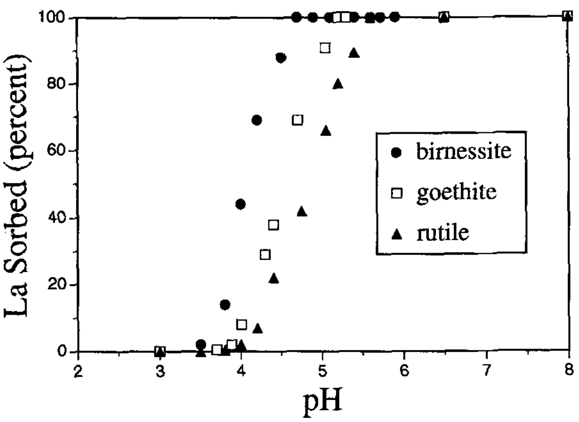

Figure 1. Sorption isotherms of La on birnessite, goethite and rutile with an initial La concentration of 1000 μM.

Microscopic Analysis

Reacted oxides, prepared as described above, were used for HRTEM analysis. After rinsing, the isolated solids were suspended in deionized water and then dispersed on a holey carbon film supported by a copper-mesh grid. After the reacted solids were mounted on grids, the specimens were air dried. Transmission electron microscopy was performed using Hitachi H-9000NAR and Topcon 002B transmission electron microscopes operating at 300 and 200 keV, respectively. Samples from each system were analyzed with both microscopes and those deemed to be most representative of the surface are shown. No significant differences occurred between the images obtained from the two microscopes. Surface structures of the reacted materials were compared with those of the unreacted solids in order to determine what alterations, if any, had been caused by the introduction of La.

RESULTS

The sorption of La on birnessite, goethite and rutile is shown in Figure 1. At pH < 3.5, only limited amounts of La sorbed on all three oxides. As the pH increased, a sharp and dramatic increase in sorption, the sorption-edge, was observed. The sorption edge on all the oxides occurred between pH 3.5 and 5.5 (Figure 1). Therefore, it is apparent that regardless of the type of oxide, the retention of La increases with pH, and above pH 5 sorption is sufficient to effectively deplete the aqueous concentration of La.

To further explore the relation between the sorption edge and retention mechanism of La, we employed HRTEM. Figure 2 shows electron micrographs of birnessite before and after reacting with La at pH 5. In

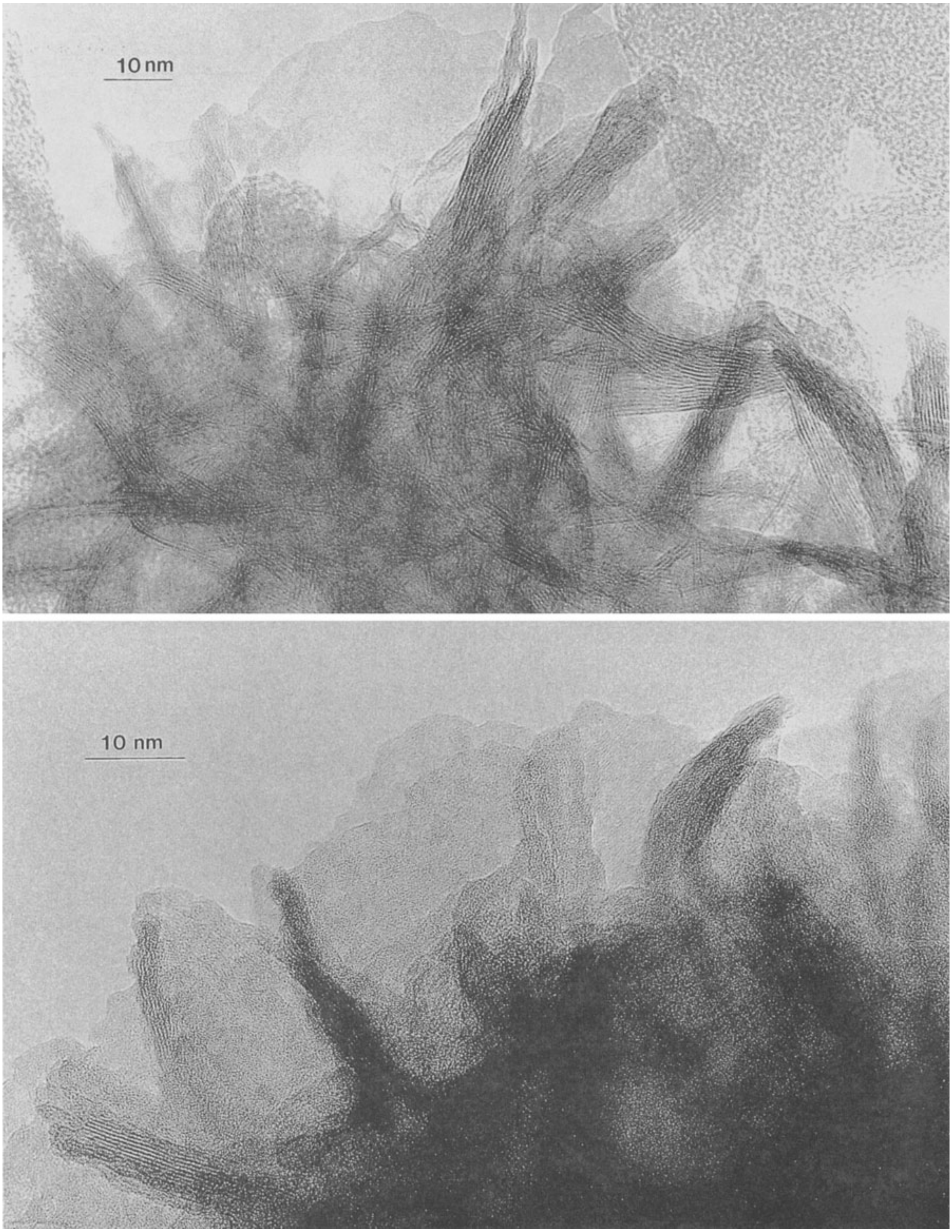

Figure 2. Transmission electron micrograph of (a) unreacted birnessite and (b) after reacting with La at pH 5.

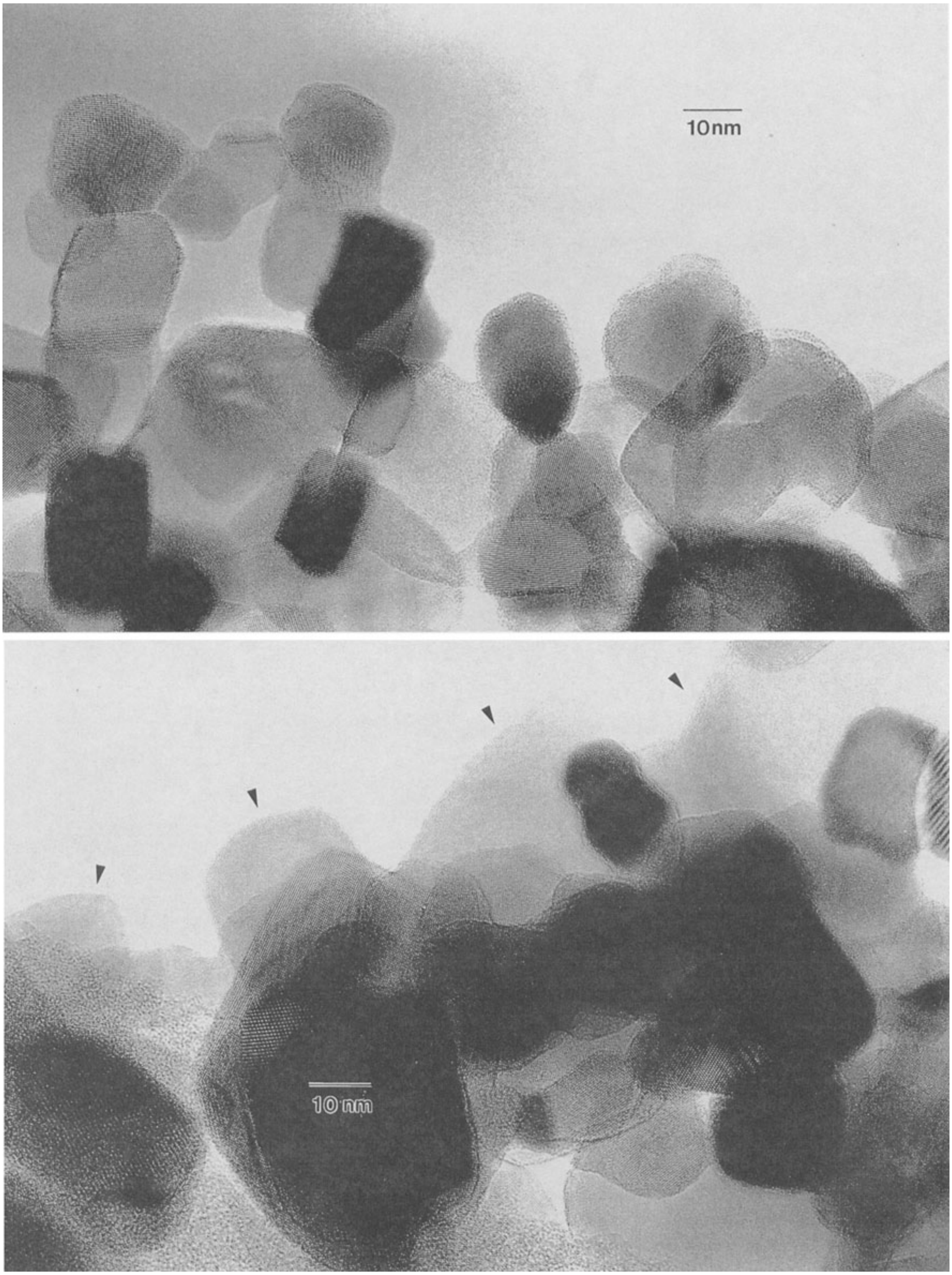

Figure 3. Surface structure of rutile as shown by HRTEM before reacting (a) and after reacting with La at pH 7 (b). Certain exposed crystallographic faces induce preferential growth of a lanthanum hydroxide surface precipitate (marked by arrows in b).

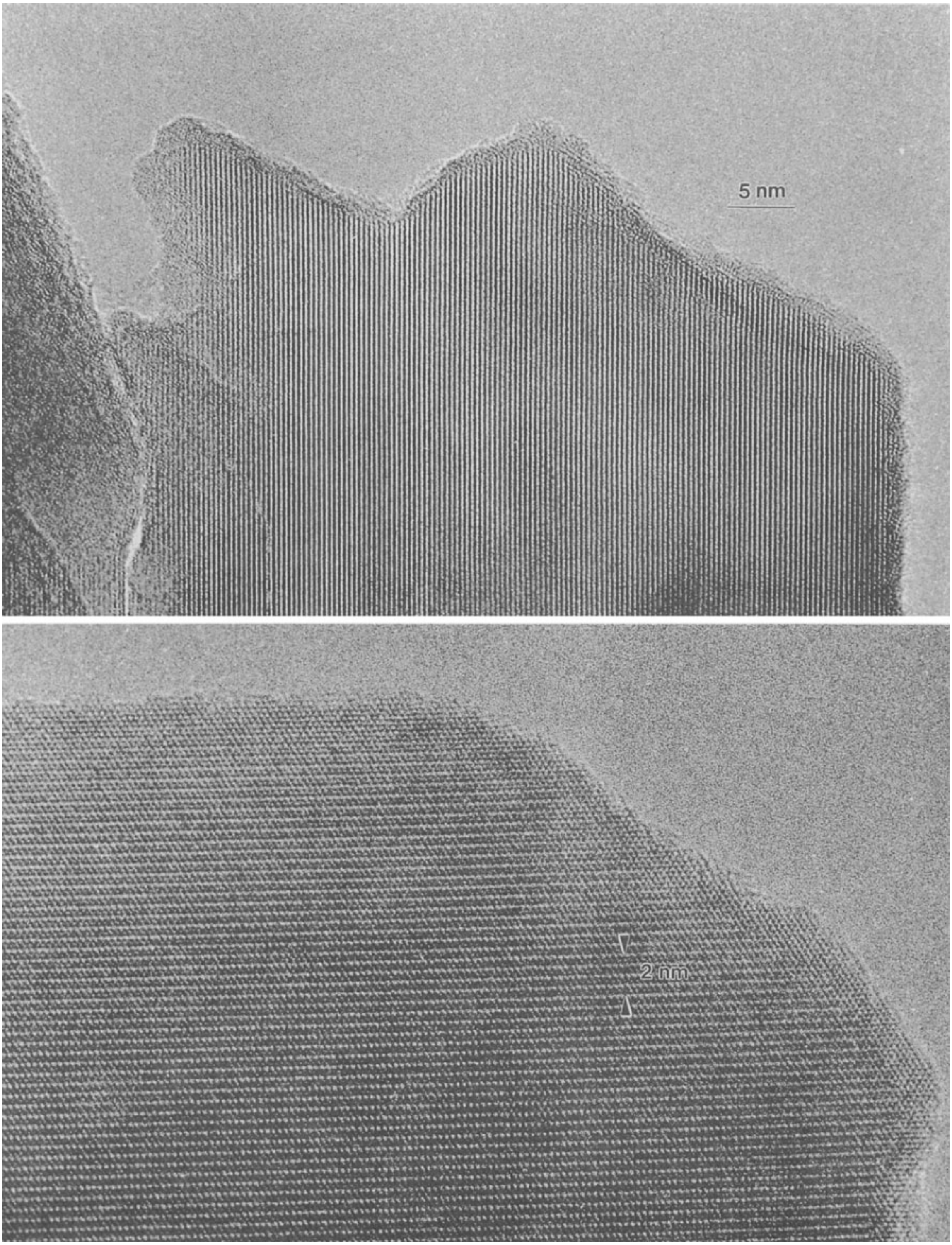

Figure 4. Transmission electron micrograph of goethite: (a) the unreacted (1$\bar{1}$1) surface; (b) along the [100] direction after reacting with La at pH 7.5; and (c) the (20$\bar{1}$) surface after reacting with La at pH 8.0. Significant surface deposition is only noted in (c).

Figure 4. Continued.

the unreacted material, the characteristic 'balls-of-needles' type structure (McKenzie 1977) can be seen. The birnessite needles possess a high degree of short- and medium-range order, as evidenced by lattice fringes visible in Figure 2a, but do not exhibit the long-range periodicity of a truly crystalline material.

After reacting with La at pH 5, a change in the surface structure of birnessite was apparent (Figure 2b). Needles protruding out of the particle centers no longer have clean atomically-ordered surfaces. Rather, an amorphous phase was deposited on the surface, which in some areas formed an extensive coating on the birnessite needles. Furthermore, reductions in overall image sharpness and clarity indicate that the beam had passed through an incoherently scattering, that is an amorphous, layer. Thus, HRTEM reveals that the original birnessite particles are coated on the top and bottom surfaces of the imaged material as well as around the edges. The precipitated material is most likely a hydrated lanthanum hydroxide: $La(OH)_x \cdot nH_2O$.

In contrast to the behavior of reacted birnessite, rutile did not exhibit extensive surface deposits of lanthanum hydroxide at pH 5. Particle surfaces remained clean and highly crystalline at this pH, although hints of small amorphous clusters were seen in isolated areas. High-resolution images show that, before reacting, the rutile phase is composed of well-crystallized, faceted grains with edges free of amorphous material (Figure 3a). At pH 7.0 a new amorphous surface phase can be discerned, which is expansive in areas of the imaged material (Figure 3b). These deposits are not as uniformly distributed over the surface as was observed for birnessite, but rather form partial coatings of individual particles as well as bridges between the rutile grains. Even when extensive deposits are present, many of the rutile faces appear to be unaltered, that is, there appears to be a crystallographic preference of the surface precipitate.

The surface reactions of La on goethite are somewhat similar to those on rutile. Even at pH 7.5, no significant alteration of the goethite surface was observed (Figure 4a). The highly crystalline, acicular goethite shards remained essentially unaltered after reaction with La throughout most of the pH range investigated. Possibly, small deposits may have formed on areas of the surface at pH 7.5. At pH values between 5.0 and 8.0, we occasionally noted a uniform layer coating the surface that is at most, only a few monolayers thick. However, up to pH 7.5 there is no indication of a significant surface precipitate as was observed on the other oxides studied (Figure 4b). A definite surface precipitate finally appears on goethite at pH 8.0 (Figure 4c). The precipitate aggregated into discrete particles attached to the surface rather than forming a layer distributed across it. Large areas of the goethite surface remain predominantly free of surface deposits even at this high pH (Figure 4c). The morphology of the precipitate and the sharp, well-defined boundary between it and the goethite surface indicate that a self-nucleated precipitation mechanism is probable, in which physical proximity allowed the developing precipitate to adhere to the surface. That is, the goethite surface does not appear to have catalyzed La-hydroxide precipitation. Using the Davies equation to correct for ionic strength effects on the activity of La and thermodynamic data from Smith and Martell (1976), one would expect $La(OH)_3$ to become saturated at pH 8.65 with a solution La concentration of 1000 μM. Thus, the solution is near saturation with respect to $La(OH)_3$ when precipitation is observed on goethite. This was not the case for rutile or birnessite, where surface precipitation occurred at pH values well below solution saturation with respect to $La(OH)_3$.

DISCUSSION

Generally, the retention of hydrolyzable ions increases dramatically with increasing pH (Schindler and Stumm 1987) and this was found to be the case for La on the oxides of Fe, Mn and Ti. The extent of La sorption on surfaces of goethite, birnessite and rutile was similar, but the sorption mechanisms differ markedly for each mineral. The sorption-edge of La on these surfaces was not correlated with the PZC of the mineral (Figure 1; Table 1). However, the PZC does appear to coincide with the onset of surface precipitation. Precipitation was observed at the lowest pH value on birnessite (Figure 2), then rutile (Figure 3) and on goethite (Figure 4) at the highest pH values investigated, following the trend of the PZC values for these materials. Therefore, it appears that the strength and sign of the electrified interface plays a fundamental role in controlling the surface precipitation of La but not in controlling the extent of its sorption.

Although surface precipitation was observed on all three oxides, the precipitates have different morphologies. On birnessite, which has needles that bend and twist among themselves, the precipitate distributes over the surface (Figure 2); no dominant surface plane is provided to allow for a preferential growth direction. Quite the opposite occurs for the sorption on rutile (Figure 3). The HRTEM images suggest La-hydroxide grows in relation to surface planes and that the specific, exposed rutile crystallite faces influence the amount and location of surface precipitation. However, the rutile grain size in our samples was extremely small (~ 10 nm), and larger, oriented single crystals would be needed to make a more definitive assessment of the relation between crystallographic orientation and precipitate growth. For goethite, the precipitate appears to be self-nucleated rather than surface catalyzed, as indicated by its particle-like morphology (Figure 4).

The onset of surface precipitation appears to account for the sorption-edge on birnessite. That is, surface precipitation rather than surface complexation (adsorption) dominates the sorption process throughout the sorption isotherm. In contrast, HRTEM analysis reveals that there are no apparent surface deposits on rutile or goethite at pH values corresponding to their respective sorption edges, and surface precipitation is only observed at pH values well above the sorption edge. This indicates that for rutile and goethite the dominant sorption mechanism is different from that for birnessite. In these two cases, precipitation is restricted on surfaces maintaining net positive charges, and when a pH is reached that causes charge reversal, La forms a surface precipitate. Since the concentration of La in solution is depleted well below these pH values, the surface moieties of La on rutile and goethite below the PZC must be produced by complexation or small multinuclear surface species.

In fact, it is commonly observed that many hydrolyzable ions are sorbed against an electrostatic gradient below the PZC. This was the case for La sorption on rutile and goethite. While many of the hydrolyzable ions, for example Cr(III) and Al(III), form strong inner-sphere complexes on hydrous oxides, La would be expected to form a weaker complex due to its large hydrated radius, especially when compared to Al and Cr. Nevertheless, the chemical affinity of the oxides overcomes the electrostatic repulsion of a net positively charged surface. As a consequence, retention becomes appreciable even at pH values below the PZC. Therefore, the chemical affinity of the oxides must dominate the sorption process of La on goethite at pH < 7.8 and on rutile below pH 6.3.

The HRTEM images clearly indicate that surface precipitation of $La(OH)_3 \cdot nH_2O$ on birnessite and rutile occurred before bulk precipitation from solution. Furthermore, the conditions producing precipitation varied between minerals. The presence of surfaces may support surface precipitation in two ways, complexation (Fendorf et al. 1994) and electrostatic charge effects (James and Healy 1972a, 1972b). Both phenomena alter the hydration environment, the hydration sphere, of the sorbing ion and catalyze cation-hydroxide precipitation. For La sorption on minerals that possess a strong negative surface charge, as would be the case for birnessite under these reaction conditions, electrostatic effects will dominate the catalysis of surface precipitation by effectively lowering their solubility relative to the bulk solution. Murray and Dillard (1979), using thermodynamic developments of James and Healy (1972a, 1972b), estimated that the K_{sp} (solubility constant) of $Co(OH)_2$ was lowered more than 100 times at the birnessite/solution interface relative to that in the bulk solution. Accordingly, based on this electrostatic model one would expect surface precipitation at the absorption edge for birnessite but not for rutile or goethite, which is in agreement with our observations.

We conclude that appreciable sorption of lanthanides on oxides will occur at pH values, ranging from 5 to 8, commonly encountered in the surface environment. Surfaces of the three oxides studied exhibited markedly different effects on precipitation and, thus, on the sorption mechanism of La. Because the sorption mechanism varies with each specific oxide, the strength of retention will also depend on which sorbent is present. Birnessite clearly had the most significant effect on the catalysis of La-hydroxide precipitation, with extensive precipitation observed on the surface at pH ≥ 5. On rutile, both surface-complexed and precipitated La must be considered, and on goethite, surface-complexed La appears to be most significant.

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