XANES studies at the Al K-edge of aluminium-rich surface phases in the soil environment

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Aluminum is highly abundant in the Earth's crust where it is present in a wide variety of primary and secondary aluminosilicate minerals, amorphous phases, and aqueous solution species. The speciation and coordination of Al in many of these phases, particularly those that are X-ray amorphous or present as thin surface coatings, are often unknown or based on indirect methods. We have utilized aluminum K-edge XANES in a study of the nature of several such phases, specifically the aluminum rich phases present in soils on the surfaces of quartz and feldspar grains in loess, and aluminum substitution in iron oxyhydroxides. In addition, the sorption products of Al-(oxy)hydroxides on synthetic α-Al_2O_3 (0001) surfaces were investigated along with model compounds. Analysis of our data suggests that the Al-rich surface phase on quartz grains in loess is gibbsite-like, while Al sorbed on synthetic quartz is boehmite-like. Surprisingly, Al substituted in goethite appears to be more similar to gibbsite than to diaspore, which is isostructural with goethite. The experimental data for corundum and Linde alumina show good agreement with calculated Al K-edge spectra from a developmental version of the full multiple scattering code FEFF8 using clusters of up to 66 atoms

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1. Introduction

Aluminum is the second most abundant cation in natural solids in the Earth's crust, where it is typically tetrahedrally and/or octahedrally coordinated by oxygen in a variety of crystalline aluminosilicates. Weathering of these phases often results in concentration of aluminum in secondary phases such as clays, aluminum oxyhydroxides, and hydroxides. Aluminum is also commonly present in thin surface coatings on primary phases such as quartz and feldspar in soils, and it substitutes for Fe(III) in a variety of crystalline and poorly crystalline iron oxides and oxyhydroxides in soils.

Sorption reactions involving Al(oxy)hydroxides at solid-aqueous solution interfaces can affect the properties of pollutant species in natural waters by reducing their bioavailability and toxicity. The toxicity of aqueous Al(III) to plants and organisms depends strongly upon its speciation; for example the tridecamer form of Al(III) in solution is considerably more toxic than the

hexa-aquo Al(III) solution complex (Bertsch and Parker, 1996). The speciation of Al(III) (coordination number, molecular structure, physical form, phase identity) in these secondary phases as well as in aqueous solutions is often unknown or based on indirect information. Synchrotron-based XAFS spectroscopy has become one of the methods of choice for studies of sorption at solid surfaces because it provides unique, element-specific information on the nature of these surface complexes or precipitates even when present at submonolayer surface coverages.

Much of our past research on the sorption of aqueous metal ions on mineral surfaces has focused on model systems using pure phases [e.g., (Brown *et al.*, 1998)] in order to develop a fundamental understanding of the mechanisms of sorption. However, these systems do not necessarily allow simulation of interfacial reactions occurring in the natural environment because they neglect the surface coatings and substitutional impurities found in natural samples. Thus our past studies and those of other groups may not have addressed important chemical effects resulting from these coatings and impurities. For example, Al(III)-rich surface phases on soil particles can dramatically affect the way these particles interact with heavy metals and organic compounds in aqueous solutions relative to the pristine soil particle surface because the Al(III)-rich surface phase may have a very different reactivity relative to the substrate. Similarly, the presence of Al(III) substituted for Fe(III) in iron oxyhydroxides can have a major effect on the uptake of aqueous metal ions (Ainsworth *et al.*, 1985; Ainsworth *et al.*, 1989; Cornell and Schwertmann, 1996). In both cases, very little is known at an atomistic level about the reason for these effects. To provide some of this atomistic-level information, we have undertaken an Al K-edge XANES study of Al-rich coatings on a natural loess samples and synthetic quartz single crystals as well as Al-substituted goethites. The local structural environment of Al in these materials has been analyzed by comparison of these spectra with spectra from various model compounds (Table 1).

Table 1
Names, formulae and coordination numbers of aluminum containing minerals discussed in this work.

Mineral Name	Formula	CN
Corundum	α-Al_2O_3	6
Topaz	$Al_2SiO_4(F,OH)_2$	6
Montmorillonite	$(Al,Mg)_8(Si_4O_{10})_4(OH)_8.12\ H_2O$	6
Gibbsite	$Al(OH)_3$	6
Kaolinite	$Al_2Si_2O_5(OH)_4$	6
albite	$NaAlSi_3O_8$	4
gamma alumina	γ-Al_2O_3	4, 6
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	4, 6
Linde alumina	α-$Al_2O_3 + \gamma$-Al_2O_3	4, 6
Kyanite	Al_2SiO_5	4, 6
Hydrotalcite	$Mg_6Al_2(OH)_{16}CO_3.\ 4H2O$	6
Goethite	α-FeOOH	6(?)
Diaspore	α-AlOOH	6

2. Experimental

Mineral samples used as standards were obtained from the Stanford Mineral Collection. The montmorillonite, gibbsite, kaolinite, γ-Al_2O_3 and Linde alumina standards were powdered samples, while the remainder of the standards were single crystals. Loess samples were collected in Göttingen, Germany and have been characterized by XPS and other techniques. A previously synthesized and characterized set of Al-substituted goethites ({Al/Al+Fe} from 1 to 9 mol %) were studied. Al-(oxy)hydroxide phases were sorbed onto a synthetic SiO_2 (0001) sample by immersion in a partially base hydrolyzed 10^{-4} M $AlCl_3$

solution for a total of 24 hours. Under these conditions, polymeric Al species are present (Bertsch and Parker, 1996).

All experimental data were collected on beamline 3-3 at SSRL utilizing YB_{66} monochromator crystals (Wong et al., 1990). Data were collected as total electron yield at a minimum pressure of 10^{-7} torr. Samples were mounted on a stainless steel holder with double-sided adhesive tape. To minimize sample charging, a conductive paint (Acheson DAG154) was applied to sample and holder. Energy calibration was periodically checked against an Al foil. Slits prior to and following the monochromator were adjusted until the desired resolution was obtained.

3. Results and Discussion

3.1 Model Compounds

Spectra of model compounds of aluminum exhibiting four- and six-coordination by oxygen are shown in Figure 1 and are listed in Table 1. The spectra are in good agreement with previous studies (Brown et al., 1983; McKeown et al., 1985; Wong et al., 1994; Ildefonse et al., 1994; Li et al; 1995; Fröba et al., 1996; Ildefonse et al, 1998) and show energy resolution with the YB_{66} monochromator comparable to that obtained using $(10\bar{1}0)$ quartz monochromator crystals in earlier studies (e.g., (Brown et al., 1983)).
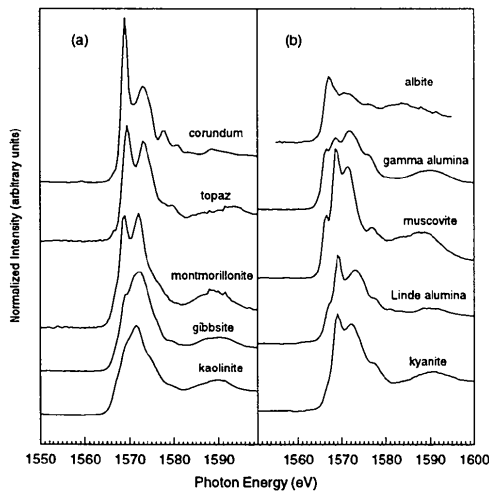

Figure 1
Al K-edge XANES spectra for a variety of aluminosilicate phases with Al in differing oxygen coordination environments; (a) six-fold coordination; (b) four-fold (albite) and mixed four- and six-fold coordination.

3.2 Al-rich surface phases on quartz and feldspar grains in loess

Loess is a fine-grained, glacially derived, wind-blown sediment that forms extensive deposits in the central United States, Europe and China, among other locations during the ice ages. The major mineral components of loess deposits are quartz, feldspar, and clays. XPS studies show that an Al(III)-Si(IV)-rich phase coats the surface of quartz and feldspar grains, and that the thickness of the covering decreases with depth in the loess deposit. These surface phases have different properties relative to the substrate, including increased reactivity relative to the host quartz or feldspar substrate. An understanding of the nature of these surface coatings is essential for understanding the processes of weathering and soil formation. Al K-edge XANES spectra were

used to characterize these layers and to investigate stratigraphic differences in a 3.2 meter deep profile from Göttingen, Germany.
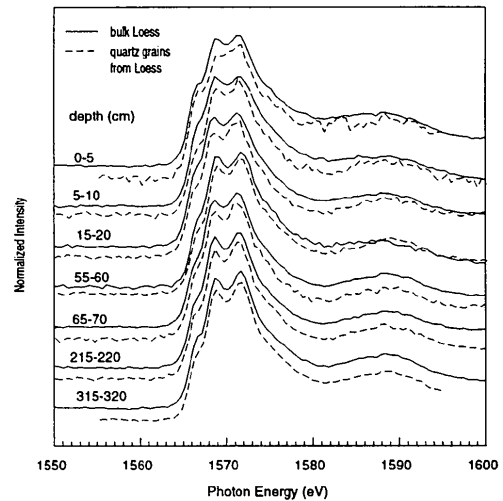

Figure 2
Al K-edge spectra of samples from a 3.2 m deep loess profile. Vertical distribution and comparison of quartz separates to bulk.
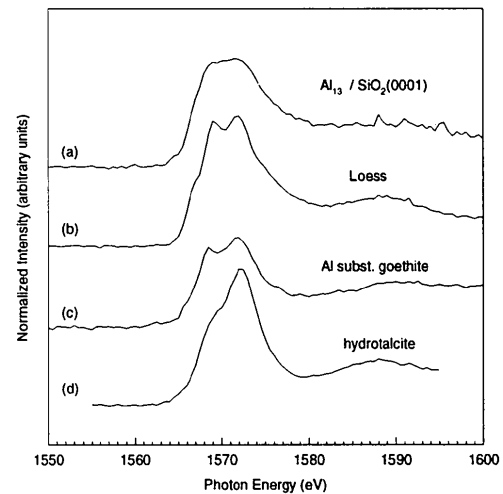

Figure 3
Al K-edge XANES spectra of samples where the aluminum coordination was to be determined.

Figure 2 shows the Al spectra for both the bulk loess samples and quartz grains separated from the bulk as a function of depth. There is little difference between spectra of the bulk loess sample and the quartz grains, indicating that the nature of the coating is similar throughout the soil. It is interesting to note that while the XPS depth profile experiments have shown that the coating thickness decreases with depth in the deposit, the nature of the surface phase does not change. This provides strong evidence that the surface phases were formed on the loess grains following deposition by interaction with Al and Si present in groundwater. The Al XANES spectra for the loess samples are similar to both the montmorillonite and muscovite spectra but show closest agreement with the previously published XANES spectra of dioctahedral illite/smectite mixed layer minerals (Ildefonse et al, 1998), although the coating contains less K than any of these phases based on XPS analysis.

A sample of Al-(oxy)hydroxide on synthetic quartz was prepared for comparison with the Al-rich coatings on the quartz

grains in the loess. The spectrum of this sample is shown along with a representative loess spectrum, in Figure 3(a) and (b) respectively, and shows poorly resolved features, somewhat consistent with the spectrum of boehmite (γ-AlOOH) (Ildefonse *et al*, 1998).

3.3 Al substitution in goethites

The spectrum for an Al-substituted goethite (Fig. 3c) shows a strong similarity to that of gibbsite, rather than the isostructural diaspore as also suggested recently (Ildefonse *et al*, 1998). This provides evidence that at low aluminum concentrations a AlOOH-FeOOH solid solution may not be present.

3.4 FEFF8 simulation of the Al K-edge NEXAFS spectrum of corundum

Simulation of the corundum spectrum using an experimental version of the full multiple scattering (FMS) code FEFF8 (Ankudinov *et al.*, 1998) was performed. Figure 4 shows some preliminary results from these calculations: (a) the experimental spectrum for a single crystal corundum sample, (b) FEFF8 result for a 66 atom cluster, considering an oriented single crystal sample, (c) FEFF8 result for the same cluster, neglecting orientation of the single crystal sample, (d) the experimental spectrum of Linde alumina (mixed α- and γ-Al_2O_3). There is reasonable agreement between the simulations and the data in terms of peak position, if not absolute intensities for both single and polycrystalline samples.
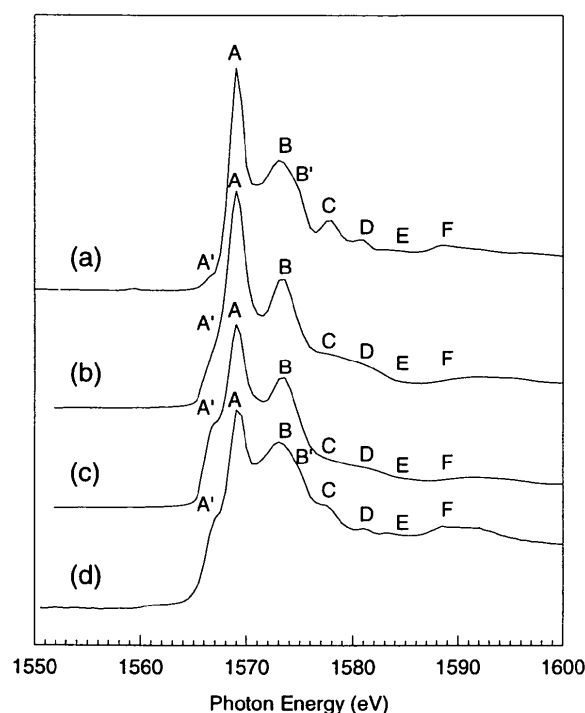

Figure 4
Comparison of experimental XANES spectra for corundum with simulation using FEFF8.

Calculations with larger clusters are being performed, the results of which will be reported elsewhere. The results of our calculations using a 66 atom cluster do not show the same level of resolution as the recent Al K-edge XANES simulation of corundum using a 164 atom cluster by Caberet *et al.* (1996) using the CONTINUUM code. However all of the relevant features except for B' (at the high energy side of B) are reproduced in our

FEFF8 simulations, and the B feature in our calculated spectrum is a good match with the energy of the B feature in the experimental spectrum.

4. Final Remarks

Aluminum K-edge XANES is an extremely useful tool for providing atomistic level information on phases found in the soil environment.

The aluminum rich surface phases found on quartz and feldspar grains in loess deposits was determined to be gibbsite-like. In contrast, Al coatings on a synthetic quartz (0001) surface are similar to boehmite rather than gibbsite.

The spectrum of aluminum substituted goethite appears similar to gibbsite, providing evidence that at low concentrations aluminum does not substitute directly for iron, as it does at higher concentrations.

Preliminary calculations for corundum and Linde alumina using FEFF8 show good agreement with the experimental spectra.

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