GIXAFS study of Fe³⁺ sorption and precipitation on natural quartz surfaces

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Grazing- incidence EXAFS has been used to characterize the structure of Fe^{3+} sorbed onto natural single crystal quartz surfaces. Fe^{3+} sorption at ca. 5% monolayer coverage on a natural crystal allowed to equilibrate in air resulted in formation of hematite nuclei with strong texturing on r- and m-planes. EXAFS calculations suggests that both O and Fe backscattering is necessary to yield acceptable structural models, that about 50% of the sorbed iron resides in nuclei, and that the approximate dimensions of the nuclei can be estimated via Feff 7.0 calculations of various nuclei sizes and shapes.

Keywords: **quartz surfaces; GIXAFS; sorption; Fe³⁺**

1. Introduction

Although aqueous ferric complexes are known to sorb strongly onto the quartz surface, little is known about the geometry of surface complexes or precipitates. In natural soils and aquifers, nanometer thin films of iron and aluminum oxides and hydroxides often cover quartz grains providing an efficient and high surface area sorbant for environmental toxins and metal contaminants (Coston et al., 1995). In these cases, and perhaps generally, metal ion sorption can be dominated by surface reactions with the oxide coatings (Davis and Kent, 1990; Sposito, 1984). Hence a knowledge of the structure of such films, their formation, and properties is valuable for estimating species transport and retention characteristics in natural systems. In particular, a better understanding of the role of drying in the growth of thin surface oxide films, and how this may affect sorbed metal complexes, is required. Surface studies of sub-monolayer to multi-monolayer coverages of Fe^{3+} aqueous complexes and polymers on quartz surfaces using XAS methods offer an approach that can shed light on these areas.

2. Experimental Details

The GIXAFS sample was prepared from 200 micromolar ferric chloride solutions adjusted to a pH of 2.75. The natural crystal (a large "Herkimer Diamond" with highly perfect crystal faces) was cleaned to remove both organics and trace inorganics then immersed in the sorption solution for three hours. XPS measurements to determine surface Fe levels were done prior to sorption and after XAS work. No detectable Fe was observed on the original cleaned crystal. Sorption density was estimated at 5-10% of a monolayer of Fe³⁺ by comparison to standards. This range is consistent with monomer sorption according to earlier bulk studies (Anderson et al., 1984).

GIXAFS data was collected at SSRL on beamline 6-2. The line was used in focusing mode with Si (111) monochromator crystals. Energy calibration was done by periodic scans of an iron foil sample. Monochromator shift was less than 1 eV over the term of the experiment. Energy

resolution was estimated to be 4 eV. The Biotechnology GIXAS apparatus was used to orient and manipulate the samples. Incident beam slits for GIXAFS were set at 100 microns height to prevent the x-ray beam from striking the front edge of the sample. Fine sample alignment was done using reflectivity scans, and data collected about 10-20% below the critical angle peak in the fluorescence to minimize sample penetration. All GIXAFS data were collected in fluorescence mode with an intrinsic 13 element Ge detector system windowed to accept only Fe K-alpha fluorescence. 40-90 individual (900 seconds each) scans were needed to produce an average spectrum with maximum useful k of 10-12 $Å^{-1}$. Analysis was done with the use of Feff 7.0 and Exafspak software.
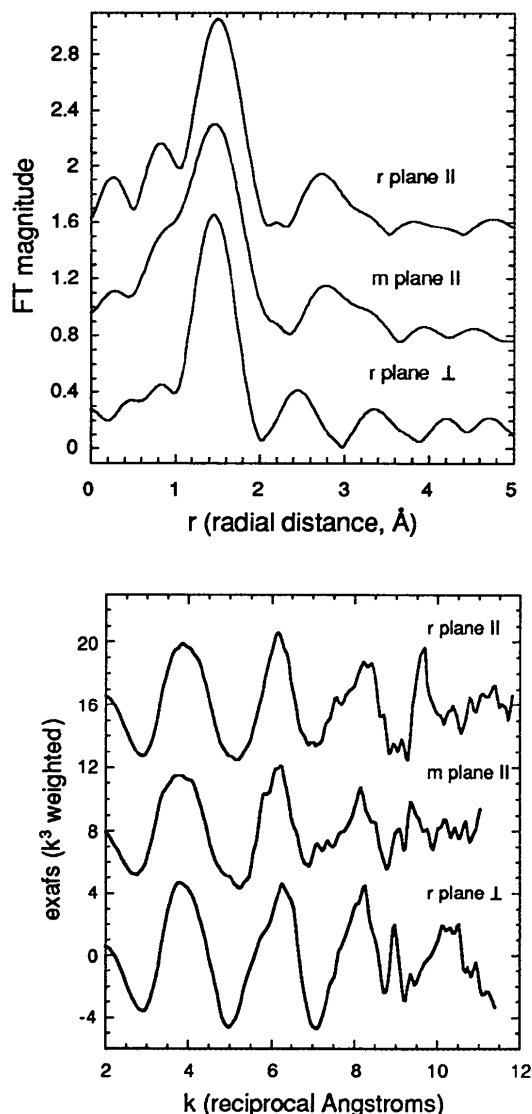

Figure 1

Top: FTs of GIXAFS measurements for Fe^{3+} sorbed on a large natural crystal. Sample equilibrated in air. Coverage ca. 0.15 mmoles/M². Bottom: Raw weighted GIXAFS data.

3. Results

Data was collected in three electric vector orientations: parallel and normal to the r-plane (10-11), and parallel to the m-plane (10-10). Two azimuthal orientations were tested in the r-plane work, but showed little sensitivity to azimuthal angle. Only one azimuthal orientation was used with the m-

plane data collection (along [0001]). The extracted EXAFS and Fourier transforms of the GIXAFS for these data are shown in Figure 1. The FTs for the parallel e-vector data sets are quite similar, with second shell contributions at ca. 2.75 and 3.3 (a shoulder), and first shells at ca. 1.50 Å (not phaseshift corrected). In contrast the r-plane normal data produced a different FT with second and third shell contributions at ca. 2.44 and 3.32 Å, respectively (not phase-shift corrected). Analysis shows that most of the backscattering is due to Fe-Fe contributions, but Fe-O contributions are also present. Fe-Si can be added to the fit, but not unambiguously, as there is interference between the phases of Fe-Fe and Fe-Si backscattering. However there is definitely clustering of the Fe^{3+} on the quartz surface despite the low average coverage. The fitted GIXAFS are shown in Figure 2. Three or four shells produced reasonable fits while remaining within the limits of the spectral information (Nyquist) limit. The fitting shells are shown in Table 1. These fits have Fe-Fe and Fe-O distances close to that expected for hematite clusters, but with very low mean numbers of metal neighbors. The variation of fitted shells with polarization direction are consistent with strong texturing of the hematite structure with respect to the surafce plane. Specifically, that the [0001] direction is normal to both the r- and m-plane surfaces.
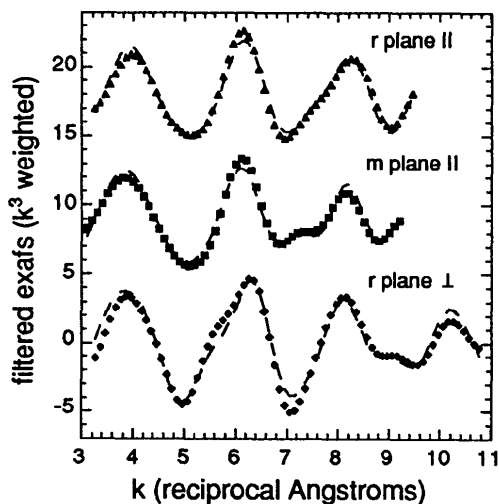
Table 1
GIXAFS fit parameters

Spectrum	Shell	r (Å)	CN	DW(Å²)	χ(fit)
r plane parallel	Fe-O	1.99	4.02	0.0057	83
	Fe-O				
	Fe-Fe	3.45	1.52	0.0065	
	Fe-Fe	3.66	0.85	0.0057	
m plane parallel	Fe-O	1.98	5.51	0.012	80
	Fe-O				
	Fe-Fe	3.43	1.70	0.0091	
	Fe-Fe	3.73	0.90	0.0055	
r plane perpendicular					
	Fe-O	1.97	3.83	0.0049	24.5
	Fe-O	2.08	0.54	0.0049	
	Fe-Fe	2.88	1.09	0.0039	
	Fe-Fe	3.89	1.69	0.013	

4. Discussion

In principle we should be able to determine the size and shape of hematite nuclei if we can assume that all Fe-X contributions to the EXAFS have similar Debye-Waller factors, and that the nuclei are oxygen terminated. The former is probably a valid assumption for second and farther neighbors, but may not be valid for first shell neighbors compared to more distant shells. Figure 4 shows the results of three calculations for differing types of clusters with [0001] polarization. In the 20 atom simulation, calculated with respect to a central Fe atom, there is a notable reduction in the amplitude of the third shell peak compared to the 50 atom cluster. To obtain a more realistic simulation, the EXAFS contributions for all different types of Fe in the cluster (surface, edge, center) were calculated and averaged. This produced a more reasonable FT and EXAFS function, but the addition of ca. 50% isolated Fe^{3+} contributions were

Figure 2
Four shell fits to polarized GIXAFS data. Fit is dashed line through solid data points. All phase and amplitude factors derived from Feff 7.0. Different k-ranges reflect signal strength for the two experimental detector positions. With perpendicular orientation the background scattering is minimal, and the detector system could be brought very close to the sample (1 cm).

For comparison the FT of the polarized EXAFS from a 50 atom hematite cluster is shown in Figure 3, calculated with all significant multiple scattering paths included and a global Debye-Waller factor of 0.005 Å². The FTs are calculated using only the central Fe atom. The 50 atom [0001] hematite FT closely matches the quartz r-plane normal FT peak positions, though with much enhanced second and third peak amplitudes. The 50 atom [01-10] hematite FT also agrees in peak positions with the r-plane and m-plane parallel FTs. These comparisons together with the GIXAFS fitting indicate that Fe^{3+} is present on the natural quartz surface as small oxide nuclei similar to hematite, but having reduced Fe-Fe correlations compared to those in the bulk structure.
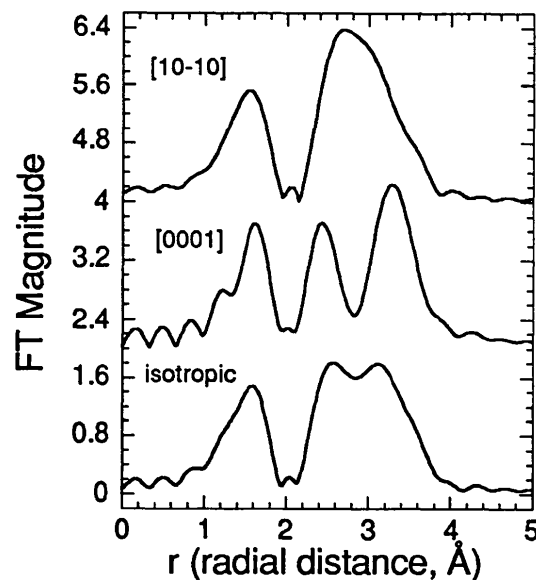

Figure 3
Theoretical polarized EXAFS FTs for two orientations of 50 atom clusters of hematite with respect to the x-ray field electric vector compared with an isotropic calculation. All correlation functions were calculated with respect to the central Fe atom. k ranges were matched to those of the data shown in figure 1.

necessary to produce a result similar to that observed in the natural sample (weighted cluster model in figure 4). The simulations performed to date suggest that the nuclei are smaller than 20 atoms in size on average with many isolated sorbed Fe^{3+} complexes on the surface. Discrete Fe-Si EXAFS contributions can be added to a fit, but the EXAFS are of insufficient quality to determine if such neighbor pairs are required. The hematite nuclei are strongly textured, with the fiducal c-axis [0001] normal to the r-plane, and [01-10] axis parallel to the m- and r-planes. The simulated clusters had roughly spherical shape, but other habits would result in different amplitudes in the second and third (mainly Fe-Fe) shells. For example, a thin platelike nucleus residing flat on the quartz surface would have enhanced parallel but reduced normal Fe-Fe contributions. Precipitate geometry associated with surface steps and defects may have particular topology and thus be distinguishable by polarized GIXAFS analysis. The similarity of m- and r-plane parallel spectra suggest that the nuclei are probably not epitaxially related to the crystal structure. This is also consistent with the inability to reliably fit Fe-Si contributions. Hence the Fe-Si relationship is either too complex for the data quality available, or there is little defined relationship.
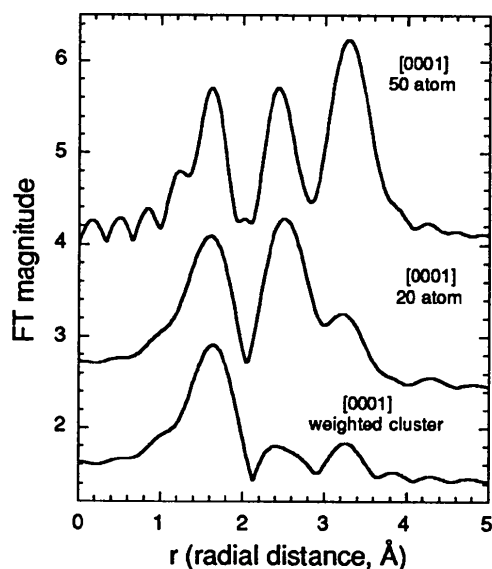

Figure 4
Theoretical polarized [0001] EXAFS FTs for Fe centered in 50 and 20 atom hematite clusters, and Fe averaged over all Fe sites in a 20 atom hematite cluster.

The natural sample was allowed to equilibrate with ambient humidity (ca. 70%) during data collection. Hence the drying effect noted in our previous Aerosil 200 studies (Waychunas et al., 1997) may have driven clustering and nuclei formation. Other studies using synthetic quartz substrates (r-, m-, and c-plane) are now in progress to investigate the mechanism of sorption in a constantly wet system, as well as further drying reactions. These types of reactions may be very characteristic of coating formation and alteration in Vadose zone conditions. More detailed Feff simulations are also in progress, using averages of "local" Fe environments from all parts of a given nucleus to assemble an EXAFS function characteristic of a particular size and shape.

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