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Spectroscopic studies of Pb(II)-sulfate interactions at the goethite-water interface

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Abstract—We used a combination of in situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and X-ray absorption fine structure (XAFS) spectroscopy to conduct molecular scale studies on Pb(II)-sulfate interactions at the solid-water interface of goethite at pH 4.5, 5.0, and 6.0. Both the ATR-FTIR studies (probing sorbed SO_4 in a flow cell setup as a function of the Pb concentration) and the EXAFS studies (probing sorbed Pb at high levels of co-adsorbing SO_4) indicated the formation Pb-SO_4 ternary complexes at the goethite surface. Based on the combined information from the IR and XAFS studies, possible Pb-SO_4 ternary complex configurations were presented and discussed by comparison to a set of reference sulfate FTIR spectra. In addition to forming ternary complexes with SO_4, adsorption of Pb also promoted SO_4 sorption to the goethite surface by changing the surface charge, leading to additional formation of inner- and outer-sphere SO_4 sorption complexes not coordinated by Pb. The relative impacts of these mechanisms (i.e., ternary complex formation versus electrostatic effects) appeared to be a function of pH and the level of Pb addition. Formation of ternary complexes was promoted (relative to the importance of electrostatic effects) at low pH values and high Pb concentrations, whereas electrostatic effects were more pronounced at high pH values and low Pb concentrations. In addition, it was found that part of the SO_4 initially sorbed at the goethite surface as inner-sphere complexes without being coordinated by Pb was transformed into SO_4-Pb ternary complexes as the Pb concentration was increased, an effect most pronounced at low pH. This study shows that co-adsorption of SO_4 and Pb may lead to changes in both the extent and mechanisms of the adsorption of these contaminants to the goethite surface relative to binary Pb/goethite and SO_4/goethite systems. The presence of co-adsorbing metals or anions may therefore significantly impact the behavior of contaminants in environmental settings. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

Sediments and soil solutions often contain many different metal cations and anions, each of which may be able to sorb to variable charge surfaces present in the mineral matrix contacting the solution phase. Numerous macroscopic studies have shown that anions may have a pronounced effect on metal sorption to mineral surfaces (e.g., Ostergren et al., 2000a,b; Bargar et al., 1998; Webster et al., 1998; Ali and Dzombak, 1996; Clark and McBride, 1985; Benjamin and Leckie, 1982), and, vice versa, that metal cations may significantly alter the sorption behavior of anions (e.g., Ali and Dzombak, 1996; Bolan et al., 1993; Marcano-Martinez and McBride, 1989; Balistrieri and Murray, 1981). Metal sorption in some cases increases (e.g., Marcano-Martinez and McBride, 1989; Gunneriusson et al., 1994), and in other cases decreases (e.g., Davis and Leckie, 1978; Elrashdi and O'Connor, 1982; Boekhold et al., 1993) in the presence of non-inert anions, depending on the sorbent, pH range, and the type and concentration of the metals and ligands being studied. Decreased metal sorption is generally explained by competition between metal-ligand complexation in solution and metal complexation to surface sites, or by competition between anions and metal ions for surface sorption sites. Explanations for promotive effects of anions on metal sorption include (1) the formation of ternary complexes, (2) reduction of the surface potential by anion sorption, making the surface more attractive to metal sorption, and (3) the formation of Me-ligand precipitates.

One of the geochemical settings where co-adsorption of anions and metal cations may be of significant importance is found in sulfide containing sediments undergoing oxidation. Submerged soils located on coastal margins commonly contain iron(II) sulfides (pyrites), which oxidize when the soils are exposed to air by a fluctuating water table or drainage (McBride, 1994). Mining operations often generate pyrite containing waste deposits at the surface, which begin to oxidize on exposure to air. Pyrite oxidation generates acidity in the form of sulfuric acid and commonly leads to release of SO_4 to solution and the formation of Fe(III) (hydr)oxide minerals (e.g., Morse et al., 1987; Bonnissel-Gissinger et al., 1998; Kamei and Ohmoto, 2000). Furthermore, trace elements such as Cd, As, Pb, and Zn associated with pyrite are released during oxidation, and the high acidity levels of the leachates may dissolve and mobilize trace elements from the rocks, soils, and sediments they contact. The retention of these elements within these sites as well as in the soils and sediments downstream may be affected by the co-adsorption of SO_4, based on results from previous studies, which generally reported increased metal sorption in the presence of SO_4 (e.g., Webster et al., 1998; Ali and Dzombak, 1996; Hoins et al., 1993; Marcano-Martinez and McBride, 1989). In turn, the retention of sulfate will likely be affected by the co-adsorption of trace metals (e.g., Ali and Dzombak, 1996; Bolan et al., 1993). A fundamental understanding of the mechanisms involved in the co-adsorption of SO_4 and trace elements and the resultant speciation of these species may help in evaluating and predicting the mobility and bioavailability of SO_4 and trace elements in such systems.

A few spectroscopic studies addressing the co-adsorption of

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sulfate and trace metals have been reported in the literature. Collins et al. (1999) studied Cd sorption to goethite as affected by SO_4 using X-ray absorption fine-structure (EXAFS) spectroscopy and concluded that enhanced Cd adsorption in the presence of SO_4 is solely due to electrostatic effects. Weesner and Bleam (1998) combined electrophoretic mobility measurements with XAFS spectroscopy to study the co-adsorption of Pb with SO_4 and PO_4 on goethite and boehmite. Phosphate induced Pb-PO_4 precipitation on both surfaces, whereas the role of sulfate was less conclusive. Sulfate sorption appeared to cause no changes in the chemical environment of Pb sorbed to the boehmite surface, but did seem to lead to the formation of $PbSO_4$ (anglesite) clusters on goethite. Ostergren et al. (2000b) used a combination of EXAFS spectroscopy and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to conduct molecular scale studies on the co-adsorption of SO_4 and Pb to goethite. In contrast to the results of Weesner and Bleam (1998), no evidence for $PbSO_4$ clustering was found, probably because of the lower reactant concentrations used in the Ostergren et al. (2000b) study. Under their experimental conditions, Ostergren et al. (2000b) found evidence for the formation of Fe-Pb-SO_4 ternary complexes at the goethite surface, with Pb increasingly sorbed via ternary complex formation as the SO_4 concentration was raised. In addition, the IR results of this study suggested that Pb sorption resulted in increased SO_4 sorption via ternary complex formation as well as via additional outer-sphere SO_4 complexation due to electrostatic effects.

The aim of this study was to provide further insight on the mechanisms involved in the co-adsorption of Pb^{2+} and SO_4^{2-} on goethite. More specifically, this study examines the effects of the Pb concentration level on the mechanisms of SO_4 complexation at the goethite surface, under experimental conditions undersaturated with respect to $PbSO_4(s)$. In addition, an evaluation of possible Pb-SO_4 ternary complex structures is provided by comparison of experimental SO_4 ATR-FTIR spectra to a set of reference SO_4 FTIR spectra. We used flow-cell ATR-FTIR spectroscopy to probe the sorbed SO_4 bonding environment on goethite and XAFS spectroscopy to characterize the local chemical environment of sorbed Pb. A recent study by Peak et al. (1999) showed that the mechanism of sulfate sorption to goethite depends on pH, a result also reported by Ostergren et al. (2000b), and further confirmed by Wijnja and Schulthess (2000). Experiments were therefore performed over a range of pH values, as well as over a range of Pb and SO_4 concentrations.

2. MATERIALS AND METHODS

2.1. Goethite Preparation

The goethite used in this study was synthesized by titrating 50 mL of a 1 mol/L ferric nitrate solution with 450 mL of 1 mol/L KOH and aging the resultant ferric oxide suspension for 2 weeks at 25°C (Schwertmann et al., 1985). Next, the goethite suspension was centrifuged, washed with DDI water and resuspended in 0.4 mol/L HCl for 2 h to remove any remaining amorphous iron oxides. The goethite was then centrifuged and washed with DDI water. Finally, the goethite was dialyzed to remove excess salts and then freeze-dried. The material was confirmed to be goethite via IR spectroscopy. The goethite had a N_2-BET surface area of 63.5 m^2 g^{-1}, and a point of zero salt effect of 8.4, as determined via potentiometric titrations in 0.1, 0.01, and 0.005 mol/L sodium perchlorate backgrounds (Peak et al., 1999).

2.2. Reaction Conditions

Experiments were performed at pH values 4.5, 5.0, and 6.0, using a background electrolyte of 0.01 mol/L NaCl. To eliminate effects of CO_2, the experiments were conducted under N_2 conditions, using either a glove box with a N_2 atmosphere, or a continuous N_2 flow into the reaction vessels. The Pb and SO_4 solution concentrations were chosen such that solutions were undersaturated with respect to $PbSO_4(s)$ (anglesite), as determined via speciation calculations in MINEQL+ (Version 3.01b; Schecher, 1994). All chemicals used were reagent grade.

2.3. ATR-FTIR Data

The FTIR experiments were conducted to probe the molecular environment of SO_4 sorbed at the goethite surface. The data were collected on a Perkin-Elmer 1720× spectrometer equipped with a purge gas generator and a liquid N_2-cooled MCT detector. Spectra were collected by using the flow cell technique described by Peak et al. (1999) and Hug and Sulzberger (1994). A 45° ZnSe ATR crystal was coated with ≈2.5 mg of goethite and placed inside the flow cell. The flow cell was placed on the horizontal ATR sample stage inside the IR spectrometer and connected to a reaction vessel containing 1 L of background electrolyte. The reaction vessel was N_2-purged, and the solution pH was adjusted to the desired value. The solution in the reaction vessel was continuously mixed by using a magnetic stir bar. The solution pH was monitored throughout each experiment and adjusted if necessary.

To start the experiment, the background electrolyte was passed through the flow cell at a flow rate of ≈1 mL min^{-1}. The effluent from the flow cell was collected as waste. A background spectrum consisting of the combined absorbances of the ZnSe crystal and the goethite deposit was collected every 15 min. Typically, after ≈3 h, there was no difference between successive background spectra, indicating that the goethite coating had equilibrated with the background electrolyte. At this time, the final background spectrum was collected as the average of 1000 scans at a 4 cm^{-1} resolution, and the sorption experiment was started by injection of sulfate into the reaction vessel. All successive spectra were collected as a ratio to this background spectrum.

The goethite deposit on the ZnSe crystal was first equilibrated with a 30-μM SO_4 solution concentration. The appropriate amount of a 1 mol/L Na_2SO_4 stock solution needed to achieve this concentration in the reaction vessel was calculated from the flow rate and the time necessary to stabilize the goethite deposit. Sulfate sorption to the goethite deposit was monitored by collecting spectra every 10 min. When the intensity of the spectra of sorbed SO_4 was stable over time, typically after ≈2 h after SO_4 injection, the final spectrum was collected and Pb was added to the reaction vessel.

The addition of Pb to the system was done in increments, with Pb solution concentrations increasing from 5 μM to 1 mM. The Pb concentrations in solution were reached by adding appropriate amounts of a 15 mM $PbCl_2$ stock solution to the reaction vessel connected to the flow cell. For every level of [Pb] in solution, the SO_4 sorption to the goethite deposit was monitored until there was no further increase in the infrared spectra of sorbed SO_4 over time. The final spectrum was then collected, the Pb concentration in the reaction vessel was raised to the next level, and the SO_4 was allowed to reach a new sorption equilibrium with the goethite deposit in the flow cell.

In addition to the sorbed SO_4 spectra, a number of aqueous reference SO_4 FTIR spectra were collected. For the FTIR spectrum of SO_4^{2-}(aq), we scanned a 0.1 mol/L Na_2SO_4 solution (in water) of pH 5.0 and subtracted out the spectrum of pure water (pH 5.0) to isolate the SO_4^{2-}(aq) spectrum. For HSO_4^-(aq), the spectrum of a 0.5 mol/L H_2SO_4 solution was collected, from which the spectrum of water was subtracted. Spectra of $MnSO_4^0$(aq), $NiSO_4^0$(aq), and $CdSO_4^0$(aq) were collected by scanning solutions of pH 4 containing 0.1 mol/L Na_2SO_4 and 3 mol/L $MnCl_2$, $NiCl_2$, or $Cd(NO_3)_2$. To isolate the spectra of the $MeSO_4^0$(aq) complexes in these scans, the spectra of the corresponding Me-salt solutions were subtracted. Speciation calculations in MINEQL+ indicated that >99% of total SO_4 in these solutions was present as $MeSO_4^0$(aq) complexes.

2.4. EXAFS Data

We used EXAFS spectroscopy to probe the molecular environment of Pb sorbed at the goethite surface. Preparation of the EXAFS samples was done in a N_2-purged glove box by using boiled DDI water. Pb was reacted with goethite for 24 h in the presence and absence of sulfate at pH 5.0 and pH 6.0. For the samples without SO_4, the goethite concentration was 0.4 g L^{-1}, and the Pb concentration was 100 μM. Pb sorption to goethite in the presence of SO_4 was done at a goethite concentration of 0.1 g L^{-1}, and Pb and SO_4 concentrations of 25 μM and 4.5 mM, respectively. Similar to the IR experiments, SO_4 was added to the goethite suspensions $\approx$2 h before Pb addition.

XAFS spectra were recorded at Beamline X-11A of the National Synchroton Light Source, Brookhaven National Laboratory, Upton, NY. Spectra were collected at the Pb L_{III} edge by using a Si(111) crystal monochromator. The premonochromator slit width was 0.5 mm. Higher-order harmonics were suppressed by detuning 25% from the maximum beam intensity. The samples were scanned in fluorescence mode at room temperature by using a Kr-filled Lytle detector equipped with an As filter and six layers of Reynolds Al foil. At least six scans were collected per sample.

Background subtraction, Fourier filtering, and data fitting were accomplished with the program WinXAS97 (Ressler, 1997), in combination with the FEFF7 code (Zabinsky et al., 1995). The χ-function was extracted from the raw data by fitting a linear function to the preedge region and a seven-knot spline function to the postedge region, and normalizing the edge jump to unity. The data were converted to k space and weighted by k^3. Structural parameters were determined with fits to the standard EXAFS equation by multishell fitting in R space. The reference compound used was β-Pb(OH)$_2$, and the amplitude reduction factor was 0.65, as determined by fits to experimental spectra of the reference compound collected in transmission mode.

3. RESULTS

3.1. ATR-FTIR Data

Figure 1 shows the effect of Pb addition on the FTIR spectra of sorbed SO_4 at the goethite surface at pH 4.5, 5.0, and 6.0. At all three pH values, SO_4 sorption increases on Pb addition, as evidenced from the increasing IR absorbance of sorbed SO_4 with increasing Pb solution concentration. Comparison of the spectra that were collected before Pb addition shows the effect of pH on the SO_4 sorption mechanism on goethite discussed by Peak et al. (1999). At pH 6.0, the spectrum of sorbed SO_4 shows two peaks: a small ν_1 peak at 975 cm^{-1} and a broad ν_3 peak centered at $\approx$1105 cm^{-1} (Fig. 1c). This spectrum is representative of SO_4 sorbed in an outer-sphere fashion at the goethite surface (Peak et al., 1999). Lowering the pH to pH 5.0 and pH 4.5 results in a more sharply defined ν_1 band, and splitting of the ν_3 band in two distinct peaks at 1055 and 1133 cm^{-1}, and a shoulder at 1170 cm^{-1} (Figs. 1b and 1a, respectively). This indicates the formation of inner-sphere SO_4 surface complexes, with increasing inner-sphere complexation as pH decreases. The inner-sphere complex has $C_{2\nu}$ symmetry and is either a monodentate bisulfate complex or a monodentate sulfate complex interacting with a proton on an adjacent goethite surface site, as determined by comparison to spectra collected in D_2O (Peak et al., 1999).

Addition of Pb not only raises the overall level of SO_4 sorption to the goethite surface but also appears to result in a gradual change of the IR spectrum of sorbed SO_4 with increasing Pb concentration (Fig. 1). To obtain the IR spectrum of the complexes that form at the goethite surface as a result of Pb addition, we subtracted the SO_4 IR spectrum collected before metal addition from the spectra obtained on increasing the Pb

solution concentrations. The resultant difference spectra are also shown in Figure 1. At all three pH values, raising the Pb solution concentration leads to the appearance of two frequencies at $\approx$1110 and 1070 cm^{-1} in the IR difference spectra, and these features become more pronounced with increasing concentrations of Pb. This type of ν_3 splitting is not observed in the spectra collected before Pb addition (Fig. 1), which indicates that increasing the Pb solution concentration leads to the formation of an additional inner-sphere SO_4 sorption complex at the goethite surface.

To study the possibility that the frequencies appearing at 1110 and 1070 cm^{-1} are an effect of sulfate surface loading on the sulfate-goethite complexation mechanisms, spectra were collected in Pb-free systems at different sulfate solution concentrations at pH 4.5, 5.0, and 6.0. Increasing the SO_4 concentration in solution leads to increased sorption of SO_4 at the goethite surface, as is the case for increasing the Pb solution concentration. At pH 6.0, raising the SO_4 concentration from 30 to 1000 μM in Pb-free systems leads to a similar increase in SO_4 sorption as raising the Pb concentration from 0 to 1 mM at a sulfate concentration of 30 μM, as judged from the increase in the integrated absorbance of the IR spectra (data not shown). At pH 5.0, the sulfate concentration has to be raised from 30 to 200 μM to achieve the same approximate increase in SO_4 adsorption obtained on raising the Pb solution from 0 to 1 mM at a SO_4 concentration of 30 μM, and at pH 4.5 the sulfate concentration needs to be increased from 30 to 100 μM. Therefore, to isolate the effect of Pb addition from possible sulfate surface-loading effects, Figure 2 compares the difference spectrum of the sulfate spectra obtained at Pb solution concentrations of 1 and 0 mM to the spectra of sorbed SO_4 forming on goethite in the absence of Pb as a result of increasing the SO_4 solution concentration from 30 to 100 μM (pH 4.5), to 200 μM (pH 5.0), or to 1 mM (pH 6.0). For further evaluation of the SO_4 sorption complexes forming on Pb addition, the following SO_4 reference spectra are also included in Figure 2: (1) SO_4 (25 μM) sorbed on goethite in the absence of Pb at pH 3.5. At this low pH value, a relatively large fraction of sorbed SO_4 is bonded in an inner-sphere fashion, and as a result, the IR absorbances characteristic of inner-sphere SO_4 complexes at the goethite surface are well-resolved; (2) SO_4 (25 μM) sorbed on hematite at pH 6.0. This spectrum strongly resembles the IR spectra reported by Hug (1997) for SO_4 sorption on hematite and represents an inner-sphere nonprotonated monodentate SO_4 surface complex.

The inner-sphere SO_4 complexes forming as a result of increasing the Pb solution concentration from 0 to 1 mM are not due to changes in the SO_4 sorption mechanism with increasing SO_4 surface loading, because the frequencies 1110 and 1070 cm^{-1} do not show in the difference spectra obtained from increasing the SO_4 solution concentrations in Pb-free systems (Fig. 2). Comparison with the spectrum of SO_4 sorbed to goethite at pH 3.5 shows that the degree (band positions) and possibly the type (number of bands) of ν_3 splitting are different for the inner-sphere SO_4 complexes formed in the presence and absence of high Pb levels. In the absence of Pb, the ν_3 band splits in three peaks centered at 1055, 1133, and 1170 cm^{-1}, whereas in the presence of Pb, ν_3 band splitting results in peaks located at 1110 and 1070 cm^{-1}. Because the appearance of these frequencies on Pb addition is not due to a surface-loading
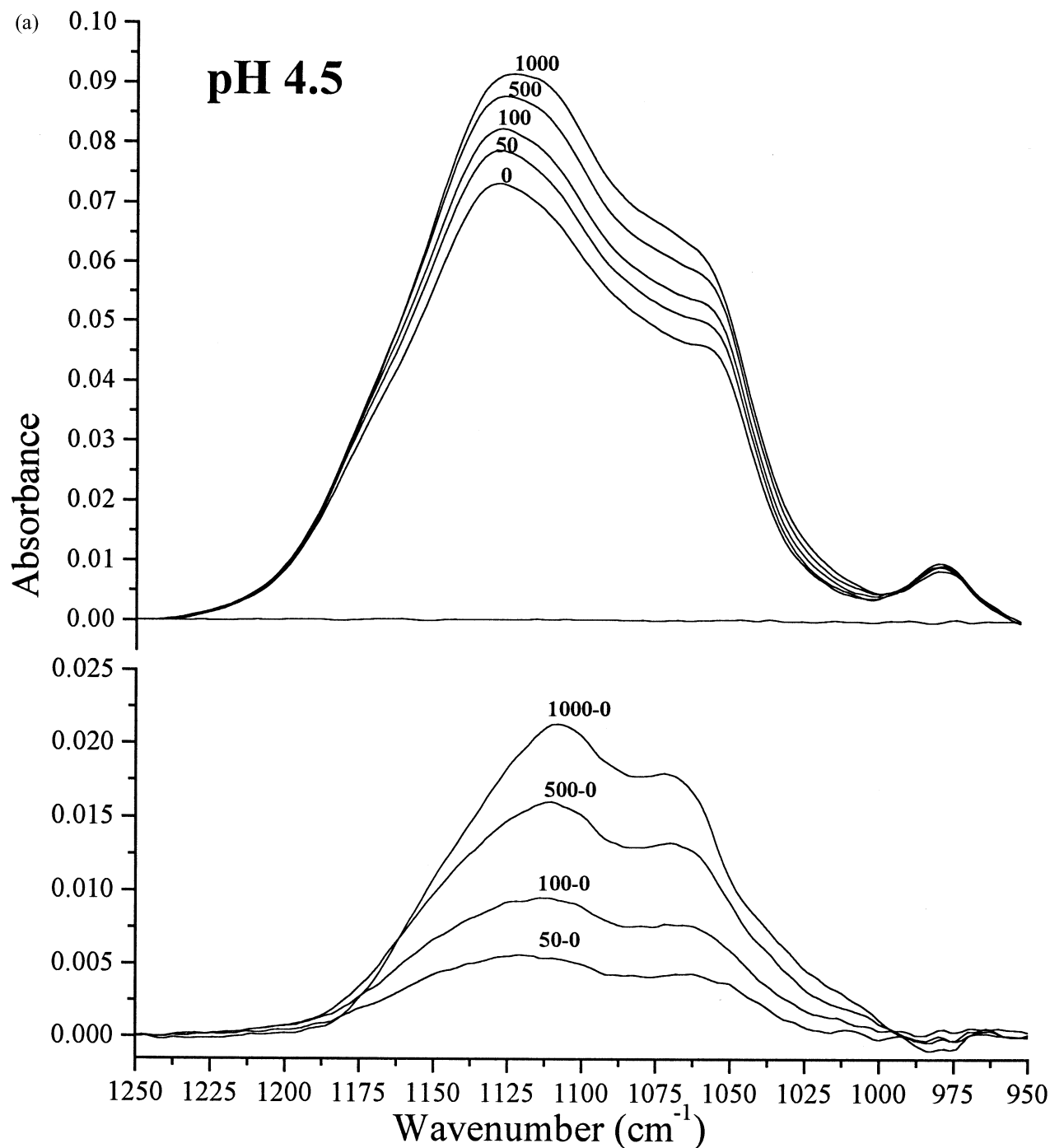
(a)

Fig. 1. Spectrum of sorbed SO_4 as a function of Pb addition at pH 4.5 (a), 5.0 (b), and 6.0 (c). The numbers indicated along the spectra denote the Pb solution concentration in μM. The spectra in the bottom part of the graphs are the difference spectra between the sulfate spectra at the various levels of Pb solution concentration and the spectrum collected before Pb addition. The SO_4 solution concentration was 30 μM in all cases.

effect, we attribute them to the formation of Pb-SO_4 ternary complexes at the goethite surface. The ν_3 band splitting of these complexes is similar, although not identical, to the ν_3 band splitting of the inner-sphere SO_4 complex that forms at the hematite surface (Fig. 2), indicating that the SO_4 present in the ternary complexes has monodentate-like symmetry.

An additional point that can be made from Figure 2 is that there is an effect of SO_4 surface loading on the SO_4 sorption mechanism to goethite in the Pb-free systems considered. In all difference spectra of the Pb-free systems shown in Figure 2 (spectra f, g, and h), the features indicative of SO_4 inner-sphere complexation are significantly more pronounced than in the
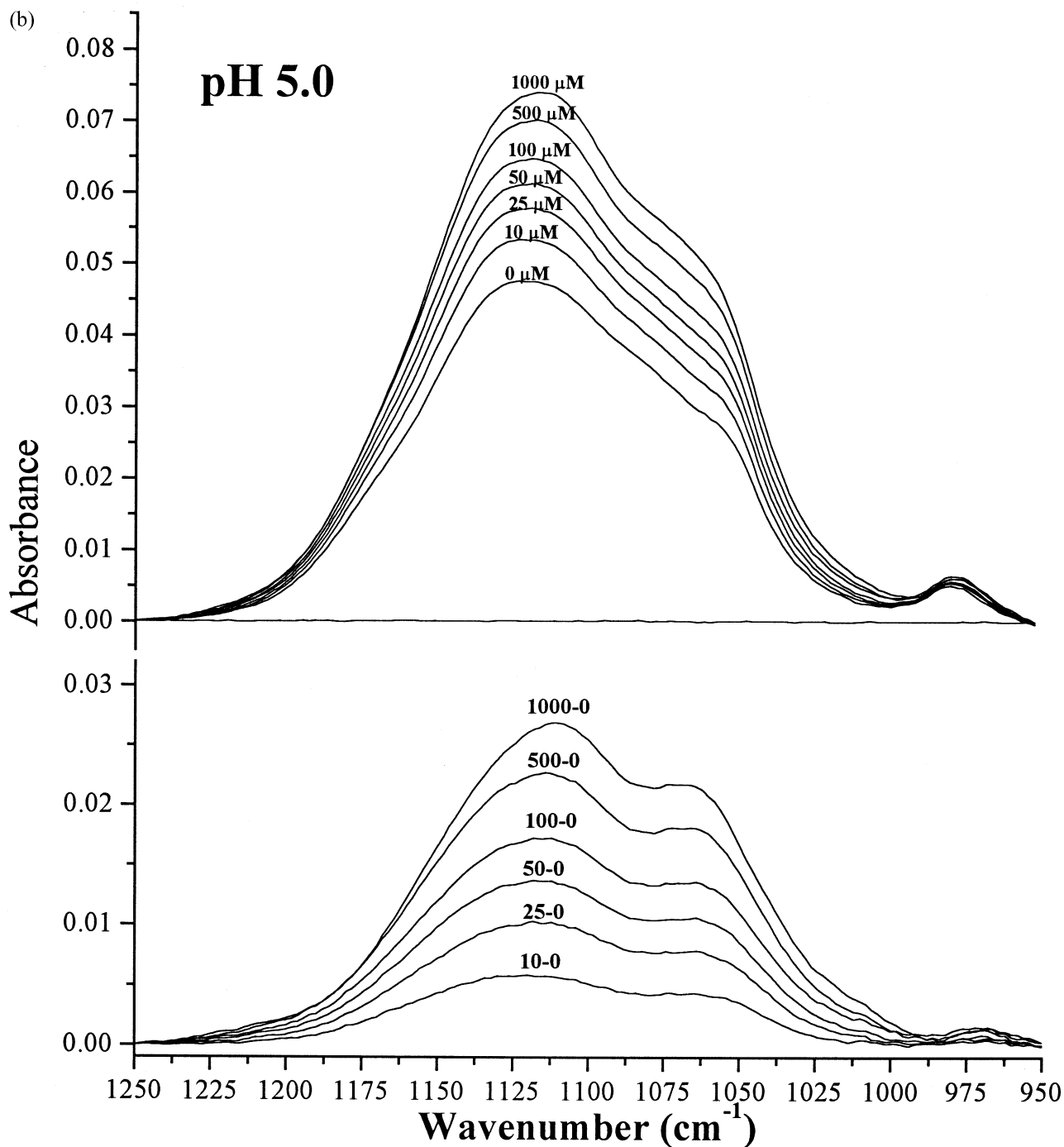
Fig. 1. (Continued).

Pb-free (0 μM Pb addition) spectra at the corresponding pH values shown in Figure 1, which were collected at a 30 μM SO$_4$ equilibrium solution concentration. This indicates that the SO$_4$ sorption occurring by increasing the SO$_4$ concentration beyond 30 μM proceeds to a larger extent via inner-sphere complexation than the sorption achieved by equilibrating the goethite with a 30 μM SO$_4$ solution concentration at a given pH value. Therefore, with increasing SO$_4$ surface loading, a larger frac-

tion of sorbed SO$_4$ is bound as inner-sphere complexes in Pb-free systems.

Ostergren et al. (2000b) report frequencies at 1150 and 1050 cm^{-1} in their in situ sulfate ATR-FTIR spectra as indicative of Pb-SO$_4$ ternary complexes. This is substantially different from the frequencies we observe ($\approx$1110 and 1070 cm^{-1}), not only in view of the overall range where ν_3 band splitting occurs on goethite under in situ conditions (between 1170 and 1050
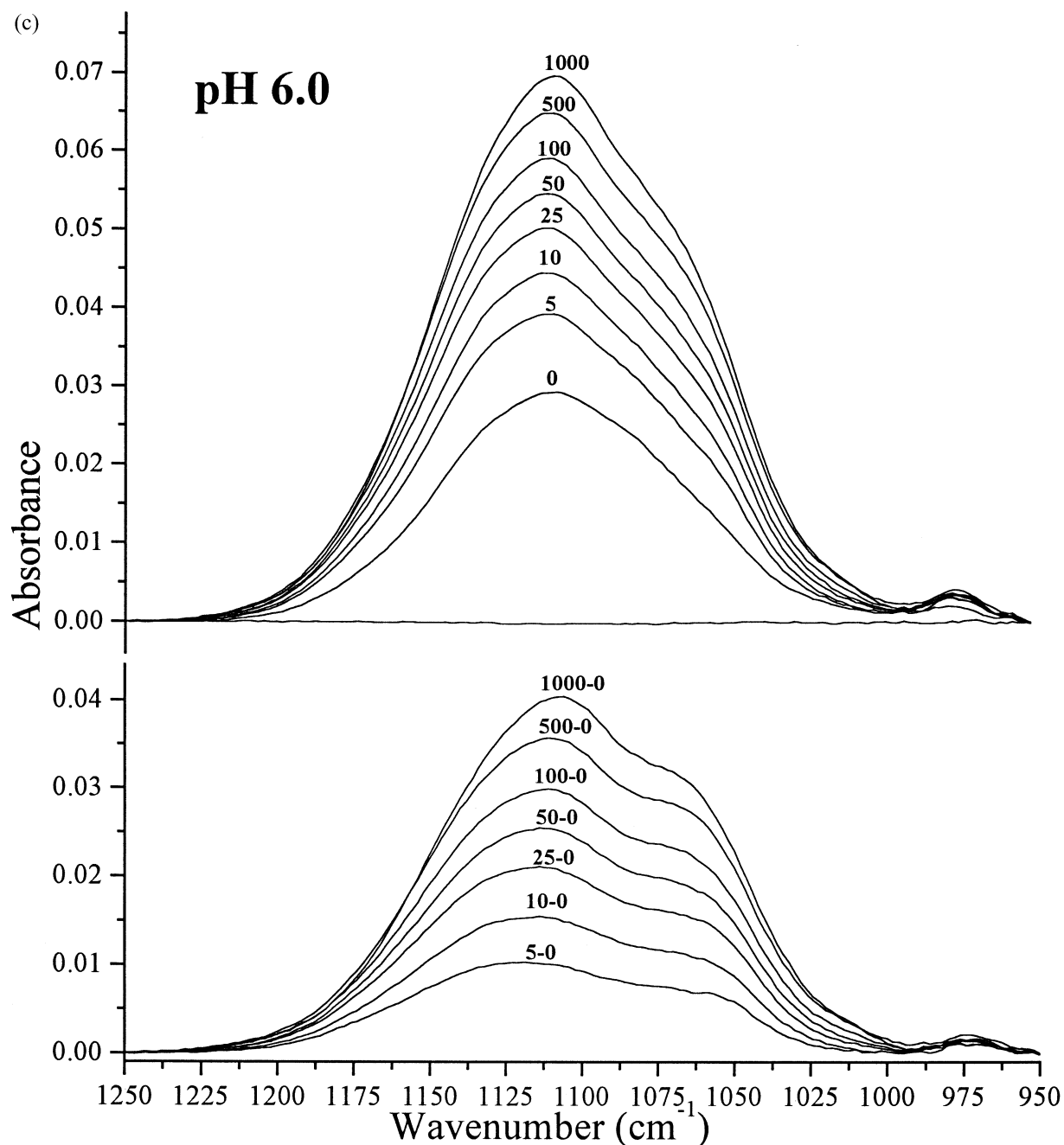
(c)

Fig. 1. (Continued).

cm^{-1}; Fig. 2 and Peak et al., 1999) but also given the fact that the SO$_4$ spectra of samples reacted in the absence of Pb presented in Ostergren et al. (2000b) have very similar band positions as our Pb-free SO$_4$ spectra (Figs. 1 and 2). The most likely reason for this difference lies in the different ATR-FTIR data collection techniques used. To isolate the IR absorbances of sorbed SO$_4$ from background absorption by water and goethite, Ostergren et al. (2000b) subtracted aqueous spectra of the supernatants from the spectra of wet solids reacted with SO$_4$ in batch experiments, followed by subtraction of supernatant-subtracted spectra of goethite pastes without sorbed SO$_4$. As

discussed in Hug and Sulzberger (1994), this technique of collecting ATR-FTIR spectra tends to be more complicated than collecting spectra with an ATR element coated with a stable layer of highly dispersed material, as was done in our study. This is due to the sensitivity of these measurements to the concentration and dispersivity of the solid particles in the proximity of the ATR crystal in samples that have adsorbate (SO$_4$) concentrations that are small compared with the H$_2$O and adsorbent concentrations, as is the case for samples in sorption studies. With coated ATR elements, the concentration and dispersivity of the probed solid material are fixed. With pastes,
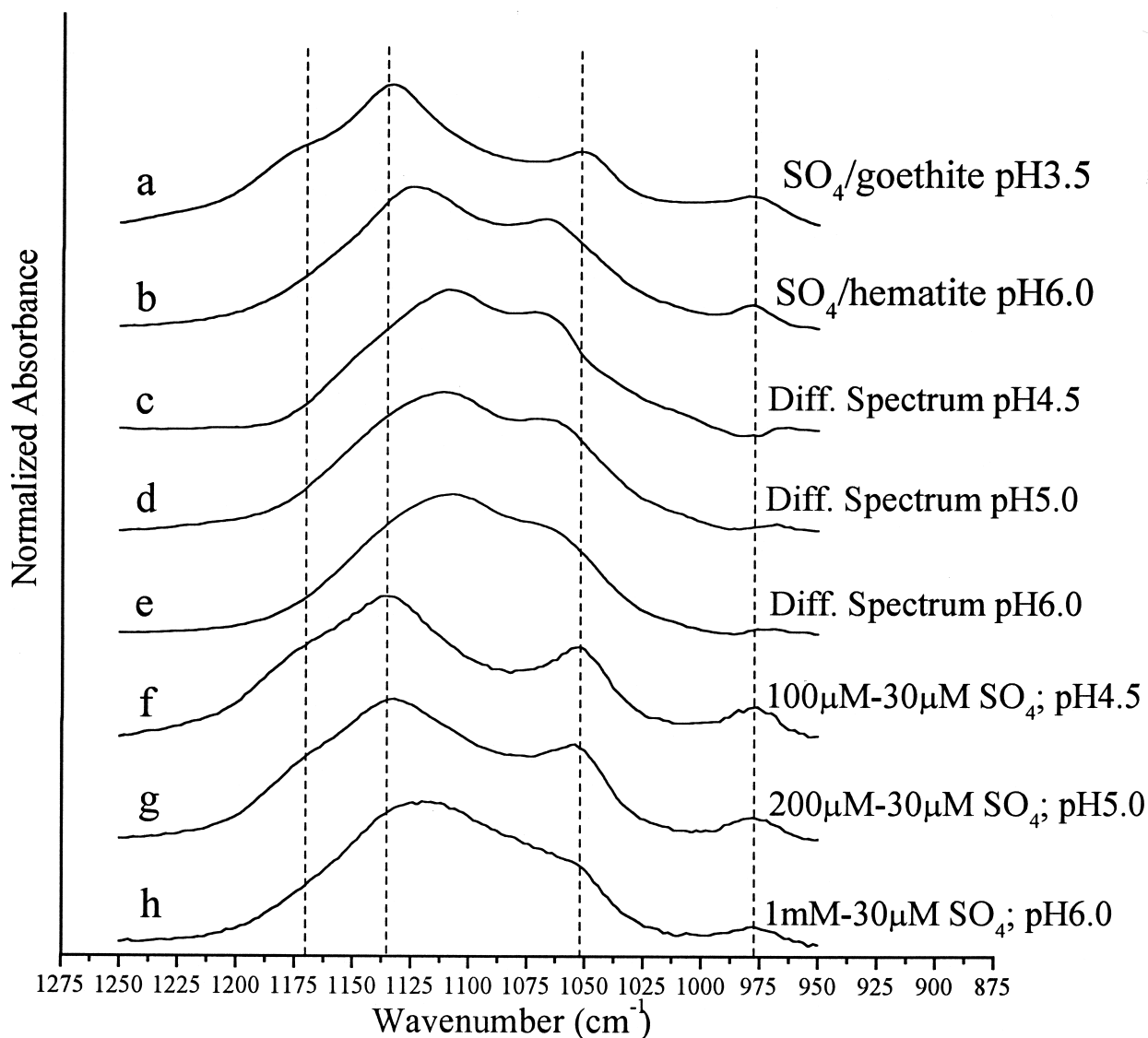
Fig. 2. The difference spectra between the SO_4 spectra obtained at 1 mM and 0 mM Pb concentrations (c, d, and e) compared with spectra of inner-sphere SO_4 complexes forming on goethite and hematite in the absence of Pb (a and b). Spectra f, g, and h are checks on possible surface loading effects, as described in the text.

however, these may vary, because the coagulation and flocculation behavior of the solid is affected by adsorption of charged species, complicating the removal of background absorbances from reacted samples by using the spectra of unreacted samples and resulting in larger uncertainties in the peak positions and overall shape of the isolated FTIR spectra. This may be of particular importance in taking the (small) difference spectrum between such spectra, as was done in Ostergren et al. (2000b), who subtracted the FTIR spectra of SO_4 sorbed to goethite in the presence and absence of Pb to isolate the frequencies of Pb-SO_4 ternary complexes, similar to the procedure used in our study.

3.2. EXAFS Data

For further characterization of the structure of the goethite-Pb-SO_4 ternary complexes, Pb L_{III} EXAFS analyses were per-

formed. Figure 3a shows the k^3-weighted χ-data (both the experimental and the fitted spectra), and Figure 3b shows the radial structure functions obtained by Fourier-transforming the experimental spectra of the XAFS samples analyzed in this study. The fit results are presented in Table 1. Consistent with the results of Ostergren et al. (2000b), both pH and the presence of SO_4 appear to influence the Pb sorption mode at the goethite surface. The pH effect is evident from the difference in the RSFs of the samples reacted in the absence of SO_4 at pH 5.0 and pH 6.0. The RSF of the sample reacted at pH 6.0 shows two peaks, whereas an additional third shell is observed at pH 5.0 (Fig. 3b). The first peak in both samples represents the first-shell oxygen atoms surrounding the sorbed Pb atom, and the second and third shells are due to the presence of Fe atoms in the local coordination environment of sorbed Pb, indicating the formation of inner-sphere Pb complexes at the goethite surface.

Data fitting results for the pH 6.0 sample (Table 1) indicated 2 to 3 O atoms at a distance of ≈ 2.3 Å, and ≈ 1 Fe at a distance of ≈ 3.35 Å from the central Pb atom, consistent with the results of Bargar et al. (1997) for Pb sorption on goethite. The Pb-Fe distance of 3.35 Å is characteristic of Pb bonding to edges of FeO_6 octahedra, i.e., the Pb atoms are coordinated to surface oxygens on adjacent corners of FeO_6 octahedra (Bargar et al., 1997, 1998). Data fitting indicated that the additional peak appearing in the pH 5.0 spectrum was due to the presence of additional Fe at a radial distance of ≈ 3.9 Å from the central Pb atom (Table 1). This Pb-Fe distance is consistent with inner-sphere Pb bonding in a binuclear bidentate fashion (i.e., corner sharing) to FeO_6 octahedra at the goethite-water interface (Bargar et al., 1997, 1998). Thus, consistent with the EXAFS results of Ostergren et al. (2000b), the fraction of Pb sorbed in corner-sharing configuration is found to increase relative to edge-sharing Pb inner-sphere complexes with decreasing pH.

The effect of SO_4 addition becomes clear by comparing the RSFs of the samples reacted in the absence and presence of SO_4 at pH 5.0 and 6.0. At both pH values, SO_4 addition results in increased scattering of Fe atoms located at 3.9 Å from the central Pb atom, as indicated by the increase of the third shell in the RSFs of the SO_4 containing samples relative to the SO_4-free samples (Fig. 3b and Table 1). This is consistent with the results of Ostergren et al. (2000b), who observed a systematic increase in Pb coordinated in bidentate binuclear fashion at the goethite surface with increasing sulfate concentrations. Similarly, Bargar et al. (1998) observed the occurrence of this Pb-bonding mode on goethite at high Cl concentrations (0.1 M NaCl) at pH 6, but not in the absence of Cl. The increased coordination of Pb to Fe atoms located at ≈ 3.9 Å in these studies was attributed to the formation of Pb-ligand ternary complexes on goethite. The presence of Fe scattering from a 3.9 Å radial distance is expressed in the χ-spectra by additional features appearing between 4.8 and 5.0 Å^{-1}, and between 6.5 and 7.0 Å^{-1} (Fig. 3a).

4. DISCUSSION

Our ATR-FTIR results indicate that Pb-SO_4 ternary complexes form at the goethite surface, especially at high Pb concentrations, and that the SO_4 ions in these complexes are bonded in an inner-sphere fashion having C_{3v} or lower symmetry. Our XAFS results show that high concentrations of co-adsorbing SO_4 stabilize Pb inner-sphere complexes that are bonded in a corner-sharing fashion to the FeO_6 octahedra at the goethite surface. The ATR-FTIR results presented in Figure 1 show that at a fixed SO_4 solution concentration, Pb-SO_4 ternary complexes at the goethite surface become increasingly important in the overall SO_4 surface speciation as [Pb] increases. It is reasonable to assume that in the reverse situation, high levels of co-adsorbing SO_4 force a relatively large contribution of Pb-SO_4 complexes in the overall Pb surface speciation at a fixed (small) Pb concentration, which is the way the EXAFS samples were prepared. Therefore, we conclude that the stabilization of corner-sharing Pb sorption complexes at high SO_4 concentration observed in the EXAFS analyses is due to the formation of Pb-SO_4 ternary complexes at the goethite surface. This is corroborated by the results of Ostergren et al. (2000b) who, as
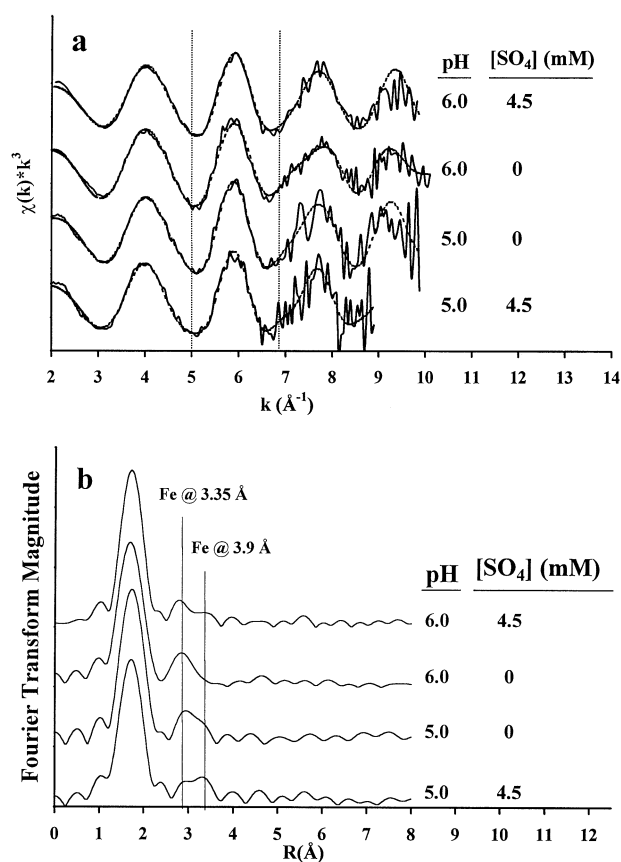
Fig. 3. (a) The raw (solid lines) and fitted (dashed lines) k^3-weighted χ-spectra of the XAS samples collected in this study. Fitting was done in R space; (b) the RSFs (not corrected for phase shift) obtained by Fourier-transforming the k^3-weighted raw spectra.

noted previously, observed a systematic increase in bidentate binuclear (i.e., bridging) Pb sorption complexes with increasing sulfate concentrations, similar to the way our FTIR results (Fig. 1) indicate an increase in Pb-SO_4 complexes in the overall SO_4 speciation as the Pb concentration is raised. Based on these considerations, the combined information obtained from the ATR-FTIR and EXAFS results point to the formation of Pb-SO_4 ternary complexes of either of the configurations shown in Figure 4.

The ATR-FTIR results indicated that formation of Pb-SO_4 ternary complexes results in splitting of the SO_4 ν_3 bands in at least two peaks, indicating inner-sphere SO_4 bonding. Therefore, to be consistent with the IR results, configuration B in Figure 4 would require Pb-SO_4 bonding to be strong and mostly covalent. In configuration A, however, covalent bonding occurs between Fe and SO_4, where SO_4 forms a monodentate inner-sphere complex, as is observed for SO_4 on hematite (Fig. 2; Hug, 1997). As a result, a mostly electrostatic interaction between Pb and SO_4 in this configuration would be required to explain the IR data. We collected the FTIR spectra of a number of $Me(II)SO_4^0(aq)$ solution complexes in an attempt to characterize the nature of Me(II)-SO_4 complexation. Unfortunately, it was not possible to collect an FTIR scan for $PbSO_4^0(aq)$, due to the low solubility of $PbSO_4(s)$: precipitation of $PbSO_4(s)$ reduced the SO_4 solution concentrations to values

Table 1. Structural parameters derived from EXAFS data fitting.

pH	[SO4] (mM)	Pb-O Shell			Pb-Fe Shell*		Pb-Fe Shell*	
		N	R (Å)	σ (Å^2)	N	R (Å)	N	R (Å)
6.0	4.5	2.2	2.27	0.004	0.6	3.34	0.7	3.92
6.0	0	2.8	2.27	0.007	0.9	3.36	—	—
5.0	0	2.5	2.29	0.005	0.8	3.36	0.6	3.93
5.0	4.5	2.6	2.28	0.007	0.4	3.33	1.4	3.89

* The Debye-Waller factors of the Pb-Fe shells were fixed at 0.01 Å^2 during fitting. Estimated errors are approximately ± 0.01 Å for R_{Pb-O}, $\pm 10\%$ for N_{Pb-O}, ± 0.03 Å for the R values of the Fe shells, and $\pm 25\%$ for the N values of the Fe shells.

below the detection limit of the IR spectrometer. The FTIR spectra of $CdSO_4^0(aq)$, $MnSO_4^0(aq)$, and $NiSO_4^0(aq)$ are shown in Figure 5. Also shown are the FTIR spectra of $HSO_4^-(aq)$, $SO_4^{2-}(aq)$, and the spectrum of the SO_4-Pb ternary complex forming at the goethite surface on 1 mM Pb addition at pH 4.5. The general appearance of the spectra of the $MeSO_4^0(aq)$ solution complexes is close to that of sulfate in aqueous solution, indicating that T_d symmetry is largely retained. The ν_1 bands are slightly active, and the ν_3 bands show a small shift toward higher wavenumbers relative to the spectrum of $SO_4^{2-}(aq)$, but no distinct splitting of the ν_3 bands is observed. This indicates that Me(II)-SO_4 ion pairing in solution is mainly due to electrostatic interactions, which lead to small distortions of the SO_4 octahedra. In contrast, the $HSO_4^-(aq)$ spectrum shows strong splitting of the ν_3 band, which indicates a strong distortion of the SO_4 octahedron, consistent with strong covalent bonding between H^+ and SO_4^{2-}.

If it is assumed that Pb-SO_4 bonding is mostly electrostatic, as is observed for the Me(II)-SO_4 complexes shown in Figure 5, then configuration A in Figure 4 would be the most plausible structure for the Pb-SO_4 ternary complexes forming at the goethite surface. This structure can be considered an analog to the inner-sphere SO_4 configuration forming in binary SO_4/ goethite systems proposed by Peak et al. (1999). In this configuration, sulfate is bonded as a monodentate complex interacting with a proton on an adjacent goethite surface site. The strong Fe(III)-SO_4 (Hug, 1997) and H-SO_4 (Fig. 5) interactions result in a relatively large splitting of the SO_4 ν_3 bands (Fig. 2). Replacing the strong H-SO_4 interaction with a relatively weak Pb-SO_4 bond, as in configuration A in Figure 4, leads to less-distorted SO_4 tetrahedra with monodentate-like (C_{3v}) symmetry, which is consistent with the IR spectra we observe for the Pb-SO_4 ternary complexes.

The $Me(II)SO_4^0(aq)$ spectra presented in Figure 5 may, however, not be representative of the $PbSO_4^0(aq)$ spectrum. The logK values of the Me(II)-SO_4 association reactions ($Me^{2+}(aq) + SO_4^{2-}(aq)$ 171 $MeSO_4^0(aq)$) range between 2.1 and 2.4 for the metals shown in Figure 5, whereas the logK value for Pb is 2.8, which indicates that Pb has a higher affinity for sulfate complexation than the other metals. Furthermore, the solubility of $PbSO_4(s)$ is much lower than the solubilities of the $MeSO_4$ salts of the metals appearing in Figure 5. Complexation between Pb^{2+} and SO_4^{2-} ions is therefore possibly more covalent than for the $MeSO_4$ complexes in Figure 5, and as a result, configuration B in Figure 4 may very well be responsible for the IR spectrum observed for the Pb-SO_4 ternary structure. In fact, this configuration was proposed by Ostergren et al.

(2000b) as the structure of the ternary complexes forming, although the possibility of formation of configuration A in Figure 4 was not considered in this study. As pointed out by these authors, configuration B may gain additional stability by SO_4 interacting with adjacent protonated surface sites via H-bonding.

The inorganic ligands Cl^- and CO_3^{2-} have the same effect on the Pb coordination to goethite as SO_4, as shown by the EXAFS results of Bargar et al. (1998) and Ostergren et al. (2000a), respectively. In these studies, increased bonding of Pb to goethite surface sites with $R_{Pb-Fe} \approx 3.9$ Å was observed in co-adsorption experiments with Cl and CO_3, similar to the effect observed for SO_4. This indicates that interactions between sorbed Pb and co-adsorbed Cl and CO_3 may be similar as for sulfate (Fig. 4), stabilizing Pb complexes sorbed in bidentate binuclear fashion at the goethite surface.
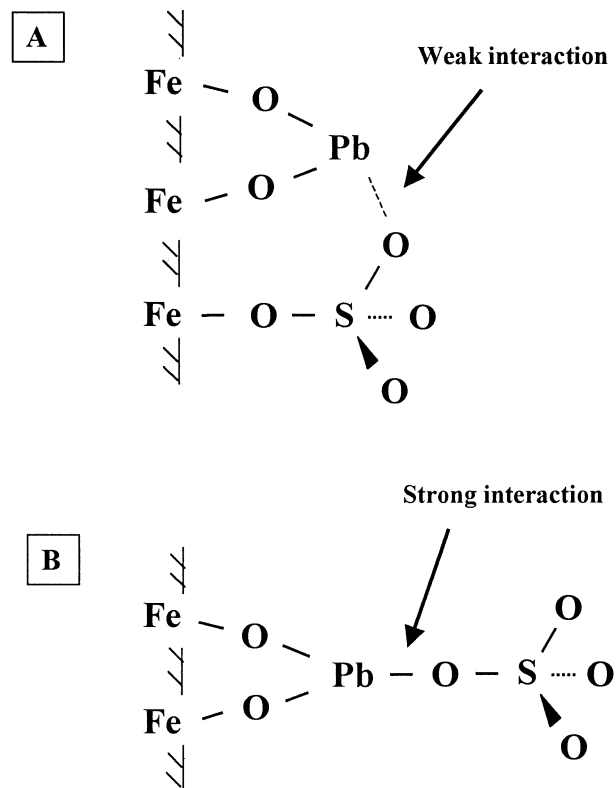

Fig. 4. Pb-SO_4-goethite ternary complex configurations consistent with the FTIR and EXAFS data.
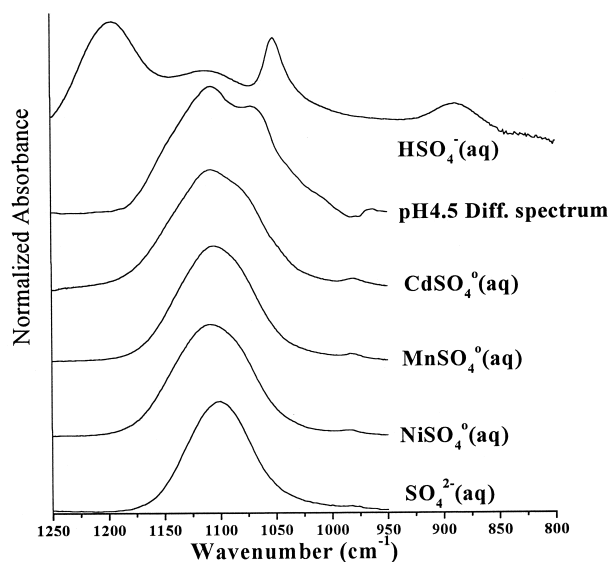
Figure 5. Comparison of the degree of SO_4 ν_3 band splitting between the pH 4.5 difference spectrum and aqueous $MeSO_4$ standards.

Closer inspection of Figure 2 shows that the difference spectra obtained from the Pb-containing systems are not the same at all three pH values, although the frequencies occurring at 1070 and 1110 cm^{-1} appear in all three difference spectra. At pH 6.0, the ν_3 bands are less well resolved than at pH 5.0 and 4.5, suggesting the presence of an additional frequency in the pH 6.0 spectrum. To isolate this frequency, the difference spectrum obtained at pH 6.0 was subtracted from the difference spectrum obtained at pH 5.0. The resultant difference spectrum (not shown) was very similar to the outer-sphere SO_4 spectrum shown in Figure 1c (pH 6.0, no Pb addition). This indicates that at pH 6.0, 1 mM Pb addition not only leads to formation of ternary Pb-SO_4 complexes, but also results in increased SO_4 outer-sphere sorption. At pH 4.5, the difference spectrum has a negative ν_1 absorbance, and the spectrum shows dips (relative to the difference spectrum obtained at pH 5.0) at 1170, 1133, and 1070 cm^{-1}, which are the ν_3 band locations of the SO_4 inner-sphere complex forming in the absence of Pb (Fig. 2). The negative absorbances at these spectral locations indicate that part of the SO_4 sorbed initially (i.e., before Pb addition) as inner-sphere complexes is replaced by or transformed into Pb-SO_4 ternary complexes on a 1 mM Pb addition at pH 4.5.

An analysis of the difference spectra between different levels of Pb addition is shown in Figure 6 to further characterize the effect of Pb addition on SO_4 sorption to the goethite surface. Shown in this figure are the successive difference spectra between the spectra obtained at Pb solution concentrations of 0, 10, 100, 500, and 1000 μM at pH 5.0. Also shown is the difference spectrum obtained from subtracting the SO_4 spectrum at a 500 μM Pb solution concentration from the SO_4 spectrum with 2500 μM Pb present (not shown in Fig. 1b). Several points can be made from this figure. Between [Pb] = 0 and 500 μM, the frequencies characteristic of SO_4 present in Pb-SO_4 ternary complexes are more sharply defined for the difference spectra of higher Pb concentrations. Further increasing the Pb solution concentration from 500 to 1000 μM leads to negative absorbances at the spectral locations of the ν_3 bands

of the inner-sphere SO_4 complex forming in the absence of Pb, which is even more pronounced in the difference spectrum of the 500 and 2500 μM Pb concentrations. The relatively broad peaks for the difference spectra obtained by incremental Pb increases of 0 to 10 and 10 to 100 μM Pb indicates that at these relatively low Pb concentrations, increased SO_4 sorption not only occurs due to formation of Pb-SO_4 complexes but also via additional inner-sphere and outer-sphere SO_4 complexation. Evidence for increased SO_4 inner-sphere complexation (in the same configuration as in Pb-free systems, i.e., with $C_{2\nu}$ symmetry, and without Pb involved in the surface complex) at low Pb concentrations is also provided by comparison of the difference spectrum of the spectra obtained at 1000 and 0 μM Pb at pH 5.0 (Fig. 1b) to the difference spectrum of the spectra obtained at 1000 and 500 μM Pb (Fig. 6). Negative absorbances at the ν_3 band spectral locations of $C_{2\nu}$ inner-sphere SO_4 complexes are observed for the 1000−500 spectrum, but not for the 1000−0 spectrum. Transformation of $C_{2\nu}$ inner-sphere complexes into SO_4-Pb ternary complexes, as indicated by negative ν_3 band absorbances of the former complexes, would appear in both the 1000−0 and 1000−500 spectra if no additional SO_4 inner-sphere complexation had occurred as a result of 500 μM Pb addition. However, negative absorbances only appear in the 1000−500 spectrum, which indicates the formation of inner-sphere SO_4 complexation ($C_{2\nu}$ symmetry) on raising the Pb solution from 0 to 500 μM, followed by transformation of these inner-sphere complexes into Pb-SO_4 ternary complexes when the Pb solution concentration is further raised to 1 mM. Similar analyses were done on the pH 4.5 and pH 6.0 systems (not shown). The main differences with respect to the pH 5.0 system were as follows. (1) At pH 4.5, the negative ν_3 absorbances in the 1000−500 and 2500−500 difference spectra are much stronger than at pH 5.0, whereas at pH 6.0 they are much weaker. Moreover, at pH 4.5, negative ν_3 absorbances already appear in the 500−100 spectrum, which is not the case at pH 5.0 and 6.0; (2) As noted before, part of the initial (i.e., before Pb addition) SO_4 sorbed as inner-sphere complexes at pH 4.5 is transformed into Pb-SO_4 ternary complexes when raising the Pb solution concentration from 0 to 1 mM Pb, as evidenced by the negative absorbances in the 1000−0 difference spectrum (Figs. 1a and 2). This was not observed at pH 5.0 and 6.0; (3) relatively strong increases in SO_4 outer-sphere sorption on Pb addition are observed in the difference spectra at pH 6.0.

These results indicate that Pb affects SO_4 sorption via electrostatic effects as well as by ternary complex formation and that the relative impacts of these mechanisms are a function of pH and the level of Pb addition. The analysis described in the previous paragraph indicates that, although ternary complex formation is observed at all three pH values studied here, it appears to be promoted (relative to the importance of electrostatic effects in the overall additional SO_4 sorption resulting from Pb addition) at lower pH values given a certain Pb solution concentration. At a given pH value, SO_4 sorption via ternary complex formation becomes more important relative to electrostatic effects as the Pb concentration is raised; moreover, it appears that part of the SO_4 sorbed at the goethite surface as inner-sphere complexes without being coordinated by Pb is transformed into SO_4-Pb ternary complexes as the Pb concentration increases, an effect most pronounced at low pH. This
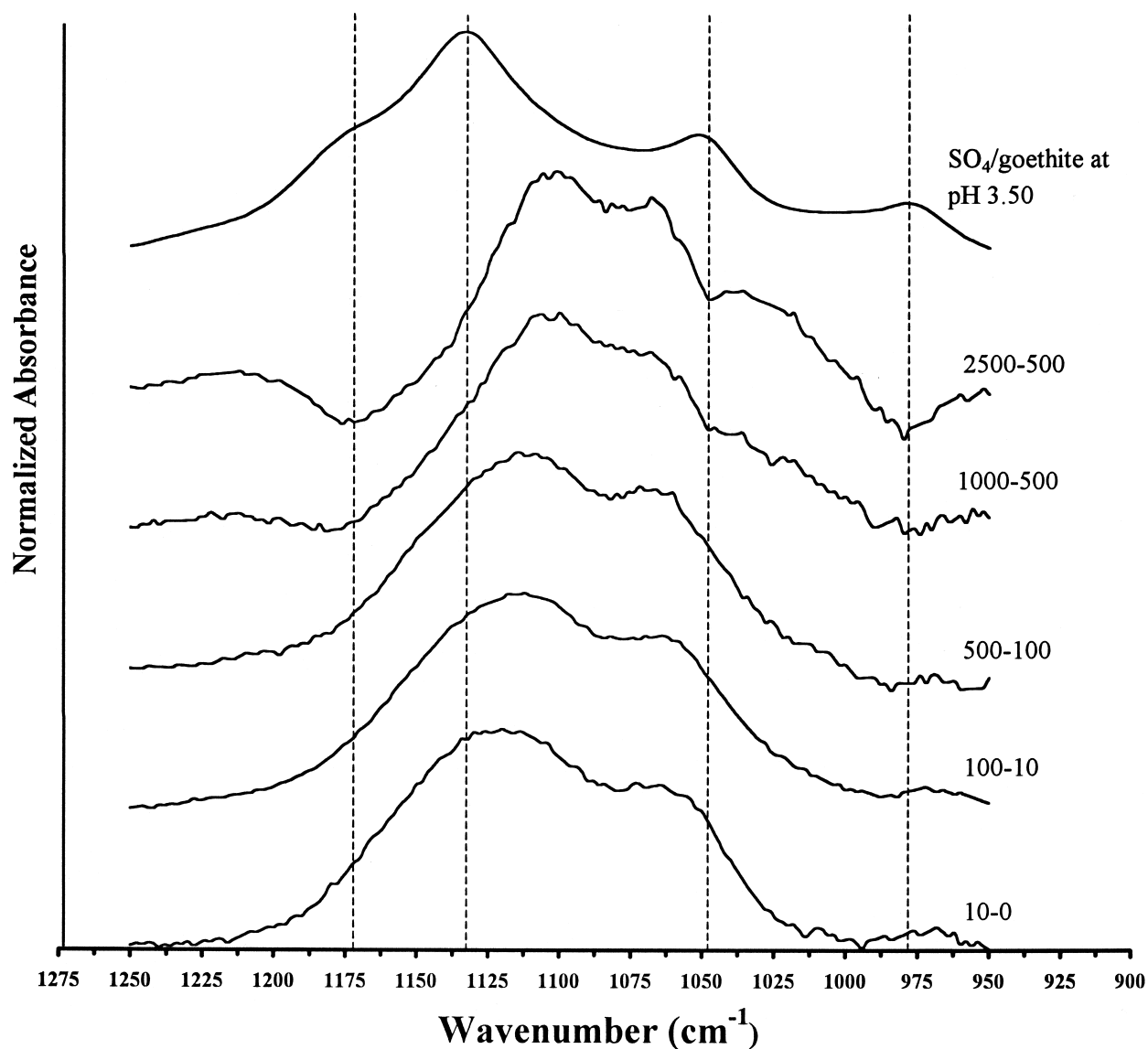
Fig. 6. Difference spectra between successive Pb additions at pH 5.0. The numbers in the figure legends refer to the Pb solution concentrations in μM. The dotted lines locate the ν_1 and ν_3 bands of sulfate inner-sphere complexes with $C_{2\nu}$ symmetry.

further increases the relative importance of SO_4-Pb-complex formation in the overall SO_4 uptake by goethite at high levels of co-adsorbing Pb.

The electrostatic effect of Pb sorption is readily explained by the fact that Pb is bonded to the goethite surface as inner-sphere complexes (as indicated by our EXAFS data, as well as by Bargar et al., 1997 and Ostergren et al., 2000a,b). Pb sorption will therefore create additional positive surface charge, which results in more favorable conditions for SO_4 sorption. At a fixed Pb solution concentration level, more Pb sorption, and therefore a larger change in surface charge, is expected at higher pH, which may explain the relatively large electrostatic effect at higher pH. The system pH value does not only affect the extent of the electrostatic effect but also affects the mechanism by which the additional SO_4 complexation occurs. At lower pH values (pH 4.5 and 5.0), the additional SO_4 complex-

ation occurs to a large extent via inner-sphere complexation, whereas at pH 6.0 a relatively large fraction adsorbs via outer-sphere complexation, which is similar to the effect of pH on SO_4 adsorption to goethite in Pb-free systems (Peak et al., 1999; Wijnja and Schulthess, 2000). Ostergren et al. (2000b) did not report any additional inner-sphere SO_4 complexation, but these authors did note that sulfate outer-sphere complexation via electrostatic effects of Pb co-adsorption was more pronounced at pH 7.0 than at pH 5.0.

The transformation of inner-sphere SO_4 complexes (with $C_{2\nu}$ symmetry) into Pb-SO_4 ternary complexes, a mechanism promoted by low pH values and high Pb additions, suggests a surface-crowding effect, where interactions occur between inner-sphere Pb and inner-sphere SO_4 sorption complexes that lead to the formation of ternary complexes. At lower pH, transformation of inner-sphere SO_4 complexes from $C_{2\nu}$ sym-

metry to ternary complexes is observed at lower Pb solution concentrations than at higher pH, indicating a more direct interaction between SO_4 and Pb (i.e., the formation of ternary complexes) given a certain Pb solution concentration at low pH relative to high pH. This may be due to the fact that more inner-sphere SO_4 sorption occurs at lower pH than at higher pH, both in absolute and relative terms, and suggests that Pb sorption to goethite is more affected by the presence of SO_4 at low pH vs. high pH, which is consistent with the macroscopic results of Pb uptake by goethite presented in Ostergren et al. (2000b). Electrostatic effects of SO_4 co-adsorption on the adsorption of metals to goethite, which based on the results of Collins et al. (1999) solely account for the increased Cd sorption on goethite in co-adsorption experiments with sulfate, should also be most pronounced at low pH, due to the increase in inner-sphere SO_4 complexation with decreasing pH.

5. CONCLUSIONS

This study indicates that the co-adsorption of Pb may have pronounced effects on the speciation of SO_4 sorption complexes on goethite. Both electrostatic effects and the formation of ternary complexes play a role in the enhanced uptake of SO_4 by goethite when Pb is introduced as a co-adsorbing species. The relative impacts of these mechanisms are a function of pH and the level of Pb addition. Ternary complex formation plays an important role at low pH values and high Pb concentrations, whereas pronounced electrostatic effects are observed at high pH values and low Pb concentrations. The electrostatic effect results in additional inner- and outer-sphere SO_4 complexation at the goethite surface, with inner-sphere complexation being more pronounced at low pH values, and outer-sphere complexation at high pH values. Our results suggest that at least part of the ternary complex formation is due to surface crowding, where interactions between inner-spherically coordinated SO_4 complexes and Pb result in the formation of ternary complexes at the goethite surface.

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