# OXIDATION OF 1-NAPHTHOL COUPLED TO REDUCTION OF STRUCTURAL $Fe^{3+}$ IN SMECTITE

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**Abstract**—Sorption and transformation of 1-naphthol by a K-smectite (K-SWy-2) were studied using batch sorption isotherms, Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). The sorbents included three preparations of the reference smectite clay (SWy-2): (1) whole clay containing naturally occurring carbonate impurities, (2) SWy-2 with the removal of carbonate impurities, and (3) the carbonate-free SWy-2 fraction amended with calcite. For the whole clay and carbonate-free clay amended with calcite, >80% of added 1-naphthol disappeared from aqueous solution within 24 h, corresponding to a sorbed concentration of $\geqslant 2$ mg/g of clay. In contrast, only 35% of the added 1-naphthol disappeared from solution in the carbonate-free clay after 24 h of exposure. For the clays from the three preparations in this study, <1% of sorbed 1-naphthol could be recovered by methanol extraction from the clays. The XRD data suggested that 1-naphthol was intercalated in the smectite, but was not conclusive because the 1-naphthol sorption range (1.5−2.8 mg/g of clay) in this study had relatively minor effects on the XRD patterns. The FTIR spectra of sorbed 1-naphthol-clay complexes demonstrated structural $Fe^{3+}$ reduction. The spectra also showed evidence of the transformation of 1-naphthol. It suggests that reduction of structural $Fe^{3+}$ may be coupled to oxidation/polymerization of 1-naphthol. Further transformation of oxidized 1-naphthol, such as by oxidative coupling reactions, is implicated by formation of a dark gray color on the clay and the inability to extract sorbed 1-naphthol.

**Key Words**—FTIR, 1-naphthol, Smectite, XRD.

## INTRODUCTION

Carbaryl (1-naphthyl *N*-methylcarbamate) is one of the most commonly used carbamate insecticides (US Department of Agriculture, 1994−2001; US Environmental Protection Agency, 1987). In 1997, estimated carbaryl usage in the United States was 50,000 kg (Barcelo and Hennion, 1997), which increased to $1.4 \times 10^6$ kg in 2001 (US Department of Agriculture, 1994−2001). It has been widely distributed in the environment. A study conducted by Larson *et al.* (1996) found carbaryl in surface water at ~0.010 μg/L in seven of eight sites in the Mississippi River Basin sampled during May to September, 1991. Carbaryl is subject to alkaline hydrolysis in aqueous media resulting in the formation of 1-naphthol. Rajagopal *et al.* (1984) reported that >50% of the soil-applied carbaryl was converted to 1-naphthol. 1-naphthol has been detected in California groundwater at concentrations up to 610 μg/L (Barbash and Resek, 1996; Barcelo and Hennion, 1997). It was reported that 1-naphthol was more toxic to soil bacteria, mollusks, invertebrate insects and marine fish than was carbaryl (Bollag and Liu, 1971; Day, 1991; Mount and Oehme, 1981).

Recent studies have demonstrated that under environmentally relevant conditions, clay minerals provide binding sites for certain aqueous-phase pesticides and organic contaminants including triazines, nitroaromatics, ureas and carbamates (Arroyo *et al.*, 2004; Boyd *et al.*, 2001; Laird *et al.*, 1992; Li *et al.*, 2003a, 2004a; Sheng *et al.*, 2001; Weissmahr *et al.*, 1998). Many organic chemicals (*e.g.* chlorinated hydrocarbons and nitroaromatic compounds) undergo a reduction catalyzed by Fe(II) associated with clay minerals (Amonette *et al.*, 2000; Cervini-Silva *et al.*, 2001; Hofstetter *et al.*, 2003; Tor *et al.*, 2000; Xu *et al.*, 2001). It has been demonstrated that phenol and phenolic compounds react with Fe(III) and Mn(III/IV) oxides as well as with silicate clays, and form high-molecular-weight products (Kung and McBride, 1988; McBride, 1987; Li *et al.*, 2003b; Naidja *et al.*, 1998; Soma *et al.*, 1986; Wang *et al.*, 1978). The degree and rate of the redox reaction depended on pH, types of minerals, exchangeable cations on clays and solution matrix (*i.e.* presence of complexing agents) (Kung and McBride, 1988; Laha and Luthy, 1990; Li *et al.*, 2003b; Naidja *et al.*, 1998; Stone and Morgan, 1984; Ukrainczyk and McBride, 1992). For example, the initial oxidation rate of phenolic compounds by Mn oxides was observed to be accelerated with decreasing pH (Laha and Luthy, 1990; Stone and Morgan, 1984; Ukrainczyk and McBride, 1992). In contrast, oxidation by Fe oxides (*i.e.* goethite, ferri-hydrite) occurred to a greater extent at alkaline pH,

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which is presumably due to the enhanced stability of the formed phenolic radicals at a relatively high pH (Kung and McBride, 1988). Wang and Huang (1986) noted that the intercalated hydroquinone in Ca-saturated nontronite (a structural Fe(III)-rich smectite) was transformed into humic macromolecules. In a subsequent study, Wang and Huang (1989) observed the transformation of 1,2,3-trihydroxybenzene into humic polymers catalyzed by Ca-saturated silicates with the sequence of nontronite > kaolinite > bentonite. Based on the difference in structural Fe content in these minerals, they implicated structural Fe(III) as an electron acceptor in humic substance-forming reactions. However, there was no direct evidence for the reduction of structural Fe(III) in the clay coupled to oxidation of polyphenols. The authors also hypothesized an alternative mechanism that mineral surface-adsorbed molecular $O_2$ was the primary agent in oxidizing 1,2,3-trihydroxybenzene (Wang and Huang, 1989).

Clay minerals have been shown to cause the hydrolysis of several pesticides including carbosulfan, carbofuran, aldicarb, pirimicarb, chlorprofan and triasulfuron (Pusino *et al.*, 2000; Wei *et al.*, 2001). Arroyo *et al.* (2004) studied sorption and hydrolysis of carbaryl by a reference smectite clay (SWy-2) and demonstrated that carbaryl was hydrolyzed to 1-naphthol in aqueous slurries of K-SWy-2. Hydrolysis of carbaryl was attributed to alkaline conditions caused by dissolution of carbonate impurities present in the reference smectite. Darkening of the clay was also observed, suggesting some chemical transformation of sorbed carbaryl or 1-naphthol. When ^{14}C-labeled carbaryl was added to slurries of SWy-2, most sorbed carbaryl was unextractable from the clay by methanol. In contrast, when carbaryl was added to slurries of SWy-2 which had been treated to remove carbonates, no hydrolysis to 1-naphthol was observed and nearly 100% of the clay-sorbed pesticide was methanol extractable (Arroyo *et al.*, 2005).

The objective of this study was to evaluate the reactions of 1-naphthol in aqueous SWy-2 slurries. Sorption and transformation of 1-naphthol by SWy-2 was studied using whole clay and the clay-sized fraction of SWy-2 which was treated, using sodium acetate solution (pH = 5.0), to remove carbonate impurities. Sorption and transformation of 1-naphthol in slurries of homoionic K-SWy-2 was evaluated using batch sorption isotherms, FTIR and XRD.

## MATERIALS AND METHODS

The reference clay, SWy-2, used in the study was obtained from the Source Clays Repository of The Clay Minerals Society (Department of Agronomy, Purdue University, West Lafayette, Indiana, USA). Milli-Q deionized (d.i.) water (Millipore Corp.) was used throughout all sample preparations. Two separate procedures were used to prepare homoionic K-SWy-2 (whole clay and carbonate-free clay). First, the reference clay used as received was suspended in water, then $K^+$ saturated by repeated washing with 0.1 M KCl solution; this material is referred to as 'whole clay'. Second, SWy-2 was suspended in water and subjected to low-speed centrifugation (58–60 g) to isolate the <2 μm particles. The <2 μm clay-size fraction was titrated to pH 6.8 with sodium acetate (pH 5.0) to remove carbonate impurities, then saturated with $K^+$ (as above). This clay sample is referred to as carbonate-free clay. After $K^+$ saturation, clays were washed with d.i. water until free of chloride as indicated by $AgNO_3$. Clay suspensions were quick frozen, freeze dried and stored. Additional details regarding clay preparation procedures can be found in Arroyo *et al.* (2005).

The 1-naphthol (>99% purity) was obtained from Sigma-Aldrich (St. Louis, Missouri), and used to prepare standard solutions in 0.1 M KCl at pH 3.0 (adjusted with HCl) protected from light. An aqueous solution containing 30 μg/mL of 1-naphthol in 0.1 M KCl solution at pH 6.5 (protected from light) was prepared and used immediately in sorption/transformation experiments.

A batch equilibration method was used to evaluate sorption of 1-naphthol by K-SWy-2 clay. 5 mL of the 30 μg/mL 1-naphthol solution was added into a 7.4 mL borosilicate amber glass vial, containing 60 mg of clay, which was closed with a Teflon-lined cap. Vials were prepared in triplicate, mixed briefly using a vortex mixer, then continuously rotated mechanically (40 rpm) at room temperature (23±2ºC) for intervals of 2, 4, 8, 12, 16, 24, 48, 72 and 96 h. Vials were centrifuged at ~3500 g for 20 min to separate solid and liquid phases and the latter were analyzed for 1-naphthol by high-performance liquid chromatography (HPLC). The supernatant pH values were measured using a pH meter. The centrifuged clay pellets were extracted with methanol and the extracts analyzed by HPLC for 1-naphthol. Amounts of 1-naphthol extracted from the clay pellets were obtained by subtracting the mass of 1-naphthol present in residual water from the mass of 1-naphthol extracted by methanol. Two additional kinetic experiments were performed to evaluate the effect of alkalinity produced by the dissolution of carbonate on the sorption and transformation of 1-naphthol. First, 1-naphthol was added to a calcite suspension, and second, was added into a carbonate-free clay suspension amended with calcite. In these experiments 5.0 mL of the 30 μg/mL 1-naphthol solution were added into 7.4 mL borosilicate amber glass vials containing 1.3 mg of calcite (with and without clay). This amount of added calcite corresponded to the amount of calcium carbonate present in the 60 mg whole clay. Vials were mixed briefly using a vortex mixer and then mechanically rotated continuously at room temperature (23±2ºC). The samples were prepared in triplicate. The 1-naphthol concentration was determined after equilibration times of 2, 4, 8, 12, 24, 48, 72 and 96 h. Sampling and analyses of 1-naphthol were as described above.

The HPLC system consisted of a Perkin-Elmer 250 pump connected to a UV-vis detector (230 nm) and a 150 × 4.6 mm Supelcosil-$C_{18}$ column (5 μm particle size and 120 Å pore size, Supelco). The mobile phase was an isocratic mixture of 71% methanol and 29% water adjusted to pH 3.2 with acetic acid. The injection volume was 25 μL and the flow rate was 1.0 mL/min.

Basal spacings of K-SWy-2 clays with and without sorbed 1-naphthol were determined by XRD analysis. Suspensions of K-SWy-2 were dropped from a glass pipette onto glass slides and allowed to air dry at ambient conditions to obtain oriented clay films. The XRD spectra of oriented films were measured at ambient air-dry condition as well as after 48 h of exposure to 1% relative humidity (RH) and 48 h of exposure to 100% RH. The XRD patterns were recorded using CuKα radiation and an XRD system consisting of a Philips 3100 X-ray generator (Philips Electronic Instrument, Inc., Mahwah, New Jersey), Philips 3425 wide-range goniometer fitted with a θ compensating slit, a 0.2 mm receiving slit, a diffracted-beam graphite monochromator, and PW1877 automated powder diffraction (Philips Electronics) control software. Diffraction patterns were measured from 4 to 11°2θ, in steps of 0.02°2θ, at 2 s/step.

The FTIR experiments were performed to evaluate the potential transformations of sorbed 1-naphthol and changes of K-SWy-2 structural Fe. Batch equilibrations of 1-naphthol in aqueous suspension of the whole clay and carbonate-free clay were mixed as described above. The vials were sampled at 48 h and 144 h and the suspensions were used to prepare self-supporting films in triplicate. The 1-naphthol-clay suspension (containing 20 mg of clay) was passed through a 0.45 μm Supor-450 hydrophilic polyethersulfone membrane (47 mm diameter) installed in a Millipore filtration system. The resulting clay deposit on the filter was protected from light, allowed to air dry overnight, and then removed from the filter (Johnston et al., 2002). Infrared spectra were obtained using a Perkin-Elmer GX2000 FTIR spectrometer equipped with deuterated triglycine (DTGS) and mercury-cadmium-telluride (MCT) detectors, an internal wire grid IR polarizer, a KBr beam splitter, and a sample compartment purged with dry air. The unapodized resolution for the FTIR spectra was 2.0 cm$^{-1}$, and 64 scans were collected for each spectrum. GRAMS/32 (Galactic Software) program was used to analyze and plot spectra.

The stretching and bending vibrational bands of the structural OH groups of SWy-2 smectite were analyzed using the non-linear least-squares peak-fitting algorithm in the GramsAI/32 Version 6.00 program (Thermo Electron Corporation, Madison, Wisconsin). Individual bands were fitted using the Voigt function (variable Lorentzian/Gaussian lineshape). The natural spectral line shape of a molecular vibration is Lorentzian; however, lineshape is influenced by the nature of the sample and sample presentation method, as well as some instrumental considerations. We have used the Voigt function to quantitatively fit the ν(OH) and δ(MOH) bands of clay minerals in a prior work (Xu et al., 2000). In the δ(MOH) region, three Voigt functions were used for the three OH-deformation bands at 916, 883 and 847 cm$^{-1}$ with a linear baseline correction between 950 cm$^{-1}$ and 820 cm$^{-1}$. The three Voigt functions, baseline and the residual spectrum (difference between the actual spectrum and the fitted spectrum) are shown in Figure 1. In the ν(OH) region, we used the same curve-fitting procedure reported recently by Zviagina et al. (2004) to fit the ν(OH) region.

## RESULTS AND DISCUSSION

Dissipation of 1-naphthol from aqueous solution is presented in Figure 2 for the suspensions of whole clay containing carbonates, carbonate-free clay, carbonate-free clay amended with calcite, and calcite. It is clearly demonstrated that ~100% of added 1-naphthol disappeared from the aqueous phase in the slurries of whole K-SWy-2 and carbonate-free clay amended with calcite after 48 h. In whole-clay slurries, ~80% of 1-naphthol initially added had disappeared from solution after 24 h, corresponding to the sorption at ~2.0 mg/g of clay. In slurries of carbonate-free clay amended with calcite, ~95% of 1-naphthol had disappeared from solution after 24 h, corresponding to the sorption at ~2.4 mg/g of clay. Disappearance of 1-naphthol from solution in carbonate-free clay slurries (not amended with calcite) occurred to a much lesser extent. Approximately 35% of the 1-naphthol added initially was lost from solution within 24 h, and ~45% at 96 h. Disappearance of 1-naphthol in the calcite suspension was ~2% at 24 h, and ~20% at 48 h. The disappearance of 1-naphthol was very similar in slurries of whole SWy-2 that naturally contains carbonate impurities (e.g. calcite, dolomite) and the SWy-2 that had been treated to remove these naturally occurring carbonates then amended with calcite. Disappearance of 1-naphthol from solution was apparently favored by alkaline pH (produced by the dissolution of carbonates) and the presence of SWy-2.

1-Naphthol present in aqueous suspension of the whole clay was transformed as indicated by a color change of the clay from off-white to dark gray, similar to the observations reported in our previous study with carbaryl (Arroyo et al., 2004) and by Wang et al. (1978). 1-Naphthol added to the carbonate-free clay slurry amended with calcite also developed a gray color, which intensified over time. In contrast, color change was not observed when 1-naphthol was added to the carbonate-free clay suspension or to the aqueous suspension containing only calcite. Thus, it was apparent that the combination of smectite and calcite facilitated 1-naphthol oxidation to produce the colorful products adsorbed by the clay.
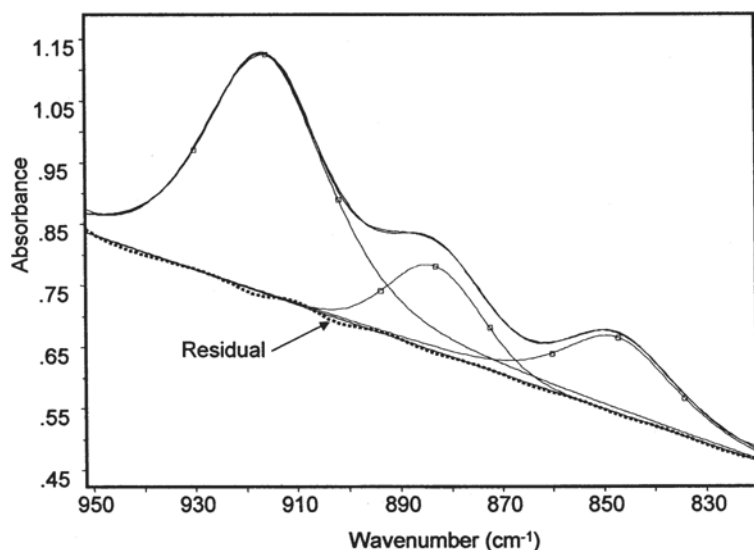
Figure 1. Voigt function fittings and residue at the three OH-deformation bands at 916, 883 and 847 $cm^{-1}$ with a linear baseline correction between 950 and 820 $cm^{-1}$.

Adsorbed 1-naphthol that could be extracted by methanol from any K-SWy-2 samples was minimal (<1%). These results are consistent with those of Arroyo *et al.* (2004) who demonstrated that ~71% of $^{14}C$ activity of ring-labeled carbaryl sorbed by the whole SWy-2 was non-extractable by methanol while the recovery of sorbed carbaryl in carbonate-free clays by methanol extraction was ~100% (Arroyo *et al.*, 2005).

The XRD patterns for air-dried films of whole clay, carbonate-free clay, and the corresponding two clays with sorbed 1-naphthol at 120 h are shown in Figure 3. In both cases the clay basal spacings increased from 10.7−10.8 Å to ~11.2 Å (Table 1) implying some intercalation of 1-naphthol and/or its transformation products between smectite layers. Similar expansions of the interlayer distances were noted for these same clay
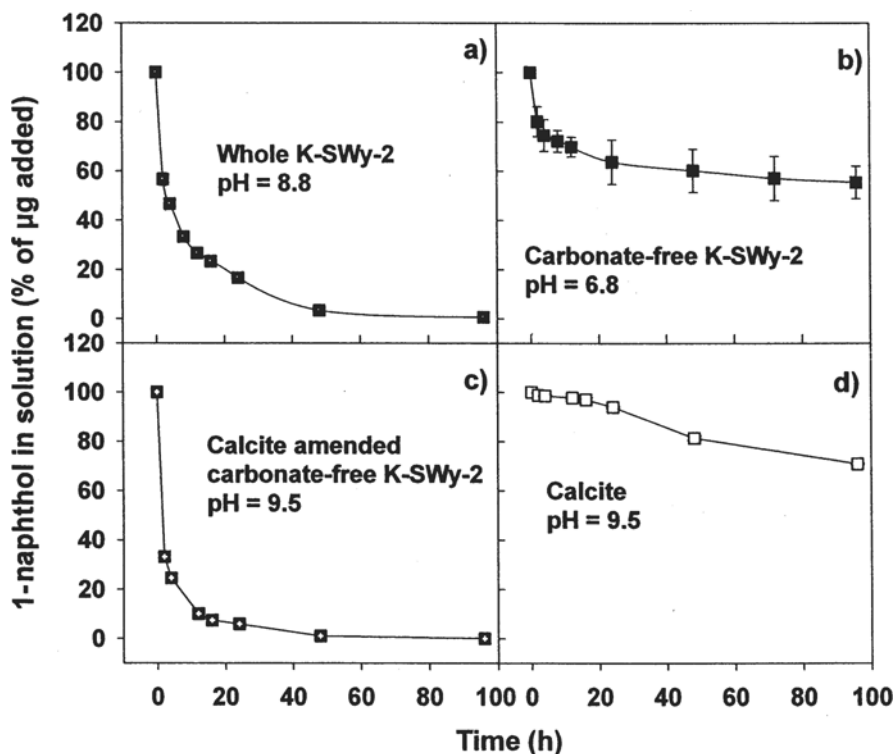


Figure 2. Disappearance of 1-naphthol from aqueous solution in the suspensions of (a) whole clay containing carbonates, (b) carbonate-free clay, (c) carbonate-free clay amended with calcite, and (d) calcite.
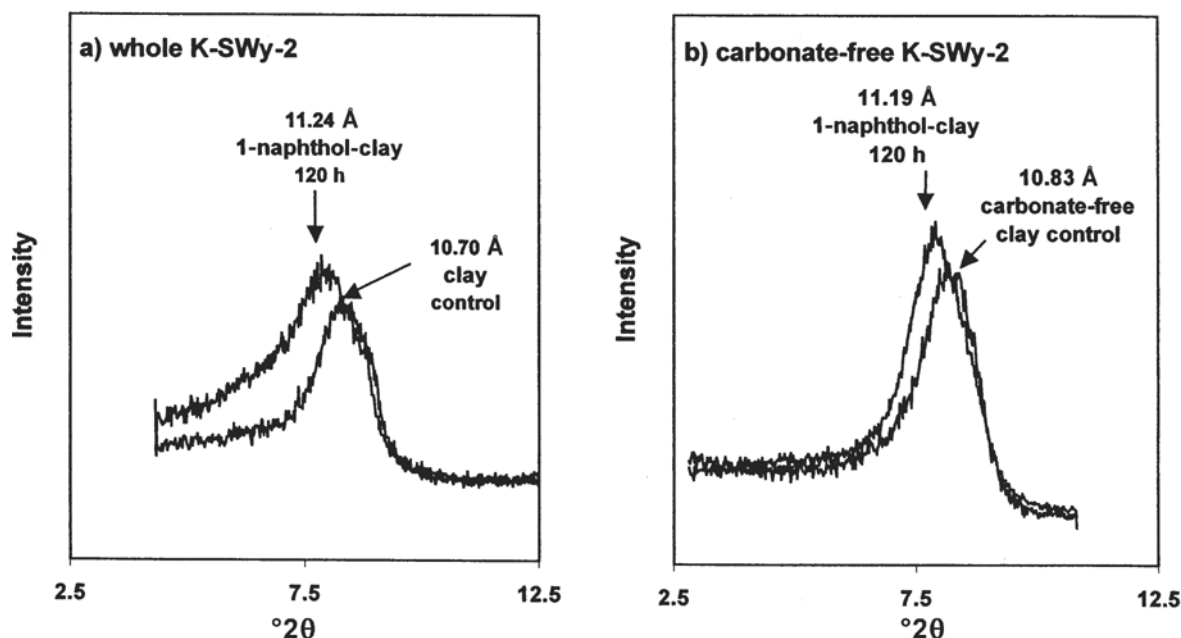
Figure 3. XRD patterns of oriented, air-dried K-SWy-2 films with and without 1-naphthol sorption: (a) whole clay and (b) carbonate-free clay.

films that were equilibrated at 1% RH (Table 1). The shapes and widths of the XRD patterns for both clays without 1-naphthol sorption (Figure 3) imply a randomly interstratified mixture of clay layers with ~10 and 12.5 Å $d_{001}$-spacings, both quite reasonable for K-saturated smectites at low humidity (MacEwan and Wilson, 1980). When 1-naphthol was added to the carbonate-free clay, there was a modest increase in the number of ~12.5 Å $d_{001}$-spacings in this mix, shifting the overall XRD peak to a slightly larger $d_{001}$-spacing (Figure 3b). This is consistent with our previous observations of intercalated aromatic compounds (Li et al., 2004b) in which the $d_{001}$ spacings of air-dried K-smectite clay films increased slowly towards ~12.5 Å as the aromatic compound (i.e. 1,3-dinitrobenzene) loading increased from 0 to 34 mg/g of clay. In the present study, the 1-naphthol loading rate is only 1.4 mg/g of clay (Figure 2b), so the XRD data are consistent with our hypothesis of weak interlayer sorption of 1-naphthol in the carbonate-free system.

Interactions between 1-naphthol and the whole clay seem to produce transformation products, as described below, and the XRD data (Figure 3a) also indicate differences in the interlayer distances induced by sorption of 1-naphthol. The maximum intensity of the XRD pattern for the 1-naphthol-whole clay systems still occurs near 11.2 Å, indicating again that most $d_{001}$ spacings are either ~10 or 12.5 Å (Figure 3a). However, the peak is much broader than that for the carbonate-free clay (Figure 3b), implying that many ~15 Å $d_{001}$ spacings are present in the K-smectite film of the whole clay after exposure to 1-naphthol. These larger $d_{001}$ spacings may indicate that some transformation products of 1-naphthol in the whole clay are nonplanar and serve to prop the layers open. Alternatively, $Ca^{2+}$ ions from dissolved carbonates occupy some interlayer cation-exchange sites and cause those interlayers to remain more swollen upon air drying.

To investigate the effect of 1-naphthol sorption on interlayer expansion by water, the air-dried clay films were exposed to 100% RH. Under these conditions the clay control not treated with 1-naphthol expanded to 15.55 Å, and the clay treated with 1-naphthol to 15.39 Å (Table 1). Note that other studies (Li et al., 2004b; Sheng

Table 1. Measured $d_{001}$ spacings (Å) for K-Swy-2, and carbonate-free K-SWy-2 with and without 1-naphthol sorption. The clay films were analyzed by XRD after each treatment of air drying and exposure to 1% and to 100% RH.

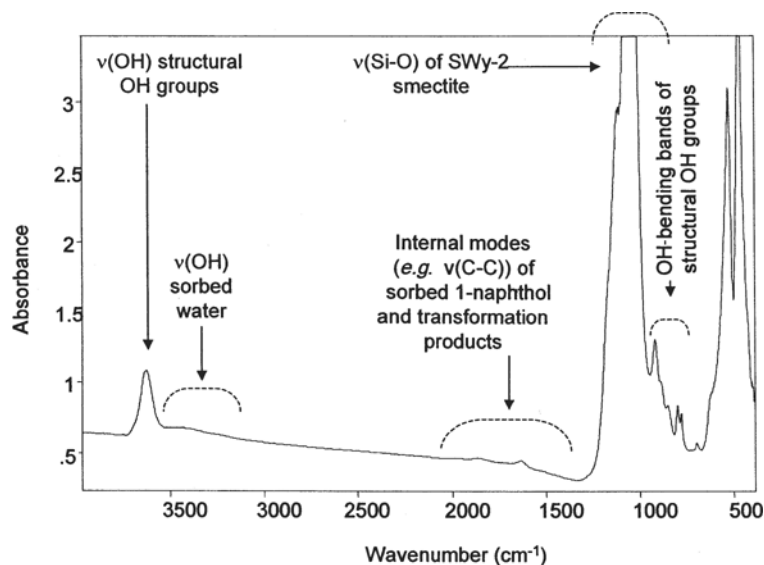| Treatment | K-SWy-2 | | Carbonate-free K-SWy-2 | |
| --- | --- | --- | --- | --- |
| | With 1-naphthol | Without 1-naphthol | With 1-naphthol | Without 1-naphthol |
| Air dried | 11.24 | 10.70 | 11.19 | 10.83 |
| Exposure to 1% RH | 11.16 | 9.99 | n.d. | n.d. |
| Exposure to 100% RH | 15.39 | 15.55 | n.d. | n.d. |

n.d. = not determined

Figure 4. FTIR spectra of 1-naphthol sorbed to the whole SWy-2 clay and carbonate-free SWy-2 in the 4000 to 400 cm$^{-1}$ region (the two spectra are overlapped).

*et al.*, 2002) have shown that intercalated aromatic compounds inhibit K-smectite swelling at 100% RH. In those studies, organic solute (*e.g.* 1,3-dinitrobenzene) sorption >8.4 mg/g of clay was sufficient to retain ~12.5 Å $d_{001}$-spacings even after exposure to 100% RH, with $d_{001}$ spacings increasing steadily towards 15.5 Å as organic solute loading rates decreased (Li *et al.*, 2004b). Thus, swelling of our clay-1-naphthol complex at the loading rate of 1.4 mg/g to a slightly lower $d_{001}$ spacing (compared to the K$^+$-saturated clay alone) upon exposure to 100% RH is again consistent with our hypothesis that 1-naphthol is intercalated in K-smectite.

The FTIR absorbance spectra of 1-naphthol sorbed to the SWy-2 and to carbonate-free SWy-2 clay are compared in Figure 4 in the 4000 to 400 cm$^{-1}$ region. An expanded area of these spectra in the 2200 to 1350 cm$^{-1}$ region is shown (baseline corrected) in Figure 5. This spectral region contains the most prominent bands from the sorbed 1-naphthol and its transformation products. As shown in Figure 4, the relative intensity of the FTIR bands from the sorbed organic species is low compared to the strong clay bands. This is consistent with the fact that a relatively small amount of 1-naphthol was adsorbed (<4 mg/g of clay). The spectra of the whole clay K-SWy-2 (carbonate-containing clay) represented by the dotted lines have additional band intensity present as a broad spectral component under the 1701, 1636 and 1531 cm$^{-1}$ bands
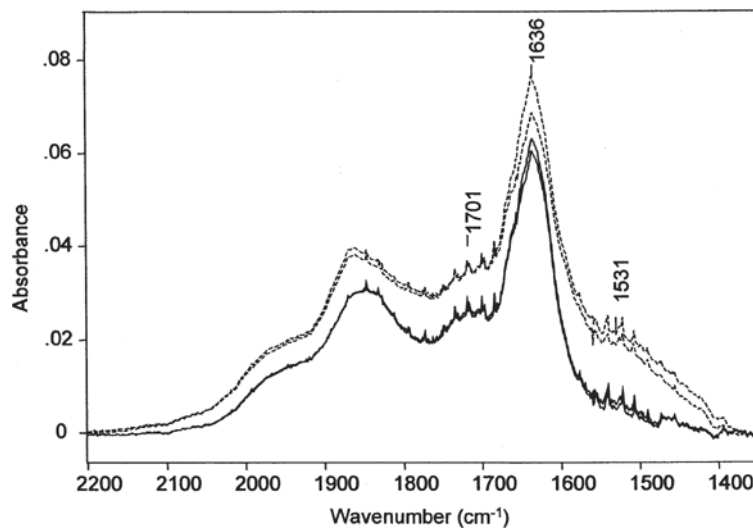


Figure 5. An expanded region in the 2200 to 1350 cm$^{-1}$ of the FTIR spectra of 1-naphthol-sorbed whole K-SWy-2 (dotted lines) *vs.* carbonate-free K-SWy-2 (solid lines). Increased band intensity present as a broad spectral component under the 1701, 1636 and 1531 cm$^{-1}$ bands is attributed to the transformation product(s) of 1-naphthol.
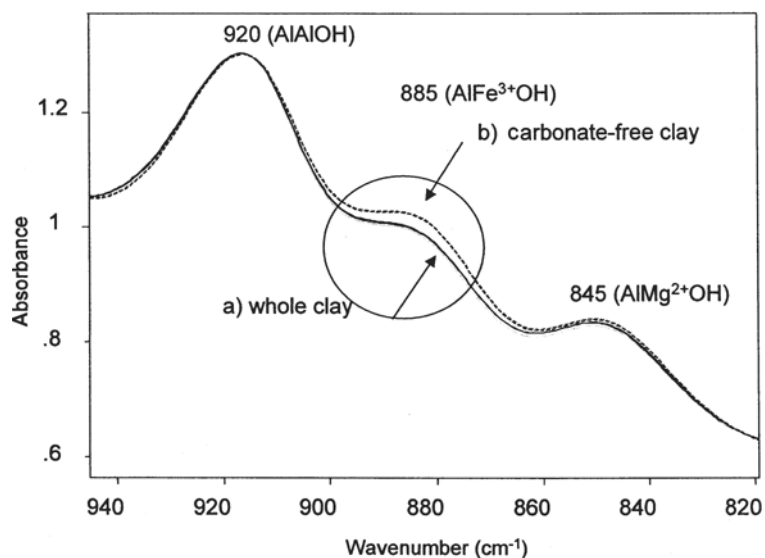
Figure 6. FTIR spectra of the structural OH-bending region of 1-naphthol-sorbed whole K-SWy-2 *vs.* carbonate-free K-SWy-2. A reduction in intensity of the AlFe$^{3+}$OH-bending mode of whole K-SWy-2 was observed relative to the intensity of this band in carbonate-free clay while no changes in the intensities of the AlAlOH and AlMgOH bands were noted.

(Figure 5). This 'new' spectral feature present in the carbonate-containing clay is attributed to the transformation product(s) of 1-naphthol. The FTIR spectra are consistent with our macroscopic evidence (*e.g.* unextractability of sorbed 1-naphthol, color change of clay) showing that a new spectral component is present in the whole clay. Unfortunately, the spectral fingerprint of the sorbed species is characterized by broad, overlapping bands that do not provide detailed clues as to the identification of the sorbed species. Similar broad, featureless bands have been observed in other chemisorption studies of other aromatic compounds on smectites. In a FTIR study of benzene chemisorption

on Cu-smectite, for example, FTIR spectra of the benzene polymerized on the clay surface showed similar broad features in this spectral region (Hinedi *et al.*, 1993).

The FTIR spectra of the OH-bending and stretching regions of the carbonate-containing and carbonate-free K-SWy-2 smectite samples are shown in Figures 6 and 7, respectively. SWy-2 has three bands at 920, 885 and 845 cm$^{-1}$ which are assigned to the structural OH-bending vibrations of AlAlOH, AlFe$^{3+}$OH, and AlMgOH groups, respectively (Farmer, 1974). The experiment was run in triplicate and there are six spectra overlaid in Figure 6 corresponding to three whole-clay samples and
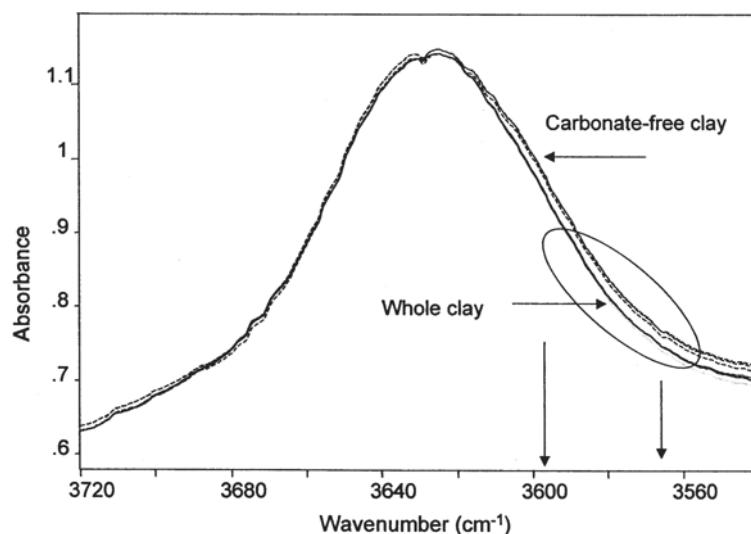


Figure 7. FTIR spectra of the structural OH-stretching region of 1-naphthol-sorbed whole clay and carbonate-free K-SWy-2 reflecting the overall contribution of AlAlOH, AlFe$^{+3}$OH and AlMgOH bands. The v(OH) band of the whole clay shows a lower intensity in the lower-energy portion (3595 to 3572 cm$^{-1}$) of this spectrum representing AlFe$^{3+}$OH and FeFeOH bands.

three carbonate-free samples. There is a consistent reduction in intensity of the $AlFe^{3+}OH$-bending mode of the carbonate-containing K-SWy-2 smectite relative to the intensity of this band in the carbonate-free clay. The $\delta(MOH)$ bands were analyzed using the non-linear least-squares peak-fitting algorithm described in the Materials and Methods section. The experimental data, three Voigt functions, baseline and the residual (difference between fitted and experimental) are shown in Figure 1 for a representative sample. This procedure was used to fit the three $\delta(MOH)$ bands for the six samples (three whole-clay samples, and three carbonate-free clay samples) and the results are shown in Table 2. The normalized intensities shown in Table 2 were obtained by summing the intensities of the three $\delta(MOH)$ bands together. These values correspond to the percent of the total area (and height) of the three OH-deformation bands. Of particular interest to this study is the change in relative intensity of the $AlFe^{3+}OH$ band in the carbonate-free clay from 23.4% (std. dev. 0.1%) of the total intensity of the OH-deformation bands to a value of 17.1% (std. dev = 1.2%). There has been renewed interest in this spectral region of smectites, and quantitative analyses of these three bands have been used to predict the extent of isomorphic substitution in smectites (Vantelon *et al.*, 2001). As shown in Table 2 and in Figure 6, there was little change in the intensities of the AlAlOH and AlMgOH bands (Figure 6). However, the reduction in band intensity of the $AlFe^{3+}OH$ band in the whole-clay fraction indicates that structural $Fe^{3+}$ is being reduced during the sorption/transformation of 1-naphthol. Reduction of structural $Fe^{3+}$ in the clay to $Fe^{2+}$ results in the loss of the hydroxyl group and concomitant decrease in the intensity of the $AlFe^{3+}OH$ population which is accompanied by a decrease in intensity of the 885 cm$^{-1}$ band. Reduction of structural $Fe^{3+}$ in smectite may be coupled via electron transfer to oxidation of sorbed 1-naphthol.

Further support for this proposed electron transfer mechanism is observed in the $\nu(OH)$ region of the structural OH group (Figure 7). The band at 3624 cm$^{-1}$ corresponds to the $\nu(OH)$ mode of the structural OH group of K-SWy-2 smectite. Because of the isomorphous substitution, there are several types of structural OH groups, similar to the OH-bending region, corresponding to AlAlOH, $AlFe^{3+}OH$, AlMgOH groups. What is observed in the 1-naphthol FTIR spectra is a composite band that reflects the overall contribution of each band. In a recent study of dioctahedral smectites, the $\nu(OH)$ band of the structural OH groups of different dioctahedral smectites was decomposed into individual components of AlAlOH (3630), AlMgOH (3601), $AlFe^{3+}OH$ (3595) and FeFeOH (3572) (Zviagina *et al.*, 2004). Of particular interest to this study is that the $Fe^{3+}$-containing components have the lowest position, relative to the AlAlOH and AlMgOH bands. Consequently, reduction of structural $Fe^{3+}$ would cause a decrease in the lower

Table 2. Non-linear least-squares peak fittings of the OH-deformation bands of the whole clay and carbonate-free clay.

| Sample | Band #1 | | | | Band #2 | | | | Band #3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Position | Height | FWHM | Norm area | Position | Height | FWHM | Norm area | Position | Height | FWHM | Norm area |
| Whole clay | | | | | | | | | | | | |
| Rep 1 | 916.1 | 0.0194 | 28.2 | 0.653 | 883.2 | 0.0069 | 21.2 | 0.156 | 847.2 | 0.006 | 26.0 | 0.191 |
| Rep 1 | 916.2 | 0.0207 | 27.3 | 0.654 | 883.5 | 0.0077 | 21.5 | 0.177 | 847.1 | 0.006 | 24.3 | 0.169 |
| Rep 1 | 916.0 | 0.0198 | 27.4 | 0.626 | 883.5 | 0.0076 | 21.7 | 0.176 | 846.9 | 0.007 | 25.8 | 0.198 |
| Average | 916.1 | 0.0200 | 27.6 | 0.644 | 883.4 | 0.0074 | 21.5 | 0.170 | 847.1 | 0.006 | 25.4 | 0.186 |
| Std. dev. | 0.11 | 0.0007 | 0.5 | 0.016 | 0.2 | 0.0004 | 0.2 | 0.012 | 0.14 | 0.001 | 0.9 | 0.015 |
| Carbonate-free clay | | | | | | | | | | | | |
| Rep 1 | 915.7 | 0.020 | 26.7 | 0.588 | 883.3 | 0.0096 | 22.9 | 0.233 | 846.9 | 0.007 | 24.5 | 0.179 |
| Rep 1 | 915.7 | 0.020 | 26.7 | 0.585 | 883.3 | 0.0096 | 22.9 | 0.235 | 846.9 | 0.007 | 24.5 | 0.180 |
| Rep 1 | 915.7 | 0.020 | 26.7 | 0.584 | 883.3 | 0.0096 | 23.0 | 0.235 | 846.9 | 0.007 | 24.5 | 0.181 |
| Average | 915.7 | 0.020 | 26.7 | 0.586 | 883.3 | 0.0096 | 22.9 | 0.234 | 846.9 | 0.007 | 24.5 | 0.180 |
| Std. dev. | 0.02 | 0.0 | 0.0 | 0.002 | 0.01 | 0.0 | 0.0 | 0.001 | 0.03 | 0.0 | 0.0 | 0.001 |

energy portion of this band and the 3595 and 3572 cm$^{-1}$ components were lost due to $Fe^{3+}$ reduction.

In order to test this hypothesis, the Zviagina model parameters were used to fit the observed $\nu$(OH) bands for the whole clay and carbonate-free SWy-2 samples. Using the same parameters as Zviagina *et al.* (2004), the $\nu$(OH) band was fitted using a set of five individual bands corresponding to the different types of structural OH groups present (Figure 8). In agreement with the observed loss in intensity of the AlFe$^{3+}$OH-deformation band, the results for the $\nu$(OH) region indicate some loss in intensity of the FeFeOH-stretching band from 7.0% (std. dev. 0.02%) to 5.7% (std. dev. 0.03%). The $\nu$(OH) band of the whole clay (carbonate-containing clay) has lower intensity in the lower-energy portion of this spectrum, precisely in the area where the AlFe$^{3+}$OH and FeFeOH components occur. Furthermore, these spectral results are correlated and supportive of the changes observed in the OH-bending region. The FTIR spectra provided direct evidence that structural $Fe^{3+}$ was involved in the transformation of 1-naphthol on the whole clay.

## CONCLUSIONS

Batch sorption experiments, XRD and FTIR spectral analysis have produced insights into the reactions of 1-naphthol with smectite clay. It is shown that upon treatment with 1-naphthol, the octahedral $Fe^{3+}$ in K-SWy-2 was reduced to $Fe^{2+}$. Furthermore, reduction of structural $Fe^{3+}$ appears to be accompanied by oxidation of 1-naphthol and the formation of dark-colored products. Alkaline pH conditions emanating from the dissolution of carbonate impurities in SWy-2 are likely to promote proton extraction from the hydroxyl groups of 1-naphthol, followed by electron transfer to structural $Fe^{3+}$ in SWy-2. It is plausible that reactive arylox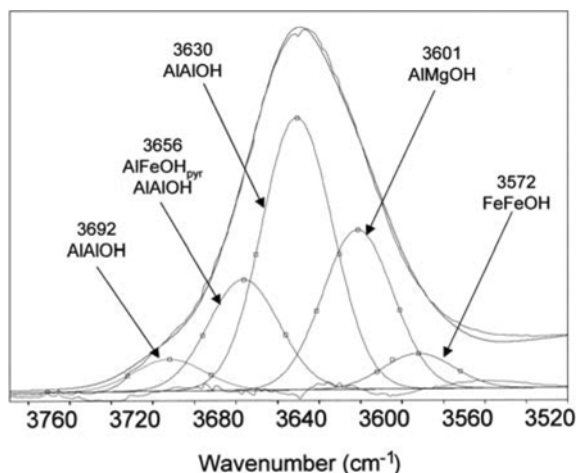y radicals produced from 1-naphthol oxidation in this fashion underwent coupling reactions on the clay surface. The presence of bound residues in the whole clay, which resist extraction by water and methanol, is consistent with the formation of higher-molecular-weight products. This type of oxidative-coupling reaction is thought to be involved in humic substance formation from polyphenols in soils (Stevenson, 1981). Our results suggest a role for smectite clays in these processes.

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Figure 8. Non-linear least-squares peak fitting of structural OH-stretching band.

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