EFFECTS OF EXCHANGE CATIONS AND LAYER-CHARGE LOCATION ON CYSTEINE RETENTION BY SMECTITES

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Abstract—This study investigates the complexes formed between amino acids, which are the natural degradation products of organic matter, and smectites. Thus, the adsorption and desorption behavior of cysteine and Na-, Ca-, Cu-homoionic smectites with different layer-charge location, a montmorillonite, and a beidellite, were studied. The clay samples were treated with Na, Ca, and Cu 1 N solutions and then with a 0.2 M cysteine solution. To test smectite-cysteine stability at acidic pH, the solids obtained were repeatedly treated with distilled water acidified to pH = 5. All treated samples were characterized by thermal, X-ray diffraction, chemical, and infrared analyses. The results showed that: 1) Na- and Ca-rich smectites adsorbed and retained small amounts of cysteine, and did not show interlayer cation-cysteine complexes, whereas the amino acid was strongly retained in the interlayer by Cu-rich smectites; 2) $d(001)$-values for Na- and Ca-rich smectites showed little or no expansion, whereas for the Cu-rich smectites the intercalation of the organic molecule produced a swelling of the structure; 3) the interaction mechanism of homoionic smectites with cysteine in an aqueous medium occurs by weak interactions, (*e.g.,* van der Waals interactions, hydrogen bonding, dipole-dipole interactions, and other electrostatic forces such as entropy-driven hydrophobic bonding), and/or by complexes involving interlayer cations and organic ligands. The formation of a stable chelate complex with the saturating ion permits cysteine to be adsorbed by Cu(II)-rich smectites and to be resistant to migration in soils and groundwaters.

Key Words—Cysteine, CMS Source Clay SAz-1, FTIR, Homoionic Smectites, Layer Charge, Thermal Analysis, XRD.

INTRODUCTION

The study of interactions between smectite and organic and/or inorganic contaminants produces insight into those chemical and biological transformations which can limit the mobilization of hazardous liquid waste in soil systems (Klumpp *et al.,* 1992; Sawhney, 1996). The increased threat of environmental pollution by organic pollutants (*i.e.,* pesticides, herbicides, fertilizers) has prompted investigations into the use of smectites as a sorbent of organic molecules. For smectite species, the magnitude and the localization of the layer charge plays an important role in their capacity to adsorb and retain organic molecules from aqueous solutions (Boyd and Jaynes, 1994).

In this study, we examine the complexes formed between smectites and amino acids, which are the natural degradation products of organic matter. The smectites include a montmorillonite and a beidellite, with different layer-charge location, saturated with alkaline (Na), alkaline-earth (Ca), and transition element (Cu) cations.

Following the HSAB theory of Pearson (Pearson, 1963, 1968) the interlayer cations and the silicate layer of smectites can be considered Lewis acids and bases, respectively (Xu and Harsh, 1992). The location of the layer charge determines the strength of the Lewis base: smectite behaves as a soft base when the layer charge is located in octahedral sites, whereas it behaves as a hard base when the charge is located in the tetrahedral sheet (Xu and Harsh, 1992). Since hard bases link preferentially with hard acids, and soft bases with soft acids, the smectite layer-charge location strongly affects the cation selectivity. Two smectites, a montmorillonite (reference clay SAz-1) and a beidellite (Rasta, Recoaro Terme, Italy) were chosen as adsorbents for their soft and hard properties, respectively. Na and Ca were selected as exchangeable cations because they are the most common smectite interlayer species and they are both hard Lewis acids. Cu was selected because of its borderline Lewis acid character. Moreover, although Cu is required in trace amounts for various metabolic processes, it may occur at higher concentrations in areas with industrial and agricultural runoff where it is toxic to the biosystem (Peijnenburg *et al.,* 1997). Of the numerous amino acids, cysteine was selected for study because it is biologically important (Gillies and Wesolowski, 1990; Sahl *et al.,* 1995).

Widespread interest in the hard-soft acid-base theory has generated studies on metal complexes of sulfur-containing amino acids (Cherifi *et al.,* 1990; Bigham and Shapley, 1991), as these ligands contain both class b (thioether or sulphide) and class a (amino and carboxylato) donors. These complexes are important in the catalysis of enzymes; for example, in the sulfur-containing amino acid cysteine [$HSCH_2CH(NH_2)COOH$] and cystine [which links two cysteine residues by a disulphide bond $HOOC(NH_2)-CHCH_2SSCH_2CH(NH_2)COOH$], the cysteine thiol group of specific protein residues may be the active or

catalytic sites of enzymes, and it can act as a hydrogen bond donor or acceptor. In addition, cystine is a cross-linking agent in protein structures because the two cysteine groups are joined by a covalent disulphide linkage (Barrett, 1985). In our study, cysteine can form complexes with cations in interlayer sites through sulfur, and/or nitrogen, and/or oxygen atoms, thus reducing the mobility of the metal.

The purpose of this study is: 1) to determine the amount of cysteine sorbed by smectites with a different layer-charge location and interlayer chemistry; 2) to determine the stability and the stoichiometry of smectite-cysteine complexes; and 3) to determine the magnitude of smectite expansion and the disposition of the cysteine-ligand molecules. In turn, these data will increase our understanding of the migration of organic compounds and inorganic pollutants in soils and fresh water.

MATERIALS AND METHODS

Minerals

The montmorillonite sample, SAz-1, from Cheto Apache Country, Arizona, USA, was obtained from the Source Clay Repository of The Clay Minerals Society. The Clay has nominal cation exchange capacity (CEC) of 120 meq/100 g; see van Olphen and Fripiat (1979). The beidellite sample is from Rasta, Recoaro Terme, Vicenza, Italy. The sample (Brigatti et al., 1996) has a structural formula of $(Si_{7.51}Al_{0.49})(Al_{2.88} Fe_{0.66}Mg_{0.50}Mn_{0.01}Ti_{0.04})(Ca_{0.24}Na_{0.20}K_{0.02})O_{20}(OH)_4$, a tetrahedral layer charge of -0.49 electrostatic valence units (evu), an octahedral layer charge of -0.20 evu, and a CEC of 78 meq/100 g.

Solutions

Stock solutions of 1 N Na, Ca, and Cu were obtained by dissolving NaCl, $CaCl_2$, and $CuCl_2$ analytical grade reagents in water, respectively. Cysteine 0.2 M solution was prepared using 99% pure reagent from Carlo Erba, Como, Italy. All reagents were added to deionized water and were filtered through a 0.2 μm membrane filter prior to use.

Preparation of homoionic clays

The clay samples were purified by suspension in distilled water and by partial settling to remove coarse grains. Homoionic clays were prepared by mixing ~10 g of each smectite with 1 L of a 1 N solution of the corresponding cation. The suspensions were stirred overnight at room temperature, and then centrifuged. The solution was then aspirated and fresh solution with the desired cation was added and the sequence was repeated three times.

Excess salts were removed from the homoionic clays by dialysis until the aspirated solution tested negative with $AgNO_3$. Filtrates from all ion-exchange experiments were analyzed by atomic absorption spectrophotometry to check the presence of metal cations used in the exchange. Finally, the smectites were air-dried and characterized.

Amino-acid adsorption experiments

Adsorption of amino acid by the smectites was performed by suspending 2 g of each homoionic sample (Na, Ca, or Cu) with 100 mL of a 0.2 M aqueous solution of cysteine. The suspensions were stirred at room temperature for 48 h. The solids were separated from the solutions by centrifugation. The following smectite-cysteine complexes were obtained: Na-rich montmorillonite-cysteine (Na-m-cys); Ca-rich montmorillonite-cysteine (Ca-m-cys); Cu-rich montmorillonite-cysteine (Cu-m-cys); Na-rich beidellite-cysteine (Na-b-cys); Ca-rich beidellite-cysteine (Ca-b-cys); and Cu-rich beidellite-cysteine (Cu-b-cys). The solids obtained were repeatedly treated with a predetermined amount of distilled water (100 mL) acidified with CO_2 to pH = 5. The suspension was shaken for 1 h at 25°C and then centrifuged. The treatment was repeated 13 times, and after each treatment a portion of the mineral was separated, air-dried, and characterized.

Characterization procedures

Elemental analysis (Elemental Analyzer, Carlo Erba 1106) was performed to determine the amount of amino acid sorbed; total S, N, and C were determined. An atomic absorption spectrophotometer (Perkin Elmer 606) and an inductively coupled plasma emission spectrometer (ICP, Varian Liberty 200) were used to analyze the quantity of metal retained.

Powder X-ray diffraction (XRD) analysis was conducted at room temperature (25°C, relative humidity (RH) = 60%) at temperature, T, of $25 \leq T \leq 500$°C, on randomly oriented and oriented mineral aggregate mounts, using a Philips PW 900 diffractometer equipped with a monochromator and an in situ heating apparatus (CuKα radiation; quartz as standard).

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed using a Seiko SSC 5200 analyzer (heating rate 10°C/min, in air). Infrared spectroscopy was performed using a standard Bruker IFS 113v Fourier transform infrared (FTIR) spectrometer. Fifty scans were recorded for each spectrum with a spectral resolution of 2 cm^{-1} in transmission mode in the region between 400–4000 cm^{-1}. A mixture of clay and KBr was pressed at 10 atm to form a pellet. Reproducibility of results was determined with four samples for each compound.

RESULTS AND DISCUSSION

Na-, Ca-, and Cu-rich smectites

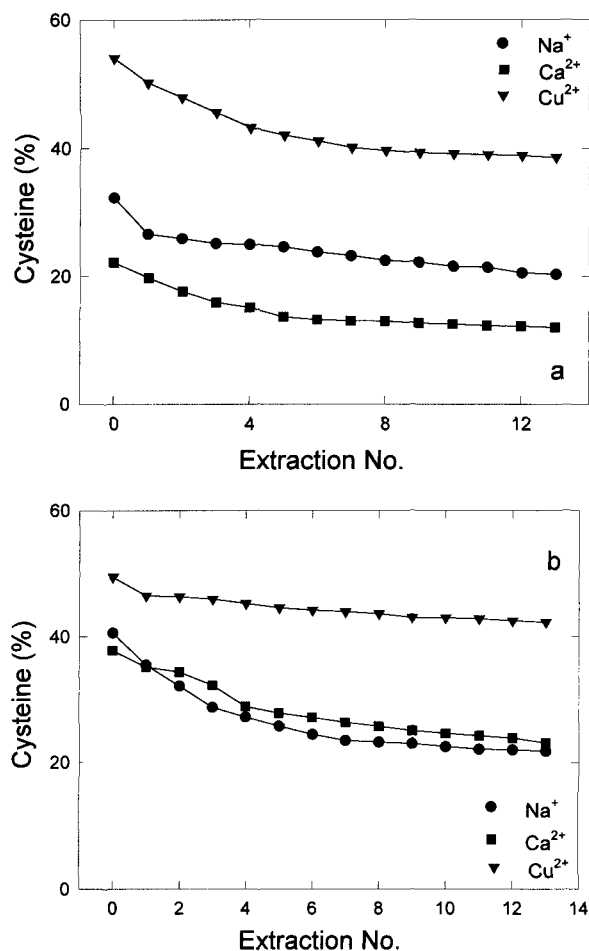The XRD patterns of homoionic Na-, Ca-, and Cu-rich smectites displayed the following $d(001)$-values:

Figure 1. Repetitive acidified (pH = 5) aqueous extractions of cysteine from Na-, Ca-, and Cu- rich smectites (a: montmorillonite; b: beidellite).

(1) montmorillonite sample, $d(001)_{Na} = 12.5$, $d(001)_{Ca} = 15.2$, $d(001)_{Cu} = 14.7$ Å; (2) beidellite sample, $d(001)_{Na} = 12.6$, $d(001)_{Ca} = 15.1$, $d(001)_{Cu} = 14.5$ Å. As expected, thermal analyses showed that dehydration of Na- and Ca-treated samples was complete at T < 200°C (Na-smectites: endothermic reaction at ~90°C; Ca-rich montmorillonite: endothermic reactions at 100 and 160°C; Ca-rich beidellite: endothermic reactions at 80 and 140°C). In Cu-rich smectites, additional endothermic reactions at T = 315°C in Cu-rich beidellite (weight loss 3.1%) and at 340°C in Cu-rich montmorillonite (weight loss 3.4%) were observed, indicating that some H_2O was bound to the interlayer cation and to the basal-plane surface more strongly than H_2O associated with the other interlayer cations. Further reactions, occurring at 450 < T < 650°C, were caused by the dehydroxylation of the octahedral sheet (Mackenzie, 1975).

FTIR spectra of homoionic Na, Ca, or Cu-rich beidellite samples were characterized by OH^--stretching frequencies at 3620 cm^{-1}, Si-O stretching at 1038 cm^{-1}, and octahedral sheet vibration by bands in the 520–470 cm^{-1} region. Bands at 794 and 915 cm^{-1} are attributed to Si-O-Al vibration and to Al-(OH)-Al [and/or Fe^{3+}-(OH)-Al] absorption, respectively (Farmer, 1997). IR-absorption bands of homoionic montmorillonite were near those of a natural sample reported by van Olphen and Fripiat (1979). Thus, there was no evidence of hydrolysis or change in the local environment of the OH groups by these treatments. The spectra show a typically broad OH-stretching band at 3620 cm^{-1}, which is the envelope for a wide range of AlAlOH and AlMgOH environments in the highly substituted and distorted homoionic montmorillonite structure. More characteristic are the well resolved OH-deformation bands at 915 cm^{-1} (AlAlOH) and 840 cm^{-1} (AlMgOH) (Russell *et al.*, 1970). In all smectites, adsorption bands of adsorbed H_2O occur at 3420 cm^{-1} and in the region of 1600–1650 cm^{-1} (Russell and Fraser, 1996).

Na-, Ca-, and Cu-rich smectite-cysteine complexes

Figure 1 shows that the amount of amino acid sorbed by homoionic smectites depends on the type of interlayer cation and on the layer charge. With hard interlayer cations (Ca and Na), the hard base (beidellite, Figure 1b) displayed a cysteine content greater than that of the soft base (montmorillonite, Figure 1a). The opposite occurred in the case of Cu-exchanged clays, where montmorillonite retained more amino acid than beidellite. In both clays, the relative amount of cysteine retained roughly followed the order: Cu > Na > Ca.

Successive extractions of the sorbed compound with acidified water (Figure 1a and 1b) showed that: 1) Ca-m-cys desorbed the amino acid nearly completely; 2) Na-m-cys, Ca-b-cys, and Na-b-cys quickly desorbed cysteine initially, however, at the end of the extraction a small amount of the organic compound was retained; 3) Cu-m-cys desorbed ~20% of the sorbed cysteine rather quickly, but at the end of the extraction a large amount of amino acid was retained. In contrast, Cu-b-cys desorbed cysteine slowly and retained a large proportion of the amino acid.

From the XRD study of the cysteine-treated homoionic smectites it is deduced that: 1) $d(001)$ for Na-m-cys showed little or no expansion ($d(001) = 12.6$ Å), whereas Na-b-cys produced a broad band at 13.6 Å; 2) both Ca-m-cys and Ca-b-cys maintained layer periodicity of ~15 Å; 3) for the Cu-exchanged smectites, the intercalation of the organic molecule produced a swelling of the clay structure: the basal spacing increased from 14.5 to 19.2 Å in Cu-m-cys and from 14.7 to 19 Å in Cu-b-cys. In Cu-m-cys, the intensity of $d(001)$ remained almost the same, indicating that layer stacking was well organized, whereas the broad band observed for Cu-b-cys is related to both great
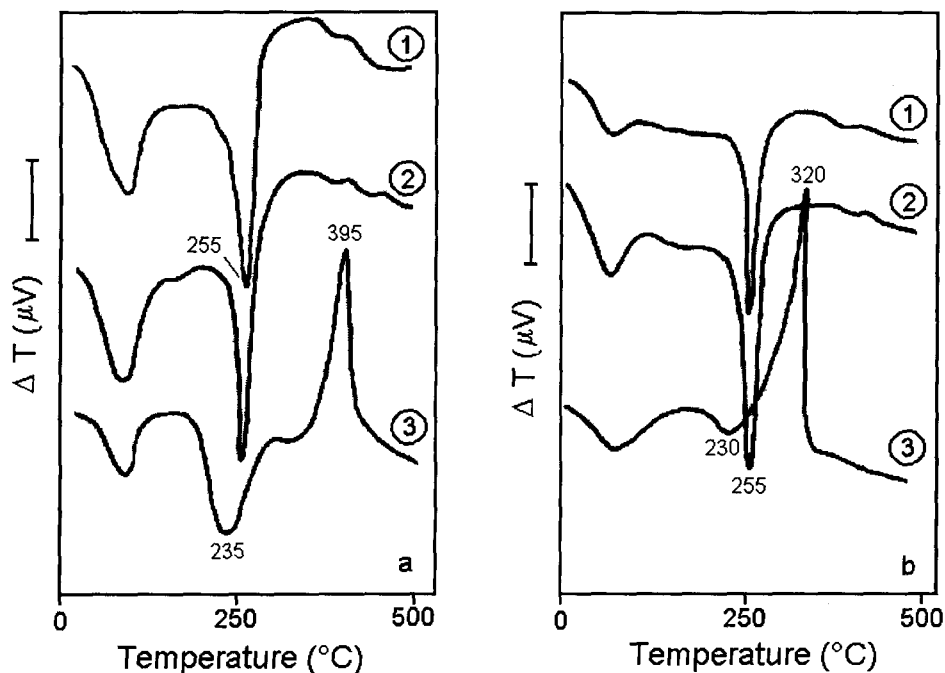
Figure 2. DTA curves for (a) montmorillonite and (b) beidellite treated with cysteine. Curves: 1) Na-rich smectites; 2) Ca-rich smectites; 3) Cu-rich smectites. The unit bar represents: (a) curve 1 = 60 μV, curve 2 = 4 μV, curve 3 = 10 μV; (b) curve 1 = 112 μV, curve 2 = 6.13 μV, curve 3 = 3.2 μV.

disorder in layer stacking and/or interstratified mixtures of layers with different spacings. The aqueous phase desorption reaction of cysteine showed little or no variation in layer periodicity.

The sorption of most organic compounds of environmental interest by smectites involves weak interactions such as van der Waals, hydrogen bonding, dipole-dipole interactions, and other electrostatic forces such as entropy-driven hydrophobic bonding (Mortland, 1986). Furthermore, complexes may form between interlayer cations and organic ligands. XRD data for Ca- and Na-rich smectites suggest that cysteine is sorbed mostly on the external particle surface, whereas the amino acid is strongly retained in the interlayer by Cu-rich smectites. The increase in the $d(001)$-value may indicate the formation of a Cu-cysteine-complex in the interlayer sites (McAuliffe and Murray, 1972). Transition metal complexes of cysteine derivatives possessing monodentate coordination of the ligand through sulfur, bidentate coordination through sulfur and nitrogen (or oxygen), or tridentate coordination with sulfur, nitrogen, and oxygen atoms were previously studied (Aizawa et al., 1988). Furthermore, Cu catalyzes the cysteine-cystine redox system. The oxidation mechanism for the reaction of copper (II) with cysteine is given by $Cu^{2+} + RSH \rightarrow RSCu^+ + H^+$ and $2RSCu^+ + 2RS^- \rightarrow 2RSCu + RSSR$ (McAuliffe and Murray, 1972).

The layer periodicity, crystal structure, and conformation of cysteine (Cody, 1985), and the ease with which cysteine oxidizes (Bigham and Shapley, 1991), suggest that the complex Cu-cysteine and/or Cu-cystine forms in the interlayer.

The results of DTA (Figure 2) show a strong endotherm at ~260°C and weaker endotherms probably relating to dehydration reactions. In Cu-rich smectite-cysteine complexes an exothermic reaction occurred at 320 and 390°C for Cu-b-cys and Cu-m-cys, respectively. There is a sequential loss of mass which is attributed to water desorption, cysteine pyrolysis, and desorption. The peak at 260°C, which was present in all homoionic smectites treated with cysteine, may be indicative of cysteine loss and may be correlated with the loss of cysteine from the lower-energy, or less-stabilized bonding sites, such as sites at the external surfaces of the particles. In this case, the amino acid is probably retained in those sites with weaker hydrophobic or van der Waals forces. For Cu-rich smectites treated with cysteine, the occurrence of successive reactions suggested stronger, more complex bonding of the amino acid, probably owing to Cu-cysteine complexes in the interlayer.

Weight loss owing to amino acid decomposition ($210 \leq T \leq 450°C$) of the cysteine-exchanged smectites subjected to successive extractions decreased with the number of extractions. In Cu-rich montmorillonite,
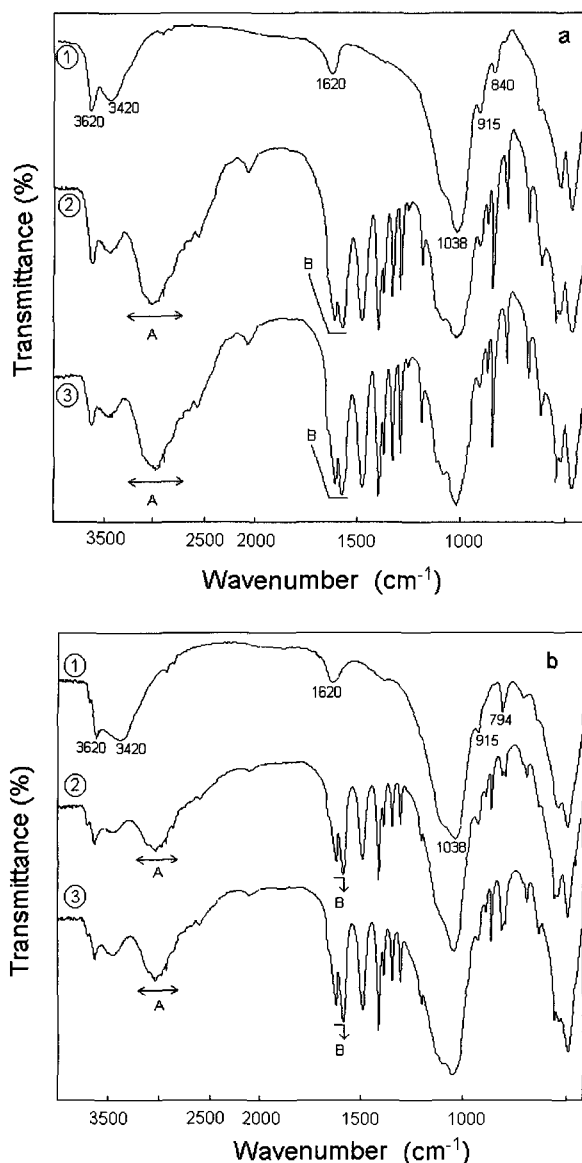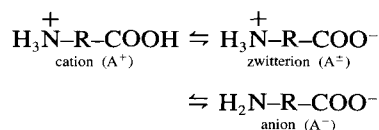
Thermal analysis was consistent both with the trend reported in Figure 1a and 1b and with XRD results, which suggested an interlayer expansion by the formation of a double-layer Cu-cysteine complex.

To understand the stabilization of organic compounds and heavy metals in soils, the precise nature of the organo-metal-clay complex formed must be determined. After the study of the adsorption/desorption mechanisms was complete, we identified the species associated with the smectites. The occurrence and stability of these forms are greatly affected by the surface properties of the adsorbent (*e.g.,* layer charge location). Proton transfer from H_2O associated with the surface of smectites to the adsorbed amino acid is highly probable. Proton transfer may shift the equilibrium between the cationic, zwitterionic, and anionic forms of amino acid thereby stabilizing one of the species:

$$\overset{+}{H_3N}-R-COOH \rightleftharpoons \overset{+}{H_3N}-R-COO^-$$
$$\text{cation (A}^+) \qquad \text{zwitterion (A}^\pm)$$

$$\rightleftharpoons H_2N-R-COO^-$$
$$\text{anion (A}^-)$$

Exchangeable cations may contribute to the stabilization of the anionic species by forming a salt, but the features of the solid surface are probably most important in these transformations (Parker, 1983). An infrared study provides information on the nature of the bonds involved in the amino acid-smectite interactions.

Band assignment (Bellamy, 1975) for the main functional groups -NH_3^+, -COOH, -COO$^-$, and -SH are: the NH_3^+ group has stretching and deformation frequencies in the 3130–3030 cm^{-1} and 1640–1610 cm^{-1} regions, respectively; an absorption corresponding to the ionized carboxylic group is found in the region 1600–1560 cm^{-1}, whereas that of the normal acid carboxylic (non-ionized) group occurs in the region 1695–1750 cm^{-1}. Moreover, S-H thiol groups are commonly found between 2400–2600 cm^{-1}. CH_2 stretching absorptions occur at 2926–2853 cm^{-1}.

For the cysteine-smectite complexes (Figures 3–5), no bands are observed near 1700 cm^{-1} for any clay-cysteine complex in the lower wavenumber region of the spectra. This result clearly indicates that no appreciable amounts of cysteine species containing a COOH group is adsorbed on montmorillonite or beidellite. Strong absorbance peaks occurring near 1600 cm^{-1} (labeled B) are assigned to NH_3^+ deformation and COO$^-$ asymmetric stretching modes (Jang and Condrate, 1972). The stretching of CH_2 and NH_3^+ groups is also observed (band labeled A). The results indicate that both the thiol and the carboxylic acid groups are deprotonated and the cysteine therefore binds in a bidentate fashion through

Figure 3. FTIR spectra of (a) Na-rich montmorillonite and (b) Na-rich beidellite. Curves 1: Na-rich smectites; curves 2: Na-rich smectites treated with cysteine; curves 3: Na-rich smectites treated with cysteine at the end of the extraction experiments. Label A refers to the stretching of CH_2 (2926–2853 cm^{-1}) and stretching of NH_3^+ groups (3130–3030 cm^{-1}); label B refers to the NH_3^+ deformation and COO$^-$ asymmetric stretching modes.

a shift of the reaction from 393 to 300°C at the end of the extraction treatments was observed. The decrease of temperature at the maximum position is ascribed to a weakening of the Cu-rich smectite-cysteine interactions. From 500 to 700°C, an increase in weight loss (~2%) with respect to the number of hydroxyl groups released in each homoionic sample was observed, and the loss of octahedral OH groups cannot be excluded.
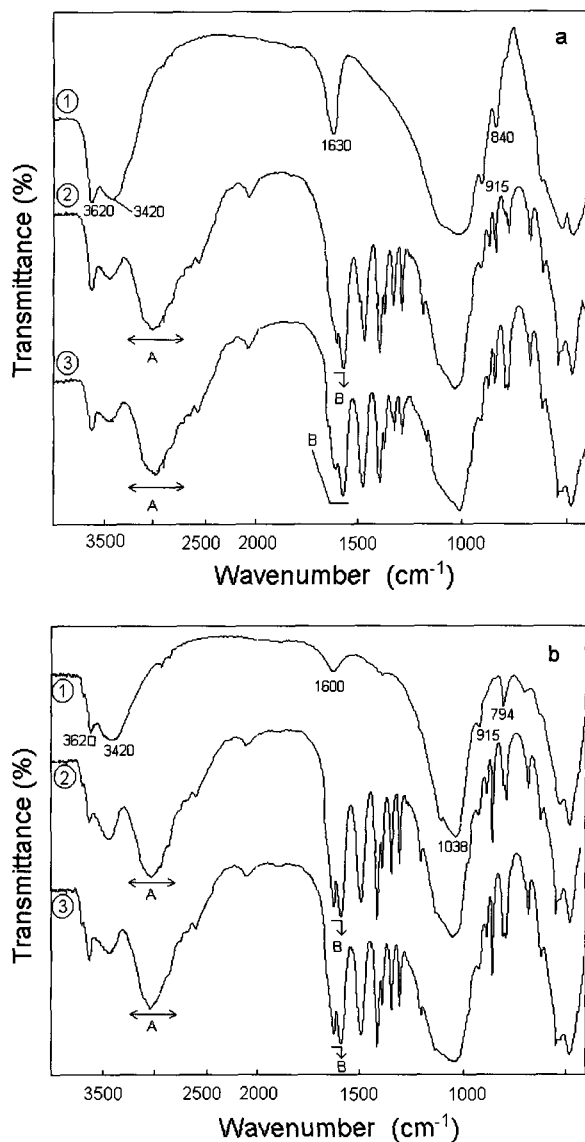
Figure 4. FTIR spectra of (a) Ca-rich montmorillonite and (b) Ca-rich beidellite. Curves 1: Ca-rich smectites; curves 2: Ca-rich smectites treated with cysteine; curves 3: Ca-rich smectites treated with cysteine at the end of the extraction experiments. Labels A and B as in Figure 3.
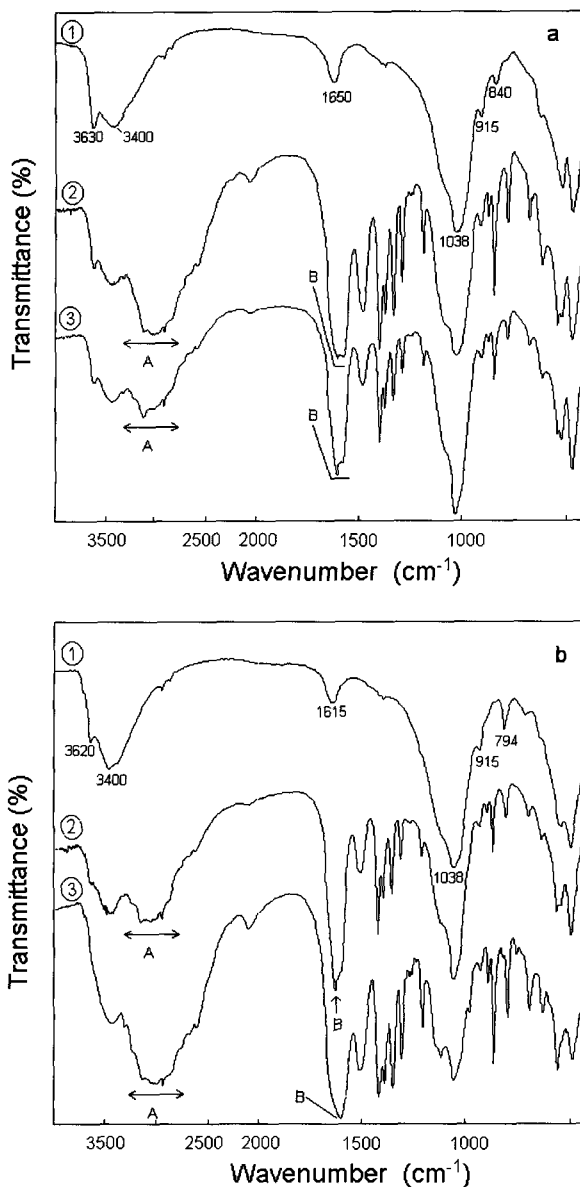
Figure 5. FTIR spectra of (a) Cu-rich montmorillonite and (b) Cu-rich beidellite. Curves 1: Cu-rich smectites; curves 2: Cu-rich smectites treated with cysteine; curves 3: Cu-rich smectites treated with cysteine at the end of the extraction experiments. Labels A and B as in Figure 3.

sulfur and oxygen (Bigham and Shapley, 1991). Furthermore, the IR spectral series essentially confirm the trend demonstrated by the XRD and thermal data. The adsorption of cysteine and the slow desorption of the amino acid as extraction proceeds is quite evident (Figures 3–5).

In addition, as indicated above, the results of the chemical analyses for the clay-cysteine complexes indicate that Cu-exchanged smectites adsorb significantly greater amounts of cysteine. The FTIR results indicate that each cysteine molecule chelates to the tran-

sition metal. Small amounts of other cysteine species may be adsorbed on these smectite complexes, but they are below detection by our methods. Chelation is expected because the cysteine zwitterion with the configuration $[^+_3HNCHSHCH_2COO^-]$ predominates in aqueous solutions, and a chelate complex can readily form by bonding one of the carboxyl oxygen atoms and the S atom of the thiol group with the Cu^{2+}. From the above, we conclude that the best model for the

adsorbed species on metal-ion substituted smectites is given by the following configuration:

$$\left[\begin{array}{c} M^{2+} \diagup S-CH_2-CH-\overset{+}{N}H_3 \\ \diagdown O-C \\ \parallel \\ O \end{array}\right]^{2+}$$
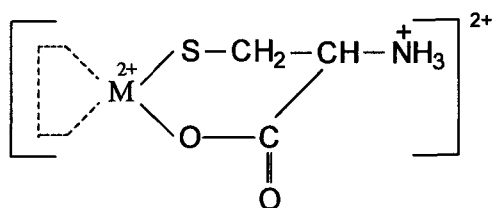
Interpretation of cysteine FTIR spectra for natural, Na-, and Ca-rich smectites indicates that cysteine molecules do not form complexes with interlayer cations, but can be present on the surface with the following configuration:

$$\left[\begin{array}{c} \overset{+}{N}H_3-CH-CH_2-SH \\ | \\ COO^- \end{array}\right]$$
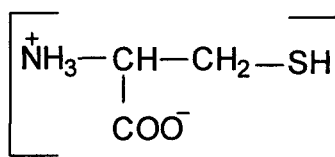
The cysteine cation possesses an ionized COO^--group and not a COOH-group. The cationic charge is maintained for this species by the protonation of the amino group.

CONCLUDING REMARKS

The formation of a stable chelate complex with the saturating ion permits heavy metal ions and cysteine to be adsorbed and retained in smectites, thereby preventing or retarding the migration of organic and inorganic contaminants in soils and ground water. This feature, which is unique for Cu ions, at least for saturating ions examined in this study, is related to the greater tendency of the cation to form stable complexes with cysteine. For Na- and Ca-rich smectites, although there was no evidence for the interaction of cysteine with alkaline earths, potentiometric studies showing the formation of a Ca-complex, which may be important in producing the outstanding resistance of spores to heat and radiation, was reported by McAuliffe and Murray (1972 and references therein). For the material studied here, the effect on cysteine sorption on Na- and Ca-rich smectites should be small, and we therefore conclude that the formation of a relatively stable complex leads to greater sorption of cysteine by the Cu-rich smectites than by Ca- and Na-saturated smectites. Although these results do not necessarily apply to a soil-water medium, cysteine interactions similar to those simulated may be nonethless important factors in the migration of heavy metals in smectitic soil.

ACKNOWLEDGMENTS

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