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ABSTRACT

Humic substances extracted from an Alfisol, Mollisol, and Histosol were sorbed to the clay (<2 μm) suite extracted from an Alfisol Bt horizon. The clays with sorbed humic substances as well as clays with indigenous organic matter and with organic matter oxidized with H_2O_2 were weathered by incubation in 0.05M H_2SO_4 for 1320 h and in 0.0025M H_2SO_4 for 1176 h. To evaluate weathering, the quantities of Mg, K, Al, Si, and Fe released and clay dissolved were monitored. In both weathering studies, Mg was preferentially released by the clays. Because Mg occurs mainly in the octahedral sheet of clays, the high release of Mg suggests preferential dissolution of the octahedral sheets. In the 0.05M H_2SO_4 dissolution study, no differences were found with respect to K, Al, Si, and Fe release from the different clays, but slightly less Mg was released from clays with sorbed humic substances. At the completion of the incubation in 0.05M H_2SO_4, 21 to 24% of the clays had dissolved. Using a less concentrated acid (0.0025M H_2SO_4), notable differences were apparent in the degree of weathering among the clays. Approximately, 3 times more Mg was released from clays with organic matter oxidized than from clays with indigenous or sorbed humic substances. Similar quantities of Mg were dissolved from clays with indigenous or sorbed humic substances. K release was similar from all clays. Using 0.0025M H_2SO_4, a larger portion (5.8%) of the clay with organic matter oxidized was dissolved than of clays with indigenous (2.6%) or sorbed humic substances (<1%). Data for Mg release and clay dissolution in 0.0025M H_2SO_4 both suggest that the weathering of clays was reduced by indigenous organic matter or sorbed humic substances. No weathering differences could be detected between clays with sorbed humic versus fulvic acids or between sources (Mollisol, Alfisol, or Histosol) of humic substances.

INTRODUCTION

The interaction of humic substances with soil minerals plays an important role in many soil processes, such as ped stability, mineral weathering, profile development, and organic matter stabilization. Available evidence indicates

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that soil organic matter binds to clay minerals resulting in a large portion of their surfaces being covered with a coating of humic substances (Stevenson, 1982). The sorption of humic substances by non-expanding (Evans and Russell, 1959; Rashid et al., 1972; Kodama and Schnitzer, 1974) and expanding (Evans and Russell, 1959; Tan and McCreery, 1975; Theng and Scharpenseel, 1975) minerals has been investigated by reacting humic (HA) and fulvic acids (FA) with clays. These studies have shown that the sorption of humic and fulvic acids by mineral specimens is influenced by the saturating cation, pH, and the type of mineral. A common factor in these studies is that the sorption data have been generated using relatively pure, well characterized minerals. The use of soil clays has been avoided because interpretation of sorption data is complicated by the heterogenous composition of soil clays.

In addition to sorbing to minerals, both humic and fulvic acids can degrade minerals (Schnitzer and Kodama, 1977). The ability of humic acids to complex metals from primary minerals has been demonstrated by Kononova et al. (1964), Ong et al. (1970), Baker (1973), Singer and Navrot (1976) and Tan (1980). Fulvic acids have also been shown to be effective in dissolving minerals (Schnitzer and Kodama, 1976; Tan, 1980; Kodama et al., 1983). Little information is available regarding the weathering of soil clays by humic substances because interpretation is complicated by the heterogenous clay mineralogy of soils. However, Schnitzer and Skinner (1963) reported that an aqueous fulvic acid solution removed 9% of the total Fe and 6% of the total Al from soil during one week of shaking. Tan (1975, 1986) has presented data indicating that humic acids will attack clay minerals, releasing Si and Al from tetra- and octahedral positions and that the release is greatest at a pH of 9.0. Tan (1986) further suggests that complexation and chelation by humic acids are especially effective at high pH values. However, under acid conditions common to many soils, it seems unlikely that humic and fulvic acids, which will be protonated, will be as effective in complexing and releasing structural cations. Other work indicates that soil humic acid does not promote Al dissolution from kaolinite at a pH of 4.2, and in fact seems to inhibit the dissolution process (Chin and Mills, 1991).

In this paper, it is hypothesized that sorbed humic substances may act as a buffer or a physical barrier which may reduce clay mineral weathering in an acid soil environment. If humic substances do retard clay mineral weathering, this could lead to different degrees of soil weathering and profile development in contiguous well-drained Alfisols and Mollisols as found in Ohio, USA. (Novak, 1989; Novak and Smeck, 1991). As indicated, data regarding the sorption of humic and fulvic acids by natural clay mineral suites and their influence on clay mineral weathering under acid conditions are generally lacking. Because Novak and Smeck (1991) have shown that there are detectable chemical and structural differences between humic acids of Alfisols and

Mollisols, the effect of humic acids from both sources will be evaluated and compared in the weathering study. Therefore, the objective of this study is to sorb humic and fulvic acids extracted from an Alfisol, Mollisol, and Histosol to a soil clay suite and assess their influence on the weathering of the soil clay mineral suite with a dilute mineral acid.

MATERIAL AND METHODS

Sorption of humic and fulvic acids and mineral dissolution studies were conducted using the total clay fraction (<2 μm) from the Bt2 (48–61 cm) horizon of a Xenia (fine-silty, mixed, mesic Aquic Hapludalf) pedon collected from Warren County, Ohio, USA. Morphological and chemical descriptions of the Xenia pedon are provided by Novak (1989).

Humic and fulvic acids were extracted from a Mollisol (Dana 2; fine-silty, mixed, mesic Typic Hapludoll), an Alfisol (Rossmoyne; fine-silty, mixed, mesic Aquic Fragiudalf), and a Histosol (Carlisle; euic, mesic Typic Medisaprist), purified, and characterized as described by Novak (1989) and Novak and Smeck (1990).

Total clay fractions were collected by two methods. In one method, H_2O_2 oxidizable organic matter was removed by treatment with H_2O_2 whereas no organic matter was removed in the other. In subsequent discussions, clays collected by the former method will be referred to as oxidized clays and those with the latter as unoxidized clays. Sorption studies were conducted with only the oxidized clays whereas weathering studies were conducted with both clay fractions. Collection of the clay fraction was facilitated by treatment with 1M NaOAc buffer (pH 5.0) to remove carbonate minerals. To obtain the oxidized clays, the clays were treated with 30% H_2O_2 to remove oxidizable organic matter. Following preliminary treatments, excess salts were removed by washing with deionized water. Following dispersion, the clay fraction (<2 μm) was separated by sedimentation (Jackson, 1975) and flocculated by saturation with 1M Ca $(NO_3)_2$. Eight sedimentation cycles were used to collect the total clay fraction. The total Mg, K, and Fe contents of the clay fraction were determined using the method of Bernas (1968). Slurries of clay specimens collected prior to and following the weathering studies were Ca- and K-saturated and pipetted onto glass slides for X-ray diffraction (Jackson, 1975). The Ca-saturated clays were X-rayed after air drying and solvation with 1% glycerol. The K-saturated clays were X-rayed after air drying, after heating to 350°C for 2 h, and after heating to 550°C for 2 h. Samples were analyzed with a Philips X-ray diffractometer using CuKα radiation, a theta compensating slit, and a diffracted beam monochromator.

The optimum conditions for sorption of humic substances by Ca-saturated clays were established in two preliminary studies. In the first study, the influ-

ence of pH on humic and fulvic acid sorption was investigated. Three 100 ml fulvic acid solutions were prepared by adding 80 ml of deionized water to 50 mg of fulvic acids and adjusting to pH values of 4, 5 and 6 with 0.1M NaOH. Three 100 ml humic acid solutions were prepared by initially dissolving 50 mg in 20 ml of 0.1M NaOH, then adding 60 ml of deionized water, and adjusting the pH to 6, 7, and 8 with 0.05M H_2SO_4. A 20:1 clay:HA or FA (wt/wt) ratio was chosen. Two hundred and fifty mg of Ca-saturated oxidized clays were added, in triplicate, to 25 ml of humic or fulvic acid solutions described above. The suspensions were shaken slowly for 24 h at $24 \pm 2°C$, and then centrifuged for 0.5 h. Supernatants were collected and the clays were washed twice with deionized water to remove humic and fulvic acids not sorbed to the clays. The clays with sorbed humic substances were then freeze-dried. The quantity of humic and fulvic acids sorbed was determined by measuring the organic carbon (OC) contents of the oxidized clays, before and after sorption, by dry combustion at 950°C as described by Nelson and Sommers (1982) and/or by measuring the humic substances remaining in solution, following sorption, with a Xertex C analyzer.

In the second preliminary sorption study, the influence of the clay:humic substances ratio (wt/wt) on sorption was investigated. Based on results of the pH study, this study was conducted at pH 6. The clay:HA ratios employed were 5, 10 and 20:1 and the clay:FA ratios were 10 and 20:1. The suspensions were shaken, centrifuged, washed, and the quantities of humic and fulvic acids sorbed to the clays at different clay:HA or FA ratios determined as described above. This study was run in triplicate and repeated three times, but not all ratios were employed each time due to a minimal supply of humic substances. Furthermore, it was necessary to employ humic substances obtained from different extractions; thus some differences can be expected between the three sorptions.

Once the optimum conditions for sorption of humic substances by the clays were determined, the clays used in the weathering studies were prepared. Sorption of humic and fulvic acids by clays was conducted using Ca-saturated clays in a suspension adjusted to pH 6 with a clay:humic substances ratio of 20:1. Following sorption, the clays with sorbed humic or fulvic acids were freeze-dried and stored in glass vials for use in the weathering studies. Greenland (1971) reported that sorption of humic substances by clays is not readily reversed following drying as stable clay–humic sols are formed.

The influence of sorbed humic substances on clay mineral weathering was investigated using clays with indigenous organic matter (unoxidized), clays with organic matter removed (oxidized) and clays with sorbed humic and fulvic acids. The clays were incubated in 0.05 and 0.0025M H_2SO_4 for 1320 and 1176 h, respectively. In the 0.0025M H_2SO_4 study, 1.33 g of clay was placed into centrifuge tubes containing 250 ml of acid. The tubes were sealed and shaken slowly for 5 s. After shaking, the caps on each tube were partially unscrewed to allow gases to exchange with the atmosphere. A control which

consisted of 250 ml of 0.0025M H_2SO_4 was also incubated in a similar manner. Each treatment and control were replicated twice and incubated at 24±0.7°C. To insure that no clays were removed when aliquots were withdrawn, all suspensions were centrifuged at 1962*g* for 0.5 h prior to sampling. Ten ml aliquots were removed from all samples at 42, 111, 184, 386, 477, 570, 663, 783, 936, and 1176 h. The aliquots were placed in plastic bottles and stored at 5°C. At the time of sampling, pH was recorded using a combination electrode. After aliquot withdrawal, the tubes were shaken for approximately 5 s before the incubation was continued. After 1176 h of incubation, the clays were quantitatively transferred to plastic beakers and freeze-dried. Procedures for clay weathering in 0.05M H_2SO_4 were similar to the 0.0025M study, except the clays were contained in dialysis tubing during the incubation to aid in the removal of solution aliquots rather than using centrifugation, suspended in 1000 ml glass beakers, and incubated for 1320 h. After freeze-drying, total clay weights were determined and compared to initial amounts in order to calculate the percent weight loss. All aliquots were analyzed for Mg using atomic absorption and K using flame emission. The concentration of Si was determined colormetrically using the blue silicomolybdous acid method of Hallmark et al. (1982). Concentrations of Al and Fe were also determined colormetrically using the ferron-*o*-phenanthroline method as described by Skougstad et al. (1979). A Beckman Du-20 spectrophotometer was used for all colorimetric measurements.

RESULTS AND DISCUSSION

Sorption of humic and fulvic acids to clays

Studies of humic and fulvic acid sorption by soil clays were conducted to determine the optimum pH and clay:HA or FA ratio for sorption. The sorption of humic and fulvic acids as a function of pH is presented in Table 1. Although, there seems to be little effect of pH on sorption of fulvic acids, sorption of humic acids by Ca-saturated clays was greatest at pH 6.0. It is also apparent that more humic acids were sorbed than fulvic acids. The greater sorption of humic acids than fulvic acids may be a function of polymer size. Due to molecular weight differences, the binding of any humic acid entity through any one reactive site results in the sorption of a greater mass than the similar sorption of any given fulvic acid entity. Because maximum or near maximum sorption of humic and fulvic acids was attained using a pH of 6, all subsequent sorptions were conducted at this pH.

The influence of clay:humic substance ratio on sorption was evaluated by comparisons of sorptions using ratios of 20:1, 10:1, and 5:1. Although precision among triplicates in a given equilibration using the same humic substance specimen was quite good, considerable variation is evident among the

TABLE 1

Sorption of humic (HA) and fulvic (FA) acids by oxidized Ca-saturated clay as a function of pH

Clays[a]	pH	Sorption[b] (mg OC/g clay)
Clay+HA	6	18.9(0.8)
	7	12.8(1.2)
	8	14.7(0.9)
Clay+FA	4	6.8(0.3)
	5	6.1(0.3)
	6	6.7(0.2)

[a]Ratio of clay:HA or FA was 20:1 in all treatments.
[b]Averages of triplicates with standard deviations given in parentheses.

TABLE 2

Sorption of humic (HA) and fulvic (FA) acids by oxidized Ca-saturated clays as a function of the clay:humic substance (HS) ratio. Values given in mg OC/g clay and % as shown

Humic substance	Rep[a]	Clay:HS (wt/wt) (mg OC/g clay)			Clay:HS (wt/wt) (%[b])		
		20:1	10:1	5:1	20:1	10:1	5:1
Mollisol HA	A	13.0(0.1)[c]	–	–	46(0.6)	–	–
	B	11.3(0.3)	13.1(0.6)	12.7(0.2)	40(1.0)	24(5.5)	11(1.0)
	C	12.0(1.0)	29.6(3.5)	13.0(0.1)	42(3.5)	46(4.5)	9(0.6)
Alfisol HA	A	13.7(0.2)	–	–	50(1.0)	–	–
	B	16.7(0.4)	11.1(0.2)	14.9(0.4)	59(1.5)	20(0.6)	14(1.5)
	C	11.2(0.5)	16.8(0.2)	13.2(0.4)	40(2.0)	29(1.5)	13(1.0)
Histosol FA	A	8.5(0.1)	7.2(0.3)	–	27(0.6)	17(1.0)	–
	B	7.7(0.6)	6.9(0.3)	–	29(2.5)	19(1.0)	–

[a]The sorption study was conducted three times (A, B, C) in triplicate.
[b]Percentage of OC sorbed to OC added.
[c]Averages of triplicates with standard deviations given in parentheses.

three equilibrations, much of which can be attributed to the use of different humic substance specimens necessitated by limited supplies. Nevertheless, in most cases, 11.1 to 16.8 mg C were sorbed from humic acid solutions and 6.9 to 8.5 mg C from the fulvic acid solutions per g of clay. It is apparent that the quantities of humic and fulvic acids sorbed at various clay:HA or FA ratios are independent of the clay:humic substance ratio within the range examined (Table 2). Evans and Russell (1959) reported that humic acid sorption by sesquioxides is also independent of humic acid concentration. These data suggest that the clays have a given capacity to sorb humic substances and

TABLE 3

Organic carbon (OC) contents of unoxidized and oxidized clays and quantity of humic (HA) and fulvic (FA) acids sorbed on clays used in the weathering studies

Clay		Organic carbon content (mg OC/g clay)	
Oxidized		7.7	
Unoxidized		14.8	
H_2SO_4 Conc	Humic substance[a]	Organic carbon content of oxidized clay with sorbed HA or FA (mg OC/g clay)	Quantity Sorbed[b] (mg OC/g clay)
0.05M	Mollisol HA	24.1	16.4
	Alfisol HA	25.8	18.1
	Mollisol FA	13.0	5.3
0.0025M	Mollisol HA	20.3	12.6
	Alfisol HA	23.9	16.2
	Histosol FA	15.5	7.8

[a]Sources of humic substances were not from the same extractions between the two weathering studies.
[b]Sorptions were conducted at pH 6 and a clay:HA and FA ratio of 20:1.

within the range examined, that capacity is attained irrespective of the amount with which it is equilibrated. It can be noted that no differences were evident between sources of humic acid (Mollisol versus Alfisol). Because the clays have a given capacity to sorb humic substances, the percentage of humic and fulvic acid sorbed by the clays increased as the amount of humic components equilibrated with the clay fraction decreased (Table 2). Because sorption of humic and fulvic acids was found to be independent of the clay:HA and FA ratio, the 20:1 clay:HA or FA ratio was arbitrarily selected for use in preparation of the clays for the subsequent weathering study. Direct comparisons of the sorption of humic substances by clays with that reported in the literature must be interpretated with caution because most of these studies have used clay mineral specimens rather than soil clays, various saturating cations, and pH values. Nevertheless, the sorptions attained in the present study were somewhat less than those attained for both humic and fulvic acids by Evans and Russell (1959) with a kaolinite and a bentonite, humic acids by Rashid et al. (1972) with an illite and a chlorite, and fulvic acids by Kodama and Schnitzer (1974) with a kaolinite but greater than fulvic acids by Kodama and Schnitzer (1974) with a bentonite and humic acids by Chin and Mills (1991) with a kaolinite.

Data for the sorption of humic substances by clays which were used in the

weathering study, discussed in the following section are presented in Table 3. The sorptions were compatible with the previous sorptions.

Clay dissolution in dilute sulfuric acid

The influence of humic substances on the weathering of soil clays was investigated by incubating clays with organic matter removed (oxidized), with indigenous organic matter (unoxidized), and with sorbed humic substances in dilute H_2SO_4. Weathering was evaluated by monitoring cation release and clay dissolution. Overall, Mg was released in the highest amounts, followed by K, Al, and then Si and Fe (Table 4). The total elemental contents of Mg, K, and Fe in the clay was 221.0, 471.3, and 1627.9 mmol kg^{-1}, respectively. Fifty-seven to 68% of the total Mg was released by the clays after 1320 h incubation in 0.05M H_2SO_4. Because Mg occurs mainly in the octahedral sheet of clays, the high release of Mg suggests preferential dissolution of the octahedral sheets which is in agreement with previous reports (Brindley and Youell, 1951). The low release of Si by the clays suggests that dissolution of the tetrahedral sheet is minimal. Furthermore, the high release of Mg relative to the other cations in the octahedral sheet (Al and Fe) suggests that there is selective dissolution of Mg from the octahedral sheet. Similar observations were made by Barshad (1960a, b), Bar-On and Shainberg (1970), and Feigenbaum and Shainberg (1975). Isomorphous substitution of Mg for Al in the octahedral sheet weakens the clay structure and because the Mg–O bonds

TABLE 4

Cation release expressed as mole ratios[a], percentage of total cation released[b] and mmol kg^{-1} clay[c] after incubation in 0.05M H_2SO_4

Clays	Cations released by clays												
	Mg	K	Al	Si	Fe	Mg	K	Fe	Mg	K	Al	Si	Fe
	----- (mole ratios) -----					------ (%) ------			---------- (mmol kg^{-1}) ----------				
Oxidized	5.3	1.0	0.8	0.4	0.5	66.5	5.9	0.9	147(8.3)	28(2.3)	23(0.1)	12(0.6)	14(0.7)
Unoxidized	5.4	1.0	0.8	0.4	0.5	68.3	5.9	0.8	151(3.5)	28(0.4)	23(0)	12(0.6)	13(0.4)
Ox. clay+ Mollisol HA	4.1	1.0	0.7	0.4	0.4	57.4	6.6	0.7	127(0.5)	31(2.5)	22(0.4)	12(0)	11(0.1)
Ox. clay+ Alfisol HA	4.7	1.0	0.8	0.5	0.4	57.4	5.7	0.7	127(1.1)	27(2.9)	22(0.7)	13(1.7)	12(0.4)
Ox. clay+ Mollisol FA	5.0	1.0	0.9	0.4	0.5	63.3	5.9	0.9	140(7.3)	28(1.5)	24(1.8)	12(0.1)	14(1.0)

[a]Mole ratios arbitrarily based on K.
[b]Percent total cation release calculated by: (mmol of cation in solution)/(total mmol in clay)×100.
[c]All values are averages of duplicates with standard deviations given in parentheses.

are weaker than the Al–O bonds, the former are preferentially attacked by protons (Shainberg et al., 1974). Less than 7% of the total K, which occupies an interlayer position in clays was released. Similar K releases have been reported by Feigenbaum and Shainberg (1975) for the dissolution of Fithian illite in acidified dilute salt solutions. The quantities of Al and Fe released in this study were much lower than that reported by Feigenbaum and Shainberg (1975).

Other than a slight decrease in the amount of Mg released from clays with sorbed humic substances, there were no detectable differences in the amounts of cations released among the various clays used in the 0.05M H_2SO_4 weathering study (Table 4). One explanation may be that the acid strength was so strong that any mollifying influence of the sorbed humic substances was masked. Quite possibly, the buffering capacity of the exchange complex of the clays and humic substances is inadequate to afford any protection from acid attack with the high H^+ concentration involved. The magnitude of clay dissolution is shown in Table 5. Twenty-one to 24% of the clay was dissolved after 1320 h incubation in 0.05M H_2SO_4. Irrespective of the extent of clay dissolution, no differences could be detected in mineralogy with X-ray diffraction between pre and post weathering clays. This suggests that acid weathering congruently attacks the clay minerals present in the soil clay mineral suite or that X-ray diffraction does not provide sufficient sensitivity. X-ray analysis indicated that the soil clay suite utilized in the weathering study consists of 25 to 35% clay mica, 25 to 35% vermiculite, 25 to 35% smectite interstratified with other 2:1 minerals, and 5 to 15% kaolinite. The clay suite has a cation exchange capacity of 84 $cmol_c\ kg^{-1}$.

In order to determine if an influence of humic substances could be detected on the weathering of soil clays under a less intense weathering environment which is more representative of a natural soil environment, a second weathering study was initiated in which the acid strength was reduced to 0.0025M. Only Mg and K concentrations were monitored in the second weathering study because they were found to be the primary cations released in the former study.

TABLE 5

Percentage of clay fraction dissolved after 1320 h incubation in 0.05M H_2SO_4

Clays	Clay dissolved[a] (%)
Oxidized	22.5(0.4)
Unoxidized	23.7(0.5)
Ox. clay + Mollisol HA	21.2(0.1)
Ox. clay + Alfisol HA	22.9(0)
Ox. clay + Mollisol FA	23.4(0.2)

[a]All values are averages of two replicates with standard deviations reported in parentheses.

Examination of the quantities of Mg and K released as a function of time (Tables 6 and 7) reveal that clays treated with H_2O_2 to remove oxidizable organic matter released much more Mg than clays with indigenous or sorbed humic substances. Similar amounts of K were released from all clays (3 to 5 mmol kg^{-1} clay) and the quantity of K released remained relatively constant after 42 h. All clays reached steady state with respect to Mg at about 400 h, although after 400 h the Mg concentration declined slowly with time for the oxidized clays.

TABLE 6

Mg release from clays (in mmol Mg kg^{-1} clay) during incubation in 0.0025M H_2SO_4 as a function of time[a]

Treatment	Incubation period (h)										
	42	111	184	278	386	477	570	663	783	936	1176
Oxidized clay	24	57	55	54	56	53	50	49	47	46	41
Unoxidized clay	1	5	10	11	13	16	13	14	14	14	13
Ox. clay+ Mollisol HA	1	4	9	10	14	16	13	12	13	13	12
Ox. clay+ Alfisol HA	1	4	8	10	13	13	12	12	12	12	12
Ox. clay+ Histosol FA	1	4	9	10	13	13	12	12	12	12	12

[a]All values are averages of two replicates.

TABLE 7

K release from clays (in mmol K kg^{-1} clay) during incubation in 0.0025M H_2SO_4 as a function of time[a]

Treatment	Incubation period (h)										
	42	111	184	278	386	477	570	663	783	936	1176
Oxidized clay	4	4	4	4	4	4	4	4	4	4	4
Unoxidized clay	5	5	5	5	5	4	4	4	4	4	4
Ox. clay+ Mollisol HA	5	5	5	5	5	5	5	5	5	5	5
Ox. clay+ Alfisol HA	5	5	5	5	5	5	4	4	4	4	4
Ox. clay+ Histosol FA	4	4	4	4	4	4	4	4	4	4	3

[a]All values are averages of two replicates.

Five to 19% of the total Mg was released by the clays after 1176 h of incubation in 0.0025M H_2SO_4 (Table 8). Clays oxidized with H_2O_2 released approximately three times more Mg than clays with indigenous or sorbed humic substances. Quantities of Mg released from clays with indigenous organic matter were similar to clays with sorbed humic substances. These data suggest that clay weathering, as measured by Mg release, is reduced by the presence of either indigenous or sorbed humic substances. No weathering differences with respect to Mg release could be detected between clays with sorbed humic vs. fulvic acids and between sources (Mollisol or Alfisol) of humic substances. Considerably more Mg than K was released from all clays. As indicated previously, the high release of Mg suggests that there is preferential dissolution of the octahedral sheet. Alternatively, Mg may have been released from Mg-hydroxy material in interlayer positions. However, not only is there no evidence that such chlorite-type interlaying exists in this clay suite, but it seems very unlikely that the large quantities of Mg released could have originated entirely from the clay interlayers.

The extent of clay dissolution by 0.0025M H_2SO_4 is reported in Table 9. Consistent with Mg release, there was less dissolution of clays coated with indigenous or sorbed humic substances than of the oxidized clays. In addition, it is apparent that more clay with indigenous humic substances dissolved than those with sorbed humic substances. This suggests that clays with sorbed humic substances are better protected from acid attack than clays with indigenous organic matter but it must be noted that the clays with sorbed humic acids contain more organic carbon than the untreated clays (Table 3).

TABLE 8

Cation release expressed as mole ratios[a], percentage of total cation[b] released, and mmol kg^{-1} clay after incubation in 0.0025M H_2SO_4

Clays	Cations released by clays					
	Mg (mole ratios)	K	Mg (%)	K (%)	Mg (mmol kg^{-1} clay)[c]	K
Oxidized	10.3	1.0	18.6	0.8	41(0.2)	4(0)
Unoxidized	3.3	1.0	5.9	0.8	13(0)	4(0.2)
Ox. clay + Mollisol HA	2.4	1.0	5.4	1.1	12(0)	5(0.1)
Ox. clay + Alfisol HA	3.0	.0	5.4	0.8	12(0)	
Ox. clay + Histosol FA	4.0	.0	5.4	0.6	12(0.2)	

[a]Mole ratios arbitrarily based on K.
[b]Percent total cation release, calculated by (mmol of cation in solution) / (total mmol in clay) × 100.
[c]All values are averages of two replicates with standard deviations provided in parentheses.

TABLE 9

Percentage of the clay fraction dissolved after 1176 h incubation in 0.0025M H_2SO_4

Clay	Clay dissolved[a]
Oxidized	5.8(0.3)
Unoxidized	2.6(0.2)
Ox. clay + Mollisol HA	0.5(0.1)
Ox. clay + Alfisol HA	0.2(0)
Ox. clay + Histosol FA	0.5(0)

[a]All values are averages of two replicates with standard deviations provided in parentheses.

Several explanations are offered for the reduction in clay dissolution and Mg release from clays with either indigenous organic matter or sorbed humic substances. First, the functional groups of the humic substance will act as a proton acceptor. Consequently, protons available to attack the clay structure are reduced. Calculations indicate that the cation exchange capacity of the sorbed humic substances (0.093 $mmol_c$) is of the same order of magnitude as the reduction in cation release afforded by the sorbed humic substances (0.086 $mmol_c$). Second, the indigenous or sorbed humic substances may act as a physical barrier which restricts the movement of protons and other cations to and from the clay surfaces. Chin and Mills (1991) have offered similar explanations for inhibition, by a soil humic acid, of kaolinite dissolution relative to dissolution observed in the abscence of a ligand. Finally because the humic substances are fully protonated under these acid conditions, no significant chelation of clay cations can occur. It is probable that all of the factors attributable to coatings of humic substances may contribute to a decrease in clay mineral weathering.

CONCLUSIONS

Whereas the sorption of fulvic acids by a soil clay was independent of pH in the range 4 to 6, humic acid sorption was highest at pH 6. In addition, sorption was found to be independent of the ratio of clay:HA or FA. Similar quantities of Alfisol and Mollisol humic acids were sorbed. These findings suggest that the clay fraction, under the conditions imposed, has a fixed capacity to sorb humic substances and that capacity is attained irrespective of the amount with which it is equilibrated.

Essentially no differences were found in the amount of cations released and clay dissolved among clays with organic matter removed, clays with indigenous organic matter, and clays with sorbed humic substances which were weathered in 0.05M H_2SO_4 except for slightly less Mg release from the latter. However, when clays were incubated in 0.0025M H_2SO_4, the amount of clay

dissolved and Mg released from clays was dramatically reduced by the presence of indigenous organic matter or sorbed humic substances. No weathering differences with respect to Mg release could be detected between clays with sorbed humic versus fulvic acids or between sources (Mollisol, Alfisol or Histosol) of humic substances. However, more clay with indigenous organic matter was dissolved than clays with sorbed humic substances. In conclusion, there is evidence to suggest that organic matter and/or humic substances sorbed to clays retard clay mineral weathering in acid environments.

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