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EFFECT OF PHOTOLYTIC OXALATE TREATMENT ON SOIL HYDROXY-INTERLAYERED VERMICULITES

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Abstract—The effects of Na-citrate-dithionite (NaCD), ammonium oxalate in the dark (NH_4Ox-D), and photolytic reaction under ultraviolet radiation (NH_4Ox-P) on the mineralogy of <2-μm fractions of selected soils from Virginia were investigated. The NH_4Ox-D treatment removed the smallest amounts of Al (<0.22%) and Fe (<0.50%) from all soils, indicating low levels of noncrystalline material in these materials. From the six soils examined, NH_4Ox-P treatment extracted 5–62% more Fe and 12–300% more Al than the NaCD treatment. The NH_4Ox-D and NaCD treatments revealed no X-ray diffraction detectable alterations to mineral phases present in <2-μm fractions of these soils. The NH_4Ox-P treatment, on the other hand, produced considerable degradation of hydroxy-interlayered vermiculites in these soils, as evidenced by a shift of the 14-Å X-ray diffraction maxima to lower spacings with heat treatment of the sample. The NH_4Ox-P treatment removed variable amounts of hydroxy-Al material from the interlayers of 2:1 layer silicates, depending on their stability and degree of development.

Key Words—Hydroxy-interlayer, Iron oxide, Noncrystalline, Oxalate extraction, Photolytic reaction, Soil, Vermiculite.

INTRODUCTION

The extractants commonly employed for the selective removal of free sesquioxides from soils generally contain either Na citrate-dithionite (NaCD) or NH_4-oxalate (NH_4Ox). The NaCD extraction is widely used to remove crystalline oxides from soils (Mehra and Jackson, 1960; Coffin, 1963; McKeague *et al.*, 1971). The NH_4Ox extraction, commonly referred to as Tamm's reagent, is used in the dark for the selective removal of noncrystalline oxides (Schwertmann, 1959, 1964; McKeague and Day, 1966) and in ultraviolet light to remove both crystalline and noncrystalline oxides from soils (DeEndredy, 1963; Schwertmann, 1964). In this paper, the NH_4Ox extraction in the dark will be referred to as NH_4Ox-D, and the photolytic NH_4Ox extraction under ultraviolet light as NH_4Ox-P.

NaCD treatment (at both 50° and 80°C) partially dissolves hematite and goethite, slightly dissolves magnetite and ilmenite, and has negligible effects on clay minerals, except for Fe-containing nontronite (Coffin, 1963; McKeague and Day, 1966; McKeague *et al.*, 1971). Mehra and Jackson (1960), however, indicated that both hematite and goethite were completely dissolved by NaCD after two or three treatments at 80°C. This discrepancy in dissolution of hematite and goethite by NaCD might be the result of differences in the temperature of extraction or in the particle size of Fe-minerals employed by different investigators. McKeague and Day (1966) showed that the dissolution of Fe-minerals by NaCD increased with a decrease in the particle size. The NH_4Ox-P treatment largely dissolves hematite, goethite, and magnetite and has a minimal effect on clay minerals, except for nontronite (DeEndredy, 1963; LeRiche and Weir, 1963; Chao and Theobald, 1976). The NH_4Ox-D treatment, on the other hand, has very little effect on hematite and goethite (−100 mesh) and only minor effect (9%) on −100-mesh magnetite (McKeague *et al.*, 1971). The severity of this treatment, however, increases with a decrease in particle size (McKeague *et al.*, 1971).

There are conflicting reports as to the susceptibility of clay minerals to NH_4Ox-D treatment. McKeague and Day (1966) reported that NH_4Ox-D treatment has little effect on kaolinite, montmorillonite, and illite. However, Arshad *et al.* (1972) found that NH_4Ox-D treatment caused considerable decomposition of finely ground trioctahedral minerals, biotite and chlorite. Pawluk (1972) observed that prolonged extraction with NH_4Ox-D treatment resulted in slight dissolution of hydrous mica and trioctahedral chlorite, and Hodges and Zelazny (1980) found that <1% of a trioctahedral vermiculite dissolved during a 2-hr NH_4Ox-D treatment.

Hydroxy-Al interlayered vermiculite is a common constituent of soils in the southeastern United States, especially in Virginia (Rich, 1968). This mineral is susceptible to dissolution by extractants employed to remove Fe-oxides, depending on the degree of development and stability of hydroxy-Al "islands" in the interlayered region of vermiculite. McKeague and Day (1966) found that some interlayer Al was removed from artificially prepared Al-chloritized bentonite during a 4-hr NH_4Ox-D treatment. They also noted that interlayer materials of natural Al-chloritized clays were only slightly affected by NH_4Ox-D or NaCD treatments. The present research was undertaken to evaluate the

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Table 1. Selected chemical, physical, and mineralogical properties of six Virginia soils.

Soil type	pH (1:1 H_2O)	Organic C (%)	Particle size (%)			Mineralogy of <2-μm fraction[1] (%)					Whole soil[2] HIV (%)
			Sand	Silt	Clay	HIV	MI	KK	QZ	GI	
Dragston sl	5.8	1.8	64.5	22.8	12.7	52	4	30	13	1	7
Dunmore sil	6.6	2.1	26.8	54.0	19.2	35	5	45	15	—	7
Groseclose sil	5.4	2.2	22.8	66.5	10.7	45	30	13	12	—	5
Litz sil	6.3	2.3	26.1	50.9	23.0	40	30	18	12	—	9
Starr sicl	6.7	2.4	10.2	58.3	31.5	39	0	50	10	1	12
Westmoreland sicl	6.2	3.5	13.0	56.6	30.4	43	30	15	12	—	13

[1] HIV = Hydroxy-interlayered vermiculite; MI = Mica; KK = Kaolinite; QZ = Quartz; GI = Gibbsite.

[2] Calculated using % clay in soil and % HIV in <2-μm fraction (clay).

effects of NH_4Ox-D, NH_4Ox-P, and NaCD treatments on X-ray diffraction properties of naturally occurring, hydroxy-Al, interlayered 2:1 phyllosilicates in soils with varying degrees of interlayer stability.

MATERIALS AND METHODS

The physical, chemical, and mineralogical properties of the Ap horizon of the six soils selected for this study are presented in Table 1. These soils were selected to represent a range in clay content and stability of hydroxy-interlayered vermiculites of soils from Virginia. Soil pH was measured using a 1:1 soil:water ratio and a 1-hr equilibration period. Organic C was determined by the modified Walkley-Black procedure (Allison, 1965), and particle size distribution by the pipet method (Day, 1965).

The NaCD treatment was carried out by the procedure outlined by Coffin (1963). A 2-g aliquot of soil was shaken for 30 min at 50°C with 40 ml of citrate buffer, which was 0.15 M with respect to Na-citrate and 0.05 M to citric acid, and contained 2 g of Na-dithionite. The suspensions were centrifuged, and the solutions were decanted and stored for analyses.

The NH_4Ox-D extraction was performed by the method of Schwertmann (1959, 1964) as modified by McKeague and Day (1966). A 2-g aliquot of soil was transferred to a 250-ml plastic centrifuge tube along with 100 ml of acidified 0.2 m NH_4-oxalate (pH 3.5) solution. The tubes were covered with Al foil to maintain darkness during the extraction. The contents were shaken horizontally on a reciprocating shaker for 4 hr, centrifuged, and the solutions stored for analyses.

The NH_4Ox-P procedure employed was the modified version (McLaren and Crawford, 1973) of the method described by DeEndredy (1963). A 100-ml aliquot of solution, which was 0.1 M in oxalic acid and 0.175 M in NH_4-oxalate (pH 3.25), was added to 2 g of soil in a 250-ml beaker. The contents were placed on a boiling hot water bath (~100°C) and irradiated from above (12.5–15.0 cm) for 2.5 hr with a 30 watt, model XX-15 Black-Ray ultraviolet lamp. The wave length of the radiation was predominantly in the near ultraviolet region. After extraction, the suspension was transferred into 250-ml centrifuge bottles with another 50 ml of extracting reagent. The contents were centrifuged and the supernatants transferred to plastic bottles, acidified, and stored for analyses.

Al, Fe, and Si in the extractants from all three treatments were determined with a Perkin-Elmer 503 atomic absorption spectrophotometer using a high temperature N_2O-acetylene flame.

Following the extractions, the <2-μm fractions of the soil residue from all three treatments were separated by centrifugation using dilute Na_2CO_3 adjusted to pH 9.5 as a dispersant. Oriented mounts of the clay fraction were prepared by depositing 250 mg of sample on a Millipore filter, saturating with Mg or K, washing free of salts, and glycolating the Mg-saturated samples. The moist membrane was placed clay-side down on a glass slide and transferred with a gentle rolling pressure of a glass rod (Drever, 1973). X-ray powder diffraction (XRD) patterns of air-dry samples and of samples heated to 105°C, 300°C, and 550°C were obtained using a Diano XRD-8300 AD X-ray diffractometer equipped with a graphite crystal monochromator, LSI-11 computer, and printout. The samples were scanned at 2°2θ/min from 2° to 32° using CuKα radiation.

Quantitative estimation of minerals in the <2-μm fractions were obtained by a combination of XRD, thermal, and chemical techniques. The gibbsite and kaolinite contents were estimated by measuring the areas under dehydroxylation endothermic peaks at 280° and 520°C in a differential scanning calorimetry pattern obtained with a DuPont 990 Thermal Analyzer equipped with a DSC cell, and by comparing the areas with standard curves derived by regression analyses for Reynolds synthetic gibbsite RH-31F and poorly crystalline Georgia kaolinite. Mica contents were calculated from total elemental analyses assuming 10% K_2O to equal 100% mica. Quantitative estimations of other clay-size minerals were obtained by proportioning integrated peak areas of the appropriate XRD patterns, using kaolinite as an internal standard and assuming the minerals detected totaled 100%.

Table 2. Quantities of Fe and Al removed from six Virginia soils by NaCD, NH_4Ox-D, and NH_4Ox-P treatments.

Soil type	NaCD (%)		NH_4Ox-D (%)		NH_4Ox-P (%)		meq Al/ g HIV[1]
	Fe	Al	Fe	Al	Fe	Al	
Dragston sl	0.22	0.16	0.09	0.12	0.28	0.28	2.0
Dunmore sil	0.97	0.25	0.05	0.10	1.14	0.43	3.0
Groseclose sil	1.28	0.26	0.15	0.11	1.34	0.29	0.7
Litz sil	2.43	0.37	0.50	0.21	3.94	1.02	7.9
Starr sicl	7.22	0.63	0.25	0.20	11.10	1.93	11.8
Westmoreland sicl	2.43	0.42	0.47	0.22	3.36	1.67	10.6

[1] Calculated with the assumption that the difference in extractable Al from NH_4Ox-P and NaCD results from dissolution of only hydroxy-Al interlayers in hydroxy-interlayered vermiculite.

RESULTS AND DISCUSSION

The mineral suites of the <2-μm soil fractions were similar, with hydroxy-Al interlayered vermiculite and kaolinite being the predominant minerals in the Dragston, Dunmore, and Starr soils and with hydroxy-Al interlayered vermiculite and mica being the dominant minerals in the Groseclose, Litz, and Westmoreland soils (Table 1). All soils contained appreciable amounts of quartz. The Starr and Dragston soils contained detectable amounts (1%) of gibbsite. Thermal analyses, before and after treatment for iron oxide removal, revealed that the six soils contained no detectable amounts of goethite either in the <2-μm fraction or in the whole soil.

Amounts of Al and Fe removed from the soils by the three extractants are presented in Table 2. The NH_4Ox-D treatment removed the smallest amounts of Al and Fe from all soils, indicating low levels of noncrystalline material in these soils. The NH_4Ox-P treatment, on the other hand, removed the most Al and Fe from the soils, followed by the NaCD treatment. These differences were more evident in the Litz, Starr, and Westmoreland soils than in the other three soils.

The NH_4Ox-P treatment extracted as much as 62 and 54% more Fe,[2] in the Litz and Starr soils, respectively, than the NaCD treatment (Table 2). In the Westmoreland, Dragston, Dunmore, and Groseclose soils, the corresponding increases in NH_4Ox-P extractable Fe were 38, 27, 18, and 5%, respectively. The wide variation in the amounts of Fe extracted by the two methods can be attributed to the efficacy with which these extractants dissolve Fe-minerals such as hematite and goethite that are normally present in soils. Dissolution of these two minerals was complete in the NH_4Ox-P treatment and incomplete (20–40%) in the NaCD treatment (DeEndredy, 1963; McKeague *et al.*, 1971; Chao and Theobald, 1976). It also is possible that the NH_4Ox-P treatment removed Fe from sources other than oxyhydroxides, such as interlayer positions.

The differences in soil-Al extracted by these methods[2] were far greater than the differences for Fe (Table 2). In the Litz, Starr, and Westmoreland soils, the NH_4Ox-P treatment removed from 170 to 300% more Al than the NaCD treatment. In the other soils, the differences ranged from 12 to 75%. LeRiche and Weir (1963) reported that the source of most of the Al extracted with NH_4Ox-P was Al-substituted soil goethite. This conclusion was based on the observation that the NH_4Ox-P treatment had no appreciable effect either on silicate minerals or on gibbsite. The source of the excess Al extracted by the NH_4Ox-P treatment (Table 2) can not be attributed to goethite because this mineral was not present in detectable amounts in these six soils. Silicon contents in the (NH_4Ox-P) extracts of these soils were <0.2% indicating that there was no significant dissolution of silicate minerals. It is possible that Al can substitute for Fe in hematite.

An examination of the <2-μm fraction of NH_4Ox-D-, NH_4Ox-P-, and NaCD-treated soils by XRD following K saturation revealed substantial dissolution of the hydroxy-Al interlayer material by the NH_4Ox-P treatment. This was evident from the change in shape and position of the 14-Å diffraction maxima, which were due to hydroxy-Al interlayered vermiculite. In the Westmoreland soil (Figure 1), where the Al extracted by NH_4Ox-P and NaCD treatments differed by a considerable margin (~300%), the diffraction maximum around 14 Å was narrow and intense in the NaCD-treated samples and broad and less intense in the NH_4Ox-P-treated samples. Furthermore, the collapse of the 14-Å peak to about 10 Å occurred at 300°C upon K saturation in the NH_4Ox-P-treated samples, whereas collapse to this extent did not occur for either the NH_4Ox-D- or NaCD-treated samples even at 550°C (Table 3). These results indicate that the NH_4Ox-P treatment removed most of the hydroxy-Al material from the interlayers of the 2:1 phyllosilicates present in the Westmoreland soil, and thus promoted collapse at a lower temperature. The effects of the NH_4Ox-P treatment on the other soils were similar to that shown by the Westmoreland soil, but less severe. In the Groseclose soil (Figure 1), where the NH_4Ox-P treatment removed only 12% more Al than the NaCD treatment, the effect due to the NH_4Ox-P treatment was minimal. However, the NH_4Ox-P treatment decreased

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[2] $[(NH_4Ox\text{-}P) - (NaCD)][NaCD]^{-1}[100\%]$.

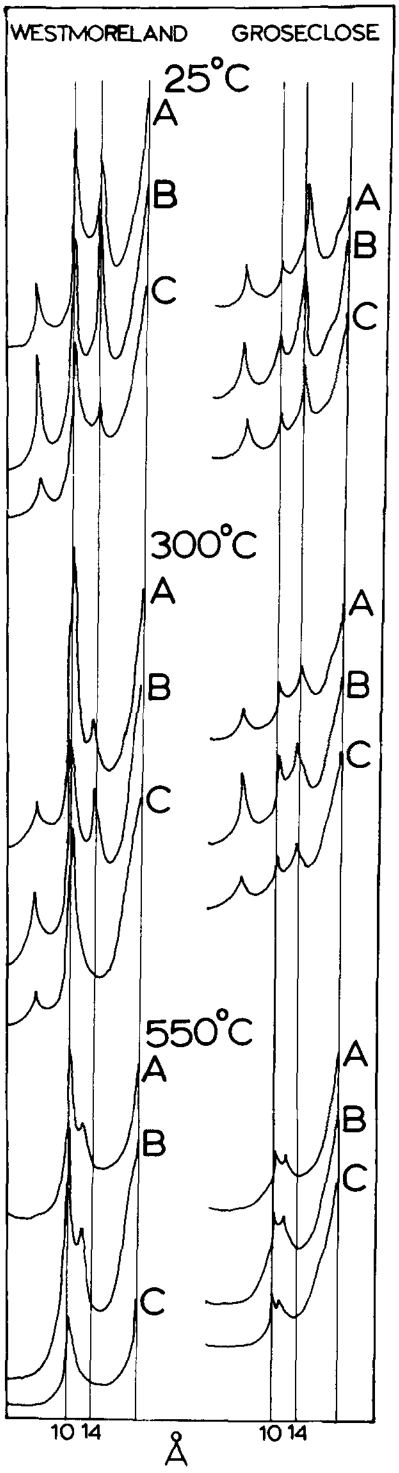

Figure 1. X-ray diffractograms of K-saturated, <2-μm fractions of Westmoreland and Groseclose soils at 25°, 300°, and 550°C following NaCD- (A), NH_4Ox-D- (B), and NH_4Ox-P- (C) pretreatments (CuKα radiation).

the thermal stability of the hydroxy-Al interlayer material in all soils (Table 3).

Differences in the severity of the NH_4Ox-P treatment among soils may be related to the degree of development, the stability, and the composition of the interlayer material (Rich, 1968; Meyers and Ahlrichs, 1973). The large differences in extractable Al[2] for the NH_4Ox-P treatment as compared to the NaCD treatment for the Litz, Starr, and Westmoreland soils are a result of the degree of interlayer development. The degree of interlayer development for these soils was greater than for the other soils examined, as evidenced by the larger amount of Al extracted per gram of hydroxy-Al interlayered vermiculite (Table 2) and the thermal stability of the diffraction maxima for the NaCD-treated samples, particularly at 550°C (Table 3). The large differences in extractable Al for the Westmoreland soil, as compared to the Litz and Starr soils, can be explained on the basis of interlayer stability. The stability of the interlayers in the Westmoreland soil was low as evidenced by the decrease in diffraction maxima at 300° and 550°C for the NH_4Ox-D and NaCD treatments. In this soil, the diffraction maximum at 14-Å collapsed partially at room temperature and completely at 300°C after the NH_4Ox-P treatment.

The small differences in extractable Al for the NH_4Ox-P treatment, as compared to the NaCD treatment, for the Dragston, Dunmore, and Groseclose soils are the result of low amounts of Al present in interlayer positions (Table 2). Of these soils, the Groseclose soil had the smallest difference in Al extracted by the NH_4Ox-P and NaCD treatments. This is probably due to its greater interlayer stability as evidenced by larger diffraction maxima at all heat treatments for all extractants (Table 3).

Schwertmann (1964) reported that varying light conditions (i.e., darkness, diffuse light, sunlight, and ultraviolet light) during the NH_4Ox extraction caused different amounts of Fe-oxide removal from soils. DeEndredy (1963) observed that the extraction of soil Fe-oxides was most efficient in the near ultraviolet region, i.e., wavelengths ~366 μm. The present study indicates that in addition to iron oxides, NH_4Ox-P treatment removes considerable amounts of hydroxyl-Al material from the interlayer region of 2:1 phyllosilicates. NH_4Ox-D treatment, on the other hand, has a minimal effect on the mineralogy of these soils (Figure 1), indicating that this method can be safely used to estimate noncrystalline oxides in soils (Hodges and Zelazny, 1980).

Table 3. Peak positions (Å) and areas (integrated intensities in cps) for the <2-μm fractions of six Virginia soils treated with NaCD, NH_4Ox-D, or NH_4Ox-P; K-saturated; and heated to 25°, 300°, and 550°C.

	25°C						300°C						550°C					
	NaCD		NH_4Ox-D		NH_4Ox-P		NaCD		NH_4Ox-D		NH_4Ox-P		NaCD		NH_4Ox-D		NH_4Ox-P	
Soil type	Peak	Area	Peak	Area	Peak	Area	Peak	Area	Peak	Area	Peak	Area	Peak	Area	Peak	Area	Peak	Area
Dragston sl	14.17	2870	14.14	4304	13.59	2090	12.88	1714	12.91	2354	12.99 10.10	1500 901	11.36	1356	11.42	1950	10.10	1510
Dunmore sil	14.03	2369	14.05	2874	13.59	2400	12.59	2968	12.92 10.23	2380 57	12.44 9.93	1650 1102	11.24	4277	11.41	1214	10.10	1920
Groseclose sil	14.60 10.68	1338 188	13.88 9.93	1615 141	14.24 10.27	1780 920	13.21 10.05	1181 3598	12.93 10.06	1139 507	13.59 10.10	1280 960	11.83 10.15	281 452	11.93 10.13	927 313	11.47 10.10	970 930
Litz sil	14.11 10.06	2245 1503	14.11 10.05	2776 2138	13.59 10.10	1590 3410	13.40 10.05	1376 1908	13.60 10.03	2459 2796	13.59 10.10	1460 4120	12.21 10.01	1373 1363	12.23 10.05	2390 1083	11.94 10.10	1280 2960
Starr sicl	14.26	1156	14.21	1062	14.24	2060	12.20	510	13.16	706	13.59	1210	11.25	788	11.90	1559	11.25	940
Westmoreland sicl	14.00 10.06	1742 1285	14.09 10.06	2619 3350	14.24 10.27	2140 5050	13.33 10.04	516 3006	13.57 10.03	1351 3878	10.10	5180	11.90 10.02	130 3697	12.03 10.05	2088 2258	10.10	1710

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Резюме—Исследовались эффекты Na-цитратного-дитионита (NaCD), оксалата аммония в темноте (NH_4Ox-D) и фотолитическая реакция в ультрафиолетовом излучении (NH_4Ox-P) на минералогию фракций размером <2 μм избранных почв Виргинии. Обработка NH_4Ox-D удалила самые маленькие количества Al (<0,22%) и Fe (<0,50%) из всех почв, указывая на низкий уровень некристаллического материала в этих почвах. Обработка NH_4Ox-P удалила от 5 до 62% более Fe и от 12 до 300% более Al, чем обработка NaCD из шести исследованных почв. После обработки NH_4Ox-D и NaCD не было никаких измеряемых рентгеновской дифракцией фазовых перемен во фракциях этих почв размером <2 μм. Обработка NH_4Ox-P, с другой стороны, вызвала значительную деградацию гидрокси-межслойных вермикулитов в этих почвах, на что указывал сдвиг 14 Å максимума рентгеновской дифракции в сторону меньших расстояний после тепловой обработки образца. Обработка NH_4Ox-P удаляла разные количества гидрокси-Al материала из прослоек 2:1 силикатов в зависимости от их стабильности и степени процесса образования. [E.C.]

Resümee—Es wurden die Auswirkungen von Na-Citrat-Dithionit (NaCD), sowie die von Ammoniumoxalat im Dunkeln (NH_4Ox-D) und bei der photolytischen Reaktion unter ultravioletter Bestrahlung (NH_4Ox-P) auf die Mineralogie der Fraktion <2 μm von ausgewählten Böden aus Virginia untersucht. Die NH_4Ox-D-Behandlung entternte aus allen Böden die geringsten Mengen von Al (<0,22%) und Fe (<0,50%), was auf niedrige Gehalte an nichtkristallinem Material in diesen Substanzen hindeutet. Aus sechs untersuchten Böden extrahierte die NH_4Ox-P-Behandlung 5–62% mehr Fe und 12–300% mehr Al als die NaCD-Behandlung. Die NH_4Ox-D- und die NaCD-Behandlungen verursachten keine mit Röntgendiffraktion erkennbaren Veränderungen an den Mineralphasen in den Fraktionen <2 μm dieser Böden. Die NH_4Ox-P-Behandlung verursachte dagegen in diesen Böden eine beachtliche Degradation der Vermiculite mit Hydroxy-Zwischenlagen, wie aus einer Verschiebung des 14 Å Maximums der Röntgendiffraktion nach kleineren Werten bei Erhitzen der Probe hervorging. Die NH_4Ox-P-Behandlung entfernte unterschiedliche Mengen an Hydroxy-Al-Material aus den Zwischenschichten der 2:1 Schichtsilikate in Abhängigkeit von ihrer Stabilität und ihrem Kirstallisationsgrad. [U.W.]

Résumé—Les effets de la citrate-dithionite-Na (NaCD), ammonium oxalate, dans le noir (NH_4Ox-D) et la réaction photolytique sous radiation ultraviolette (NH_4Ox-P) sur la minéralogie de fractions <2-μm de sols sélectionnés de Virginie, ont été investigués. Le traitement au NH_4Ox-D a enlevé les plus petites quantités d'Al (<0,22%) et de Fe (<0,50%) de tous les sols, indiquant de bas niveaux de matériel non-cristallin dans ces matériaux. Dans les six sols examinés, le traitement au NH_4Ox-P a extrait de 5–62% plus de Fe et de 12–300% plus d'Al que le traitement au NH_4Ox-D. Les traitements au NH_4Ox-D et au NaCD n'ont révélé aucune altération détectible à la diffraction aux rayons-X des phases minérales présentes dans les fractions <2-μm dans ces sols. Le traitement au NH_4Ox-P, d'un autre côté, a produit une dégradation considérable des vermiculites à intercouches hydroxy dans ces sols, mise en évidence par un déplacement des maxima 14 Å de la diffraction aux rayons-X à des espacements plus bas, avec traitement de l'échantillon à la chaleur. Le traitement NH_4Ox-P a retiré des quantités variables de matériel Al-hydroxy des intercouches silicates à couches 2:1, dépendant de leur stabilité et de leur degré de développement. [D.J.]