COMPOSITION AND ORIGIN OF SMECTITE IN SOILS DERIVED FROM BASALT IN NORTHERN IRELAND

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Abstract—The sand and silt fractions of soils derived from Tertiary basalt in northeastern Ireland exhibit unusually high cation-exchange capacities. Smectite was identified by X-ray powder diffraction in all size fractions and was selectively dissolved by treatment with 1 N HCl and 0.5 N NaOH. Structural formulae, based on chemical analysis of the dissolved material, suggest that the smectite is intermediate in composition between a di- and a trioctahedral mineral and that the octahedral cation occupancy, together with the numbers of Mg and Fe atoms per unit cell, decreases with decrease in particle size of the soil fraction examined. The mean formula for the smectite in the clay separates is: $M^+_{0.40}(Si_{3.33}Al_{0.67})(Al_{1.07}Fe^{2+}_{0.09}Fe^{3+}_{0.41}Mg_{0.82})O_{10}(OH)_2$. Similar analysis of smectite present in clay-size material separated from weathered basalt rock taken from the bases of the soil profiles showed that it had close to the full trioctahedral occupancy. It is suggested that the soil smectite is a weathering product of the trioctahedral smectite inherited from the weathered basalt.

Key Words—Basalt, Octahedral occupancy, Selective dissolution, Smectite, Soil, Weathering.

INTRODUCTION

Tertiary basalts cover an area of approximately 4000 km² in northeastern Ireland. The lava pile is built of many successive flows and varies in thickness from 100 to perhaps 1000 m, but its original thickness or the length of time required for its emplacement are unknown (Charlesworth, 1963). Mineral transformations probably took place between successive outpourings of lava and where water-saturated flows were buried beneath fresh lava (Charlesworth, 1963). According to Patterson (1955), the most abundant minerals in the basalts are labradorite, augite, and olivine. Smith (1957) identified vermiculite and kaolinite in apparently unweathered rock. He considered that the vermiculite was an alteration product of olivine and that the kaolinite was secondary to labradorite. Walker (1960) identified saponite throughout 800 m of basalt intersected by the Langford Lodge borehole. These occurrences indicate that the saponite formed prior to present-day weathering of the lavas.

The area is covered by glacial drift, generally of local origin. Most of the soils are classified as brown earths (Brown, 1954) and are characterized by high levels of extractable Fe and Al, high phosphate retention (Evans and Smillie, 1976), large cation-exchange capacities (CEC) and, commonly, high amounts of exchangeable Mg (McConaghy and McAleese, 1957). The sand and silt fractions contribute substantially to the total soil CEC (McAleese and McConaghy, 1957). The clay mineral composition has been reported to be vermiculitic (Smith, 1957) and to vary from kaolinitic to montmorillonitic to vermiculitic (McAleese and Mitchell, 1958).

The purpose of this paper is to show that a smectite mineral, inherited from the parent rock, is responsible for the high CECs of the soils and the soil separates and to discuss changes in its chemical composition during pedogenesis.

MATERIALS AND METHODS

Samples from two soil profiles derived from basaltic till at Woodburn and Upper Woodburn, County Antrim, Northern Ireland, were analyzed. The Woodburn profile showed some mottling in the B horizons, indicative of drainage impedence, whereas the Upper Woodburn profile appeared to be freely drained. Some properties of these soils are given in Table 1. Sand, silt, and clay fractions were separated by the usual sieving and sedimentation procedures following dispersion of the soils using a Rapidis 150 ultrasonic vibrator, according to the method of Genrich and Bremner (1972). After destruction of organic matter (OM) by H_2O_2 treatment, the separates were Ca-saturated, washed free of excess salt, and dried. Clay samples were also separated from fragments of weathered basalt by first crushing them in a mortar and then dispersing them ultrasonically.

Free Fe and Al in the size fractions were extracted using dithionite-citrate-bicarbonate (DCB) (Mehra and Jackson, 1960). Noncrystalline material was dissolved by boiling DCB-treated samples in 0.5 N NaOH (Hashimoto and Jackson, 1960). The Fe released by this treatment was extracted by an additional DCB treatment. CEC was determined on deferrated, NaOH-treated samples using a $BaCl_2$ solution buffered at pH 8.2 with triethanolamine. Potassium fixation was estimated by the method of Alexiades and Jackson (1965). Removal of interlayer Al was attempted on selected samples using the sequential sodium citrate extraction procedure of Frink (1965).

X-ray powder diffraction (XRD) analysis was carried out on deferrated, NaOH-treated samples of the sands, silts, and clays using a Philips X-ray diffractometer and Ni-filtered $CuK\alpha$ radiation at 40 kV and 20 ma. The sands were prepared as random powders, whereas the silts were sedimented onto glass slides. The clays were divided into coarse (2–0.2 μm) and fine (<0.2 μm) fractions by centrifugation. Subsamples were saturated with K^+ and Mg^{2+}, pipetted onto glass slides, and air dried. The K-saturated samples were also heated at 300° and

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Table 1. Some properties of the soils containing smectite.

Horizon	Depth (cm)	pH	CEC (meq/100 g)	Base sat. (%)	Organic matter (%)	Sand[2] (%)	Silt (%)	Clay (%)
Woodburn[1]								
A11	0–20	6.13	58.3	52.6	9.25	21.8 (38.4)	42.9 (36.1)	35.3 (60.5)
A12	20–35	5.56	53.0	39.5	5.61	17.3 (36.0)	42.6 (34.2)	41.1 (63.1)
B2	35–65	5.78	54.3	18.3	4.15	22.3 (55.5)	55.7 (46.0)	22.0 (67.3)
B3/C	65+	5.92	54.7	64.2	1.00	20.8 (54.87)	51.5 (46.8)	27.7 (65.7)
Upper Woodburn[1]								
A11	0–20	6.00	62.9	36.4	10.51	19.8 (35.9)	48.3 (40.7)	31.9 (64.3)
A12	20–35	5.62	60.4	25.3	8.88	18.4 (36.7)	46.3 (40.3)	35.3 (67.3)
B2	35–65	5.70	57.6	16.1	5.35	26.4 (47.0)	49.9 (41.6)	23.7 (71.6)
C	65+	5.55	54.7	44.5	0.98	18.1 (54.0)	46.8 (56.7)	35.1 (69.9)

[1] Both soils are classified as Dystric Eutrocrepts.
[2] Sand = 2 mm–50 μm; silt = 50–2 μm; clay = <2 μm.
Numbers in parentheses are CEC values (in meq/100 g) for deferrated, NaOH-treated samples of corresponding particle size separate.

550°C in a muffle furnace for 2 hr. A Mg-glycerol sample was prepared by suspending a Mg-saturated sample in 1 ml of 10% glycerol in water. Differential thermal analysis (DTA) was performed on samples of clay (<2 μm, Ca-saturated), equilibrated for at least 4 days in a desiccator over a saturated $Mg(NO_3)_2$ solution, using a Stanton-Redcroft 673-4 instrument at a heating rate of 20°C/min in a nitrogen atmosphere. Al_2O_3 was used as reference.

Acid dissolution of samples, previously treated with DCB and NaOH to remove free oxides and amorphous silicates, was carried out by digesting 100 mg of sample (Ba-saturated) in 50 ml of 1 N HCl on a water bath at 80°C for 24 hr. The residues were washed with 25 ml of 1 N HCl. The wash solutions were combined with the supernatants and brought up to volume. The residues were treated with boiling 0.5 N NaOH for 2.5 min. Si and Fe^{2+} in the extracts were determined colorimetrically (Pruden and King, 1969). Al, total Fe, Mg, Ca, K, and Na were determined by atomic absorption spectroscopy. The effect of time on acid dissolution of selected silts was assessed by subjecting the samples to acid treatment for from 2 to 45 hr. The residues were boiled in 0.5 N NaOH as before.

RESULTS AND DISCUSSION

Properties of the soils

The CECs of the soil samples were quite high (Table 1). The values were relatively uniform within the profiles, despite the decrease in organic matter with depth. Ca was the dominant exchangeable cation, but ex-

changeable Mg was also high, reaching 15.6 meq/100 g (data not shown) for the B3/C horizon of the Woodburn profile. The ultrasonic vibration procedure produced more 'clay' (31.5%), on average, than the conventional 'Calgon' method (25.8%). McAleese (1954) attributed the abnormally high CECs of the coarse fractions of similar soils to the presence of composite grains which, even after repeated reduction with sodium hydrosulphite followed by shaking with ammonium hydroxide, did not disperse. In the present study, microscopic examination of sand fractions confirmed the presence of composite grains containing phyllosilicate material. Walker's (1960) observation that saponite occurs at all depths in the basalt at Langford Lodge suggests that the composite grains are rock fragments and that the materials composing them are alteration products of the primary basalt minerals. Some of these materials are undoubtably clay size, but because their aggregation is geologic rather than pedologic, their complete dispersion, even if it could be achieved, would not be appropriate for the characterization of soil texture.

Properties of the particle size separates

The sand, silt, and clay separates contained large amounts of DCB-extractable Fe and Al and substantial

Table 2. Extractable Fe, Al, and Si in particle size separates.

Extractant and component extracted[1]	Sand		Silt		Clay	
	Mean	Range	Mean	Range	Mean	Range
DCB Fe_2O_3 (%)	6.1	3.6–8.5	4.5	3.7–5.7	5.7	3.6–8.1
DCB Al_2O_3 (%)	1.8	0.9–3.2	1.9	0.8–3.4	3.8	1.3–6.6
NaOH Al_2O_3 (%)	2.7	1.5–4.6	3.2	1.6–4.9	7.4	5.7–10.1
NaOH SiO_2 (%)	4.5	3.0–5.7	8.8	5.9–13.7	11.1	8.8–14.3
DCB Fe_2O_3 (%)[2]	0.7	0.5–0.8	0.6	0.5–0.7	0.7	0.5–0.9
DCB Al_2O_3 (%)[2]	0.2	0.1–0.3	0.2	0.1–0.4	0.4	0.3–0.6

[1] Separates were sequentially treated with dithionite-citrate-bicarbonate (DCB), 0.5 N NaOH, and again with DCB.
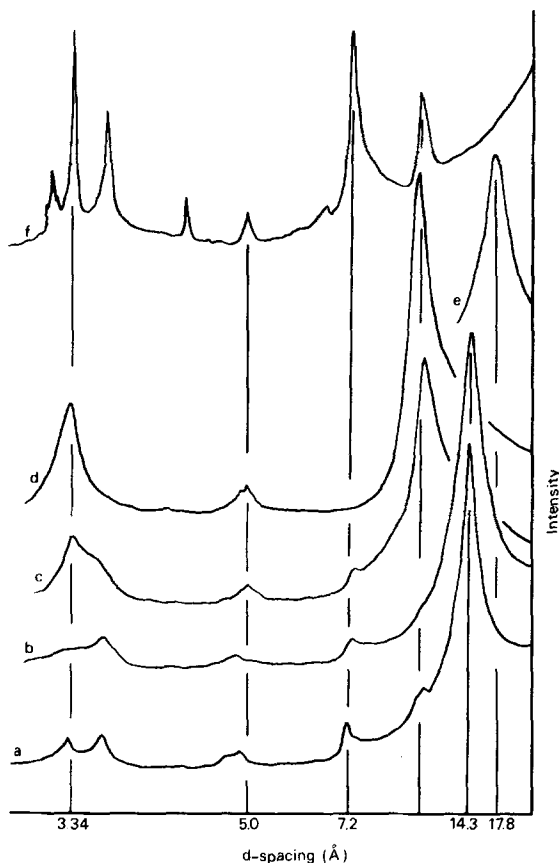[2] Amounts extracted from the samples after NaOH treatment.

Figure 1. X-ray powder diffractograms for clays (DCB and NaOH treated) from Upper Woodburn A12: (a) coarse clay (2–0.2 μm), Mg-saturated, (b) fine clay (<0.2 μm), Mg-saturated, (c) fine clay, K-saturated and heated at 300°C, (d) fine clay, K-saturated and heated at 550°C, (e) fine clay, Mg/glycerol, and (f) acid residue of clay (<2 μm), Mg-saturated.

Figure 2. X-ray powder diffractograms for Mg-saturated samples of (a) basalt clay (<0.2 μm), (b) Upper Woodburn A12 silt (50–2 μm), and (c) acid residue of Upper Woodburn A12 silt.

quantities of noncrystalline aluminosilicates, as defined by the Hashimoto and Jackson (1960) dissolution procedure (Table 2). The CEC data (Table 1) show, however, that the crystalline fraction is the main source of negative charge in the samples. A member of the smectite group was the dominant mineral in both fine and coarse clays (Figure 1). Small amounts of kaolinite, mica, and quartz (in coarse clays) were also present. The silt and sand separates also contained smectite along with labradorite, quartz, and augite (Figure 2). The smectite, therefore, must be responsible for the high CECs.

Representative DTA traces of the clay fractions are presented in Figure 3. All samples gave quite similar patterns. The large, low temperature endotherm at 130°C is characteristic of expanding 2:1 phyllosilicates. The dehydroxylation endotherm between 540° and 550°C is close to that of beidellite (550°C) and nontronite (500°C), but is low compared with that of dioctahedral montmorillonite, which occurs at about 700°C.
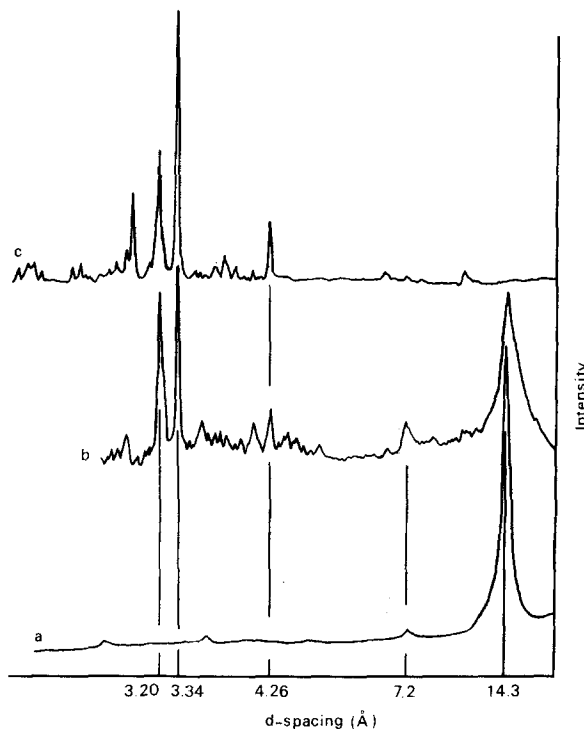
Greene-Kelly (1957) suggested that the shift of the dehydroxylation peak of smectites to lower temperatures may be due to increased tetrahedral substitution. Mackenzie (1970) concluded that substitutions such as Si by Al, Al by Fe, and Mg by Zn tend to decrease the dehydroxylation temperatures, probably due to strains set up in the structure due to different sizes of the ions.

Selective dissolution of smectite

Calculation of smectite composition by applying corrections for the other minerals present was successfully employed by Sawhney and Jackson (1958) and Mackenzie (1960). The low temperature of smectite dehydroxylation in the study clays precluded quantitative determination of kaolinite by DTA or by the dissolution procedure of Hashimoto and Jackson (1960). Acid treatments have been used for the selective dissolution of chlorite (Brindley, 1961) and vermiculite (Ristori et al., 1974). The partial dissolution of smectite at low pH during CEC determinations (Curtin, 1979) suggested that smectite might be selectively dissolved using dilute acid. The smectite was completely dissolved by an acid dissolution procedure similar to that of Ristori et al. (1974). The residues consisted of kaolinite, mica, and quartz with a trace of feldspar in the clay separates, whereas quartz, augite, and feldspar
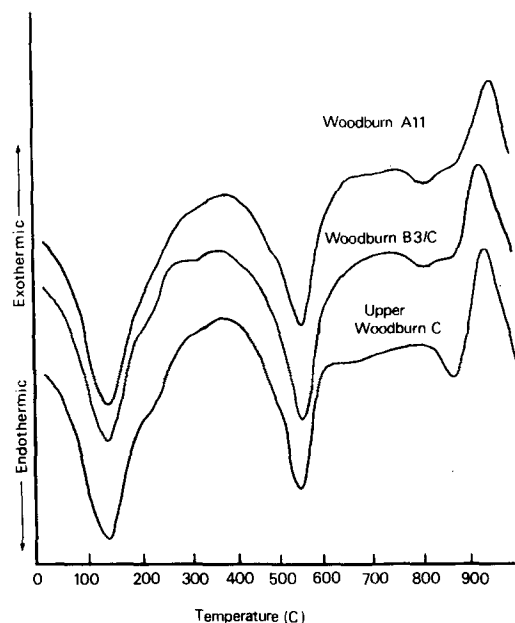
Figure 3. DTA traces of clays (<2 μm).

remained in the silt and sand separates (Figures 1 and 2).

Chemical analyses of the HCl and NaOH extracts of the sand, silt, and clay separates from the Upper Woodburn profile are given in Table 3. The data for the Woodburn samples are similar and are not presented. Most of the clay fraction was dissolved by the treatment. The solubility of pure kaolinite and the amount of K in the HCl extracts (Table 3) indicate that the nonsmectite

minerals in the clay fractions were partially dissolved by the treatment. However, the intensities of the kaolinite, mica, and quartz diffraction peaks were much increased by the treatment, showing that substantial concentration of these minerals had occurred. Because the initial amount of kaolinite, mica, and quartz in the clay separates was low (e.g., $K_2O = 0.22–0.80\%$) it is unlikely that the partial dissolution of these minerals led to a significant error in the calculation of smectite composition.

The solubility of the silt and sand fractions was lower than that of the clay fractions. The alteration of the nonsmectite minerals in the >2 μm fraction was assessed by subjecting silt samples, which had been pretreated with DCB and NaOH, to acid treatment for 2–45 hr. Typical dissolution data are presented in Figure 4. HCl-soluble Mg showed little increase after 2 hr of acid treatment. The amount of Fe extracted increased substantially between 2 and 8 hr, but longer extraction periods removed little additional iron. Although Al extracted by HCl also increased substantially between 2 and 8 hr, subsequent increases were relatively small. The amount of Al dissolved by the 2.5-min NaOH-boiling treatment decreased as the duration of the acid dissolution increased. The amount of Si dissolved by the two reagents paralleled fairly closely the total Al dissolution data. The fact that little or no increase with time was noted for Mg suggests that augite, which has a high Mg content, was not being attacked by the acid. Some dissolution of feldspars occurred as indicated by the presence of Ca, Na, and K in the HCl extracts (Table 3). Plagioclase feldspars are increasingly susceptible to acid attack as the Ca content increases. However, an

Table 3. Elements dissolved from Upper Woodburn samples by the 1 N HCl and 0.5 N NaOH treatments (% of oven-dried samples).

Horizon	SiO_2 (HCl) (%)	Al_2O_3 (HCl) (%)	MgO (%)	FeO (%)	Fe_2O_3 (%)	CaO (%)	Na_2O (%)	K_2O (%)	SiO_2 (NaOH) (%)	Al_2O_3 (NaOH) (%)	Total (%)
Sand fraction											
A11	12.08	7.76	4.59	1.31	4.74	0.56	0.18	0.05	10.08	0.27	41.62
A12	12.42	7.59	4.66	1.24	5.06	0.55	0.15	0.05	9.58	0.27	41.57
B2	12.42	8.61	6.37	1.44	6.33	0.44	0.08	0.15	12.50	0.27	48.61
C	11.75	7.99	8.84	1.69	6.89	0.29	0.05	0.05	14.80	0.27	52.62
Silt fraction											
A11	12.63	8.28	3.40	0.89	4.20	0.38	0.15	0.07	10.19	0.38	40.57
A12	12.50	8.13	3.55	0.88	4.21	0.42	0.13	0.09	9.88	0.34	40.13
B2	12.78	8.59	4.31	1.07	5.03	0.23	0.11	0.22	10.38	0.34	43.06
C	13.31	11.15	5.91	0.89	6.44	0.35	0.08	0.07	16.88	0.50	55.58
Clay fraction											
A11	13.60	14.94	5.31	1.25	5.79	N.D.	0.07	0.14	21.92	0.57	63.59
A12	13.33	14.40	5.47	1.58	5.53	N.D.	0.06	0.16	21.43	0.72	62.68
B2	14.60	14.31	6.63	1.27	5.78	N.D.	0.08	0.27	19.96	0.61	63.51
C	12.67	16.20	6.05	0.81	5.56	N.D.	0.07	0.12	26.30	0.95	68.73
Kaolinite (<2 μm)	3.74	2.74	—	—	—	—	—	—	3.27	2.05	—

N.D. = not detectable.

average of only 12.5% of the total Ca in the sands and silts was dissolved by HCl, indicating a limited dissolution of feldspar. The results of Kiely and Jackson (1965) suggest that silt- and sand-sized quartz should be little affected by this treatment. These patterns of dissolution are consistent with the conclusions of Grim (1968) that alkaline earth cations are removed more rapidly during acid attack on smectite than are Al or Fe and that Fe is removed more rapidly than Al. A very high correlation coefficient of r = 0.98 was found between CEC and the sum of the oxides ($SiO_2 + Al_2O_3 + FeO + Fe_2O_3 + MgO$) dissolved by HCl and NaOH. This relationship may indicate that the dissolution procedure was highly selective for the smectite. Extrapolation of the relationship between CEC and total dissolved oxides indicates that the mineral has a CEC of about 100 meq/100 g.

Although the dissolution procedure was highly selective for smectite, ratios of the dissolved oxides were not constant, but varied substantially with particle size. In general, with decreasing particle size, Mg and Fe decreased relative to both Al and Si. The Si/Al ratio also decreased with decreasing particle size. Structural formulae (Table 4), based on the amounts of Si, Al, Mg, Fe^{3+}, and Fe^{2+} dissolved by HCl and NaOH and on the CEC values, were calculated according to the procedure of Marshall (1949).

The tetrahedral sheet was relatively constant in composition and had a high negative charge. Twenty of the 24 samples analyzed were in the relatively narrow range $Si_{3.3}Al_{0.7}$–$Si_{3.5}Al_{0.5}$. The remaining samples contained slightly more tetrahedral Al. Much of the tetrahedral charge is neutralized by the positively charged octahedral sheet. The tetrahedral origin of the negative charge may account for the ability of these samples to fix small amounts of K (Table 5) and for the fact that they expand with some difficulty.
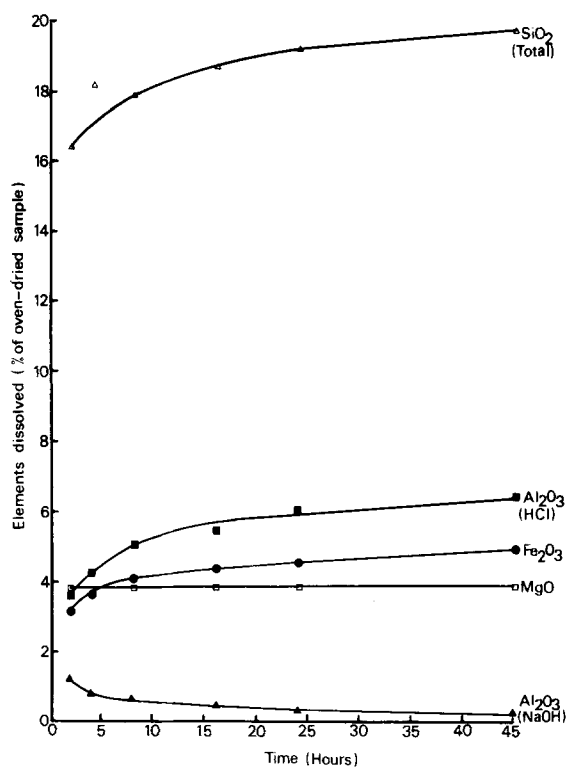
The composition of the octahedral sheet is appar-

Figure 4.   Effect of duration of treatment with 1 N HCl on the amounts of SiO_2, Al_2O_3, Fe_2O_3, and MgO dissolved from the silt fraction of Woodburn A12.

ently about midway between that of a dioctahedral and trioctahedral mineral, but the number of octahedral cations per half unit cell apparently decreases with a decrease in the particle size of the initial separates. Octahedral Al increases, whereas Mg, and to a lesser extent Fe decreases, with decrease in particle size. The calculated formulae are consistent with the finding of McAleese (1954) that heating Li-saturated silts and

Table 4.   Structural formulae for smectite in size fractions of Woodburn and Upper Woodburn soils and in clays separated from basalt rock.[1]

	Sand fraction		Silt fraction		Clay fraction		Basalt clays	
	Mean	Range	Mean	Range	Mean	Range	Fine	Coarse
Tetrahedral								
Si	3.32	3.19–3.42	3.40	3.31–3.50	0.33	3.22–3.40	3.30	3.38
Al	0.68	0.58–0.81	0.60	0.50–0.69	0.67	0.60–0.78	0.70	0.62
Octahedral								
Al	0.66	0.36–0.83	0.90	0.81–0.99	1.07	0.96–1.20	0.28	0.58
Fe^{2+}	0.15	0.09–0.17	0.11	0.08–0.13	0.09	0.06–0.13	0.46	0.78
Fe^{3+}	0.57	0.51–0.62	0.50	0.43–0.55	0.41	0.36–0.43	0.42	0.02
Mg	1.17	0.92–1.58	0.90	0.79–1.03	0.82	0.67–1.01	1.65	1.45
Total	2.54	2.39–2.73	2.41	2.35–2.46	2.39	2.32–2.50	2.81	2.83
Layer charge	0.37	0.32–0.42	0.37	0.33–0.41	0.40	0.37–0.42	0.38	0.36

[1] Formulae were calculated from elements dissolved by 1 N HCl and 0.5 N NaOH and are based on an $O_{10}(OH)_2$ structural unit.

Table 5. Potassium fixation by deferrated clays and silts.

	CEC (Ca//Mg)[1] (meq/100 g)	CEC (K//NH$_4$)[2] (meq/100 g)	K fixed (meq/100 g)
Clay fraction			
Woodburn A11	57.4	43.8	13.6
Woodburn A12	55.6	45.1	10.5
Upper Woodburn A11	61.4	48.1	13.3
Upper Woodburn A12	63.1	48.8	14.3
Upper Woodburn B2	56.4	47.4	9.0
Upper Woodburn C	62.4	50.3	12.1
Silt fraction			
Upper Woodburn B2	34.9	33.3	1.6
Upper Woodburn C	53.6	45.3	8.3

[1] Ca-saturated sample: Mg displacement.
[2] K-saturated sample heated to 110°C: NH$_4$ displacement.

Table 6. Aluminum and iron in sodium citrate extracts of deferrated, NaOH-treated clays.

	Woodburn A11		Woodburn B3/C	
Extract	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)
1	0.06	0.16	0.06	0.16
2	0.07	0.15	0.08	0.13
3	0.07	0.09	0.09	0.06
4	0.07	0.06	0.07	0.05
5	0.08	0.07	0.07	0.03
6	0.05	0.04	0.03	0.02
7	0.05	0.04	0.03	0.02
8	0.05	0.04	0.03	0.02
Total	0.50	0.65	0.46	0.49

clays of similar origin to 200°C resulted in only marginal decreases in CEC, thereby excluding the possibility of the smectite being a dioctahedral mineral with predominantly octahedral substitution.

The increase in the calculated number of octahedral Al atoms per unit cell as particle size decreased could be due to an increase in the number of hydroxy-Al interlayers. The assignment of Al from this source to the smectite structure was suggested by Sawhney and Jackson (1958) as an explanation for montmorillonite formulae with high octahedral occupancies. The present formulae were calculated for samples which had been given a NaOH and two DCB treatments, a sequence which would be expected to remove much of the interlayer Al. Most methods for selective removal of hydroxy-Al interlayers cannot be used with the present samples because of the composition of the smectite. The procedure of Dixon and Jackson (1959) involves heating samples at 400°C followed by the dissolution of the dehydroxylated interlayer material in hot NaOH. However, when this method was employed, large amounts of both Si and Al were removed, indicating that some dehydroxylation of smectite had taken place even at this low temperature. Procedures involving the use of acid (Rich, 1966) obviously cannot be used because of the solubility of the smectite. The less severe procedure of Frink (1965), which involves repeated extraction with 1 M sodium citrate on a water bath at 80°–90°C, was tried on selected samples. The total amount of Al removed in eight, hour-long extractions was quite small (Table 6). The pattern of its extraction with time and its ratio with extracted Fe is indicative of attack on the smectite structure. It is concluded from these results that little interlayer Al was present in NaOH-treated clays.

Composition of smectite in basalt fragments

Although an average octahedral cation occupancy of 2.4 per $O_{10}(OH)_2$ was estimated from the chemical data,

the above clays gave a weak 060 reflection at 1.54 Å, indicating that the smectite has the structure of a trioctahedral mineral. Smectite was also present in fine and coarse clays separated from weathered basalt fragments. The basalt smectite gave a strong 060 reflection at 1.54 Å. The XRD data (Figure 2) showed that it also had a more ordered structure than the smectite in the soil separates. Because the chemical composition of the soil smectite varied considerably with particle size, and hence degree of weathering, the composition of the basalt smectite may represent that of the original mineral. Prior to acid treatment the basalt clays were pretreated with DCB and NaOH. The smectite was completely dissolved by the acid treatment, leaving feldspar as residue in the case of the coarse clay. Little of the fine clay remained. Structural formulae (Table 4), calculated from the elements dissolved by HCl and NaOH, suggest that the composition of the tetrahedral sheet was similar to that of the smectite in the soil separates. Octahedral cation occupancy, however, was close to 3 per half unit cell. In general, the basalt smectite is richer in Mg and Fe but poorer in octahedral Al than the smectite in the soil separates. The most significant difference between the two basalt clay fractions was the Fe^{2+}/Fe^{3+} ratio. Almost all of the iron in the coarse clay was in the ferrous form whereas, in the fine clay, much of it was in the oxidized state.

This mineral, though chemically considerably different from the trioctahedral smectites discussed by Weaver and Pollard (1973), can be classified as a saponite. In particular it differs in its Mg content which is lower than the values usually given for saponite (i.e., >2 Mg atoms per half cell). Saponites are quite rare in soils. According to Borchardt (1977), basic rocks, even those high in Mg, tend to produce iron-rich montmorillonite (nontronite).

Most of the published work on clay mineral transformations refers to environments which are warmer and wetter than that of northeastern Ireland. Eswaran and De Coninck (1971) summarized the clay mineralogy of basaltic soils as being of allophane, halloysite, ka-

olinite, and gibbsite under well-drained conditions and montmorillonite under impeded drainage conditions. They found montmorillonite in all basaltic soils in tropical environments, although only minor amounts were detected in Oxisols. They found that the amount of montmorillonite increased with wetness and depth and concluded that montmorillonite was unstable in such environments, and was in the process of alteration to halloysite. Reports on the clay mineralogy of basaltic soils commonly assume that the soils and their clay minerals are contemporaneous. The clay mineralogy of the soils of the present study is dominated by an inherited smectite, probably of hydrothermal or deuteric origin. This mineral is unstable in the soil environment and, although its alteration products are fairly uniform in composition, there is no evidence that it has reached a stable phase.

CONCLUSION

The alteration products of primary minerals of the basalts of Northern Ireland include a trioctahedral smectite. This mineral occurs in rock fragments of sand and silt size and imparts to these separates exceptionally high values of CEC. The mineral is unstable under the conditions prevailing in the soil, and substantial changes in its composition occur. Mg and Fe seem to be lost from the octahedral sheet during the weathering process, thereby reducing the octahedral cation occupancy from close to 3, as in the smectite in clays isolated from the basalt rock, to approximately 2.4 per $O_{10}(OH)_2$, although the 060 spacing of 1.54 Å indicates a retention of the trioctahedral structure. Such intermediate formulae have been considered by many workers, including Mering (1975), to be incorrect. Assignment of Si and Al from noncrystalline materials or crystalline minerals to the structure of a trioctahedral mineral could lead to underestimation of the octahedral cation occupancy. Similarly, values of between 2 and 3 per half cell could be obtained if interlayer Al/Fe or exchangeable Mg are assigned to a dioctahedral mineral. Neither possibility explains the present formulae because noncrystalline and interlayer materials were removed by treatment with DCB and NaOH prior to dissolution of the smectite, and dissolution of the other crystalline minerals during the acid treatment was small. Another possible explanation might be the occurrence of a mixture of di- and trioctahedral phases. However, the XRD data gave no evidence of the presence of a second smectite. The results suggest the existence of smectites with octahedral cation occupancies intermediate between di- and trioctahedral minerals; such minerals were formed as weathering products of trioctahedral smectites.

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Резюме—Песчаные и илистые фракции почв, полученных из третичного базальта в северо-восточной Ирландии, показывают необыкновенно высокие катионо-обменные способности. При помощи рентгеновской порошковой дифракции во фракциях всех размеров был обнаружен смектит, который был селективно растворен путем обработки 1 N HCl и 0,5 N NaOH. Структурные формулы, основанные на химическом анализе растворенного материала, указывают на то, что смектит имеет промежуточный состав между двух- и трехоктаэдрическими минералами и что как катионное заполнение октаэдрических мест, так и количество атомов Mg и Fe в элементарной ячейке уменьшаются с уменьшением размера частиц исследованной фракции почв. Средняя формула для смектита во фракциях глин:

$$M^+_{0,40}(Si_{3,33}Al_{0,67})(Al_{1,07}F^{2+}_{0,09}Fe^{3+}_{0,41}Mg_{0,82})O_{10}(OH)_2.$$
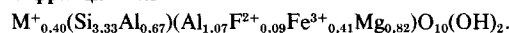
Похожий анализ смектита, присутствующего в материале размера глины, выделенного из выветренной базальтовой породы основы почвенных профилей, показал, что этот материал был близкий к вполне трехоктаэдрическому заполнению. Можно предположить, что почвенный смектит является продуктом эрозии трехоктаэдрического смектита, унаследованного их выветренного базальта. [E.C.]

Resümee—Die Sand- und Siltfraktion von Böden, die aus tertiären Basalten in NE Irland entstanden sind, zeigen ein ungewöhnlich großes Kationenaustauschvermögen. Aufgrund der Röntgenpulverdiffraktometerdiagramme handelt es sich in allen Kornfraktionen um Smektit. Der Smektit wurde selektiv durch Behandlung mit 1 N HCl und 0,5 N NaOH gelöst. Strukturformeln, die auf der chemischen Analyse des gelösten Materials beruhen, deuten darauf hin, daß der Smektit in der Zusammensetzung zwischen einem di- und einem trioktaedrischen Smektit liegt, und daß die oktaedrische Platzbesetzung zusammen mit der Zahl der Mg- und Fe-Atome pro Elementarzelle mit abnehmender Partikelgröße der untersuchten Bodenfraktion abnimmt. Die allgemeine Formel des Smektit aus der Tonfraktion lautet: $M^+_{0,40}(Si_{3,33}Al_{0,67})(Al_{1,07}Fe^{2+}_{0,09}Fe^{3+}_{0,41}Mg_{0,82})O_{10}(OH)_2$. Eine ähnliche Analyse von Smektit, der aus der Tonfraktion des verwitterten Basalts von der Basis des Bodenprofils genommen wurde, zeigte, daß er eine nahezu vollständige trioktaedrische Besetzung hat. Es wird angenommen, daß der Boden-Smektit ein Verwitterungsprodukt des trioktaedrischen Smektit aus dem verwitterten Basalt ist. [U.W.]

Résumé—Les fractions de sable et de vase dérivées d'un basalt Tertiaire d'Irlande du nord-est exhibent des capacités d'échange d'électrons inhabituellement élevées. La smectite a été identifiée par diffraction poudrée aux rayons-X dans les fractions de toutes tailles et a été sélectivement dissolue par un traitement au 1 N HCl et 0,5 N NaOH. Des formules structurales, basées sur une analyse chimique du matériau dissolu suggèrent que la composition de la smectite est entre un minéral di- et trioctaèdre et que l'occupation du cation octaèdre, ainsi que les nombres d'atomes de Mg et Fe par maille décroissent proportionnellement à la décroissance de la taille de particule de la fraction de sol examinée. La formule moyenne pour la smectite dans les argiles est: $M^+_{0,40}(Si_{3,33}Al_{0,67})(Al_{1,07}Fe^{2+}_{0,09}Fe^{3+}_{0,41}Mg_{0,82})O_{10}(OH)_2$. Une analyse semblable de smectite présente dans le matériau de taille de l'argile séparé d'une roche de basalt altérée prise des bases des proviles de sol montre qu'elle avait près de l'occupation trioctaèdre totale. On suggère que la smectite du sol est un produit d'altération de la smectite octaèdre héritée du basalt altéré. [D.J.]