

Soil-Saprolite Profiles Derived from Mafic Rocks in the North Carolina Piedmont: II. Association of Free Iron Oxides with Soils and Clays¹

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ABSTRACT

The association of free Fe oxides with soils and clays from two Enon sandy loam (Ultic Hapludalfs, fine, mixed, thermic) soil-saprolite profiles was studied. Goethite was the dominant Fe oxide identified. Lepidocrocite was detected in trace amounts in some samples. Fe^{CBD}/clay ratios were highest in the epipedons of these soils suggesting the concentrating of Fe oxides as a result of aluminosilicate mineral weathering. External (BET-N₂) surface area measurements of non-deferrated and deferrated clays were analyzed in conjunction with electron micrographs of selected clay fractions to determine the association of free Fe oxides with aluminosilicate clays as a function of depth in the profile. Free Fe oxides were found to exist mainly as small, discrete clusters in the A and B horizons of both profiles and specific of the clay surface decreased as a result of treatment for Fe removal. However, external surface areas increased for the saprolite (Cr) horizon clays after deferration. One subfraction identified as having an increase in surface area after deferration was fine clay from the Cr2 horizon, Enon (metagabbro) profile. Chemical data and electron micrographs suggest that either partial dissolution of small, poorly crystalline aluminosilicate clays or removal of some Fe or non-Fe oxide aggregating agent results in breakdown of the fine clays into smaller particles of higher net specific surface.

Additional Index Words: weathering, gabbro, Alfisols, Argillic horizon.

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IRON IS THE FOURTH most abundant element in the earth's crust (after O, Si, and Al), comprising 5% by weight (Brownlow, 1979). During weathering of Fe-bearing primary minerals, the Fe, predominantly bound in the reduced (Fe²⁺) state, is released through

a combined hydrolytic and oxidative reaction of the following type: $-\text{Fe}^{2+} -\text{O}-\text{Si} + \text{H}_2\text{O} = -\text{Fe}^{3+} -\text{OH} + \text{OH} - \text{Si} \pm e^-$ in which atmospheric oxygen takes up the electron ($\text{O}_2 + 4e^- = 2\text{O}^{2-}$) (Schwertmann and Taylor, 1977). Due to the extremely low solubility of Fe³⁺ oxides in the normal pH range of soils, the Fe released is precipitated as an oxide or hydroxide (Garrels and Christ, 1965). (In this paper, "Fe oxides" will represent oxides, hydroxides and oxyhydroxides, and free Fe oxides will refer to reductant soluble Fe).

Oades (1963) divided the occurrences of free Fe oxide accumulations in soils into four general categories: i) Fe concretions; ii) illuvial deposits in lower B horizons of podzolic soils; iii) laterite crusts; and iv) Fe oxides of agricultural soil and brown earths, which are not found as local concentrations due to thorough mixing of the soils.

The free Fe oxides include nine crystalline oxides of which goethite, hematite, and lepidocrocite are the most common forms. Of these, goethite ($\alpha\text{-FeOOH}$) is the most frequently occurring form of Fe³⁺-oxide in soils. Thermodynamically, goethite is the most stable under most soil conditions (Schwertmann and Taylor, 1977). Also, "amorphous" free Fe oxides have been reported (Mackenzie, 1949). Recently, Schwertmann et al., (1981) have identified a poorly crystalline Fe oxide, ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$), which they believe is the so-called "x-amorphous" form, soluble in acid ammonium oxalate. Moreover, they have identified several diffuse x-ray diffraction (XRD) reflections for ferrihydrite thus establishing that the material is not truly amorphous.

Iron concretions in soils are normally Fe-Mn concretions. Their properties have been reported in detail by numerous authors including Gallaher et al., (1973a, 1973b), Schwertmann and Fanning (1976) and Ciric and Skoric (1973). These workers have generally observed that Fe-Mn concretions occur between the winter and summer water table levels in hydromorphic soils with impeded internal drainage. The presence of alternate oxidation-reduction conditions in that zone suggests that concretion precipitation is physico-

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chemical in nature (Oades, 1963). By repetition of a cyclic process of oxidation-reduction, more and more Fe and Mn accumulate in the given zone until it becomes so densely precipitated in the soil fabric that diffusion processes grow less and less effective. Deposition finally occurs only on the outer concretion surfaces. In this way, a concretion may form and slowly grow, cycle by cycle (Marshall, 1977).

Silicate clay minerals have Fe associated with them in several ways: i) as an essential constituent, ii) as a minor constituent within the crystal structure, and iii) as Fe oxide on the surface of the minerals (Carroll, 1958). Added to this list should be Fe oxides as discrete particles in the clay fraction (Greenland et al., 1968).

The question of whether Fe oxides exist as coatings on clay particles has been the subject of several investigations. Using selective dissolution techniques, some authors (Davidtz and Sumner, 1965; Roth et al., 1969; Sumner, 1963) have concluded that Fe oxides occur as coatings on kaolin or vermiculite minerals. The evidence they use is a resultant increase or decrease in cation exchange capacity of the aluminosilicate clays after deferration. Davidtz and Sumner (1965) list three possible situations resulting from Fe oxide removal: i) positive and negative charges both increase, ii) positive and negative charges both decrease, or iii) positive charges increase and negative charges decrease or vice versa. The particular response depends on pH, kind of clay mineral, and isoelectric points of the mineral and Fe oxide. However, Greenland (1975) studied a goethite-kaolinite system and determined that the mixed system behaved as would be expected with each mineral contributing independently to the total charge. Analyzing specific surface area (area per unit weight) changes upon deferration, Deshpande et al., (1968) stated that in all but one instance, removal of free Fe oxides led to a reduction in specific surface area. The results indicate that most of the free Fe oxides in the soils they studied are present as small discrete particles. However, an acid treatment (that removed Al but not Fe oxides) caused an increase in the specific surfaces of the samples. Deshpande et al., (1968) concluded that the acid treatment dissolved Al and Si oxides and hydroxides that served as bonding agents for mineral surfaces (Jones and Uehara, 1973) made accessible to nitrogen (BET-N₂ procedure) after their removal. In a similar study, Greenland et al., (1968) found high contents of "free Fe oxide" but little "active iron" (Fe soluble in acid ammonium oxalate solution) in some "old, highly weathered soils" (Ultisols, Oxisols) they studied. They concurred with Deshpande et al., (1968) that the "active" inorganic material in their soil samples, in terms of its influence on physical properties, is primarily Al oxide. They also qualified this statement by suggesting that the situation in younger soils or those subject to alternating oxidation-reduction conditions may be quite different.

Utilizing a combination of selective dissolution techniques and electron microscopy, Greenland and co-workers (Greenland and Mott, 1978; Greenland and Oades, 1968; Greenland et al., 1968; Greenland and Wilkinson, 1969) have decided that most Fe oxides present in the clay fraction are small, discrete parti-

cles, which have relatively little effect on the physical and the physico-chemical properties of the soil. However, precipitates of Fe hydroxide have been shown to envelop clay particles (Greenland and Mott, 1978) or be attached to edges of kaolin plates or halloysite tubes (Greenland et al., 1968), but this was considered more the exception than the rule. Greenland and Oades (1968) concluded that the association of Fe hydroxides with clay surfaces is dependent on the surface characteristics of the Fe compound and the clay and on the properties of the medium in which they are dispersed.

This study was undertaken to determine the form and distribution of Fe in soil and saprolite material formed from gabbro and metagabbro rocks.

MATERIALS AND METHODS

Soil and saprolite samples from two Enon sandy loam (fine, mixed, thermic Ultic Hapludalfs) profiles were analyzed in this study. The profiles are described in a previous paper (Rice et al., 1985). Particle size distribution was determined by the pipette method (Kilmer and Alexander, 1949). Centrifugation-decantation was used to determine fine clay content (Jackson, 1975). External surface areas of the clays were determined in duplicate by nitrogen gas adsorption using a Quantachrome Quantasorb Surface Area Analyzer.³

Sodium hypochlorite was used for soil organic matter destruction prior to clay fractionation (Jackson, 1975; Anderson, 1963). The Na-saturated clays were dialyzed against distilled water and lyophilized (Malcolm, 1968).

Free Fe, Mn, Al, and Si were extracted from clays with sodium citrate-dithionite solution (CD) (Coffin, 1963). Free Fe was removed from the fine-earth fraction ($< 2 \times 10^{-3}m$) with sodium citrate-bicarbonate-dithionite solution (CBD) (Mehra and Jackson, 1960). "Amorphous" or poorly crystalline Fe, Al, and Si were extracted from the clays ($< 2 \times 10^{-6}m$) with an ammonium oxalate-oxalic acid buffer (O^x) adjusted to pH 3.0 with HCl (McKeague and Day, 1966) and were quantified using atomic absorption spectroscopy.

Each of the fine and coarse clay fractions was then mixed as a $< 0.5\%$ weight/volume suspension in pH 10 Na₂CO₃ solution using an ultrasonic probe (Branson Sonified Cell Distructor, Model W-350, micro tip, moderate power) for 2 min. The suspensions were passed through a specially designed high gradient magnetic filter similar to that described in Schulze and Dixon (1979). The suspension flow rate through the filter during the high gradient magnetic separation (HGMS) was fixed by means of a short piece of glass capillary tubing placed in the end of the plastic outlet tubing.

The fine and coarse clay suspensions were each passed through the filter a total of three times (passes) at a flow rate of $0.83 \times 10^{-3}LS^{-1}$. Between each pass, the magnetic fraction, i.e., that retained by the filter, was flushed out and collected. Then, the nonmagnetic tailings were re-run through the filter. The magnetic fractions for each of the three passes of the coarse clay samples were collected separately. The magnetic fractions for the three passes of the fine clay samples were combined.

After HGMS, the suspensions containing the nonmagnetic tailings and magnetic fractions were flocculated by lowering the pH to 4.5 with *M* HCl, dialyzed against distilled water until the clays were free of salt and the dialyzing medium had conductivity readings below the equivalent of 1 mg L⁻¹ as NaCl, and then lyophilized.

³ The use of trade names in this publication does not imply endorsement by the North Carolina Agricultural Research Service of the products named, or criticism of similar ones not mentioned.

Table 1. CD-extractable Fe, Mn, Al, and Si and OX-extractable Fe, Al, and Si from total clay; external surface area for the untreated, CD-extracted, and OX-extracted total clays; and free iron extracted with CBD ($< 2 \times 10^{-3}$ m basis).

Horizon	Depth 10^{-2} m	CD-extractable				OX-extractable			Fe _{OX}	Surface area (BET-N ₂)			Fe _{CBD} ($< 10^{-3}$ m basis)	Fe _{CBD} clay
		Fe	Mn†	Al	Si	Fe	Al	Si	Fe _{CD}	Natural	CD	OX	g kg ⁻¹	g kg ⁻¹
Enon (metagabbro) profile														
A	0-10	97	6	13	3	14	7	1	144	66	57	69	8	267
E	10-20	148	7	16	5	21	6	2	140	96	66	83	7	99
BE	20-33	99	3	12	4	10	5	1	101	86	74	84	14	79
Bt1	33-51	56	t	7	3	4	4	1	67	97	103	100	33	45
Bt2	51-71	42	t	5	3	3	4	1	71	98	98	98	17	54
BC	71-81	31	1	5	4	4	4	1	129	79	91	87	17	41
Cr1	81-114	23	1	5	4	4	6	1	174	58	74	69	--	--
Cr2	114-147	33	1	5	4	4	5	1	121	56	69	60	--	--
Cr3	147-188	29	1	5	4	4	6	1	137	57	72	60	4	105
Enon (gabbro) profile														
Ap	0-18	131	3	13	3	25	6	1	191	112	122	115	20	117
Bt	18-43	70	t	7	4	13	5	1	188	114	108	117	27	63
BC	43-64	106	t	8	5	21	6	1	198	112	109	120	23	99
C	64-86	76	1	7	8	15	5	2	197	113	125	115	5	179
Cr1	86-135	63	1	5	9	9	4	2	145	116	141	120	--	--
Cr2	135-165	80	1	6	9	10	4	2	125	111	133	110	--	--
Cr3	165-203	97	1	6	9	17	5	2	175	111	132	113	4	190

† t = trace ($< 0.1\%$).

RESULTS AND DISCUSSION

Chemical Analyses

Free Fe content in the fine-earth fraction ($< 2 \times 10^{-3}$ m) generally increases as clay content increases in both profiles (Tables 1, 2). However the Fe^{CBD}/clay ratios (Tables 1) show decreases from the surface horizons to a minimum in the argillic horizons of both Enon profiles. The presence of Fe-Mn concretions in upper soil horizons of both profiles and high Fe^{CBD} values suggest that Fe oxides concentrate while aluminosilicate clays are selectively removed by eluviation, weathering, and/or erosion in these surface horizons. The increase in Fe^{CBD}/clay values in deeper saprolite horizons is attributable to the very small amount of clay in these zones, and implies that Fe oxide is one of the first weathering products removed from aluminosilicate structures. The extremely low solubility of the ferric oxides results in a concentrating of these materials relative to the amount of clay pro-

duced. Oxidation of ferrous Fe is the earliest change during the chemical weathering of the ferro magnesian primary minerals in the parent rocks (Carroll, 1970).

Sodium Citrate-Dithionite Extraction of Clays

Enon (Metagabbro) Profile.—Amounts of Fe(CD) extracted from the clays are higher in the A, E and BE horizons and generally decrease with depth (Table 1). Manganese, Al, and Si values follow the same trend. The CD treatment resulted in a decrease in external specific surface area for clays from the A, E and BE horizons, a slight increase in the Bt1 horizon, and no difference in the Bt2 horizon (Table 1). Below the Bt2 horizon surface area after deferration increased. A decrease in surface area upon deferration implies that the free Fe oxides in the upper horizons occur as small discrete particles. Several factors may explain the surface area increases: i) the free Fe oxide removed may act as an aggregating agent or as a coating, binding smaller particles together, ii) the free Fe oxide may

Table 2. Particle size distribution expressed as weight percent of the fine-earth fraction.

Horizon	Depth 10^{-2} m	2000-1000	1000-500	500-250	250-100	100-50	50-20	20-5	5-2	2-0.2	<0.2
		μ m	μ m	μ m	μ m	μ m	μ m	μ m	μ m	μ m	μ m
Enon (metagabbro) profile											
A	0-10	9.2	11.5	7.1	9.5	9.8	26.6	19.6	3.7	2.3	0.7
E	10-20	18.1	13.9	4.3	5.5	6.9	22.2	17.2	4.8	0.4	6.7
BE	20-33	14.2	10.2	3.5	4.6	5.8	20.3	17.5	6.1	7.3	10.4
Bt1	33-51	1.8	2.1	1.3	1.6	1.6	12.2	5.8	0.4	25.3	47.9
Bt2	51-71	3.5	8.6	7.7	5.8	3.1	17.2	16.5	6.2	1.2	30.3
BC	71-81	4.6	3.1	4.7	7.7	5.9	19.3	28.9	7.9	3.1	14.1
Cr1	81-14	12.7	5.1	5.3	8.0	6.2	18.4	27.6	6.8	1.1	1.8
Cr2	114-147	19.6	11.0	7.9	7.4	5.3	16.3	21.7	5.8	3.7	1.4
Cr3	147-188	17.0	19.8	10.4	7.4	4.7	15.3	16.6	5.1	2.6	1.2
Enon (gabbro) profile											
Ap	0-18	12.8	11.1	10.4	17.3	11.6	13.1	5.0	1.3	6.0	11.1
Bt	18-43	0.7	1.3	5.0	14.7	11.3	16.3	5.6	2.2	6.3	36.8
BC	43-64	2.8	12.2	18.7	19.3	9.0	10.9	3.5	0.7	6.2	17.0
C	64-86	6.3	28.1	30.7	18.5	6.5	6.1	1.0	0.1	0.3	2.5
Cr1	86-135	8.8	26.3	28.5	19.7	6.4	6.4	0.8	0.2	1.7	1.4
Cr2	135-165	9.1	27.4	31.4	19.9	5.8	4.8	0.5	0.1	0.6	0.5
Cr3	165-203	9.2	29.2	31.8	17.0	5.2	5.0	0.6	0.1	1.1	1.0

exist as large discrete particles with average specific surface areas smaller than the surface areas of material left after deferration, iii) the free Fe may be removed from the structures of aluminosilicate clays causing their breakdown into smaller units after deferration, and/or iv) some substance other than Fe oxide, such as Al oxide, may act as a cementing agent binding smaller particles together.

Enon (Gabbro) Profile.—The free Fe content of the clay fraction is highest in the Ap horizon and then decreases irregularly with depth. The fact that most of the clay (Table 2) found in the lower four horizons was located in clay seams along fractures in the saprolite may account for the irregular decrease with depth. The Al values generally follow the irregular pattern of the Fe data. However, the Si contents appear to generally increase with depth.

Surface area values were higher than in the metagabbro profile and removal of Fe oxides (CD) resulted in apparent decreases in clay surface area (N_2) in the Bt and BC horizons but increases in surface areas of the clays in the Ap, C, Cr1, Cr2, and Cr3 horizons.

Acid Ammonium Oxalate Extraction of Clays

The amounts of Fe removed by acid ammonium oxalate extraction are consistently lower than Fe values for the CD-extraction method (Table 1). This extraction procedure is thought to almost completely remove a poorly crystalline Fe oxide called ferrihydrite (Schwertmann et al., 1981).

Enon (Metagabbro) Profile.—Assuming that the oxalate extraction is selective for ferrihydrite and that ferrihydrite is also removed in the citrate-dithionite extraction, the Fe_{OX}/Fe_{CD} data show that from 6.7% to 17.4% of the free Fe in the clay samples is ferrihydrite. Schwertmann and Taylor (1977) report that organic compounds retard the crystallization of Fe oxides, and therefore, ferrihydrite contents should be higher in organic-rich surface horizons. This would explain the higher values in the clays of the upper three soil horizons. The higher Fe_{OX}/Fe_{CD} values in the saprolite horizons may be explained if lepidocrocite, (γ -FeOOH) is present. The Fe oxide may also be soluble in acid ammonium oxalate (Pawluk, 1972). Its presence was not detected by XRD which is not surprising if present in very small quantities.

The fact that ferrihydrite is reported to have a high surface area ($600 \text{ m}^2 \text{ kg}^{-1} 10^{-3}$; Schwertmann et al., 1981) and there are only slight decreases in clay surface areas from two horizons (E and BE) after the oxalate extraction suggests that the absolute amounts of ferrihydrite are small. The increases in BET- N_2 surface areas after oxalate extraction are also small in all other horizons indicating that the poorly crystalline Fe oxides have little influence on the net external surface areas of the clays.

Enon (Gabbro) Profile.—The Fe_{OX}/Fe_{CD} data indicate that from 12.5% to 19.8% of the free Fe in the clays is "active" and assumed to be ferrihydrite. Lepidocrocite was detected in this profile and would be expected to contribute to that value. The values irregularly decrease with depth. No marked decrease in the Fe_{OX}/Fe_{CD} ratio in the argillic horizon is present as in the Enon (metagabbro) profile.

The slight increases or decreases in surface area after oxalate extraction indicate that the poorly crystalline Fe oxides contribute little to the overall net surface area of the clays.

Sodium Citrate-Dithionite Extractions of HGMS Clay Fractions

The CD-extractable Fe, Al and Si data for clay from selected horizons are shown in Table 3. The Fe data agree well with the XRD data (Table 4) that show goethite is concentrated in the magnetic clay fractions. As mentioned earlier, this separation treatment is more effective in the coarse clays than in the fine clays. Nevertheless, the fine, clay, magnetic fractions for the E, Bt1 and Cr2 horizons, Enon (metagabbro) profile, contain the highest percentage of free Fe of all the fractions in each horizon. In contrast, the highest percentage of free Fe in the Bt horizon, Enon (gabbro) profile, is in the coarse clay, magnetic fraction. The data demonstrate that the free Fe in the Enon (metagabbro) profile is concentrated in smaller size fractions than in the Enon (gabbro) profile.

Calculation of mole percent Al in Fe + Al in the CD extract is based on the assumption that all the Al removed in the extraction process was contained in an Fe oxide structure, e.g., goethite. Some of the results (Table 3) are considerably higher than the 30–33 mole percent frequently quoted as the maximum allowable Al in goethite (Golden et al., 1979; Norrish and Taylor, 1961). The values may be inflated due to a contribution of Al from the dissolution of poorly crystalline aluminosilicate clays by the citrate buffer. However, the data suggest that the goethites are highly Al substituted, which is a common finding (Bowen and Weed, 1981). Use of the equation shown in Table 3 to calculate the Fe oxide surface area assumes that all gravimetric weight loss (W factor) is due to free Fe oxides and that the contribution of a physical fraction to the clay surface area is additive. However, some poorly crystalline aluminosilicate clays or aluminosilicate clays with isomorphously substituted Fe are likely dissolved in the extraction procedure (Coffin, 1963) and contribute Al to the extract. The higher mole percent Al values (Table 3) for the fine clay (total) and nonmagnetic fractions support these conclusions.

Measured surface areas decreased as a result of treatment for deferration in all clay fractions except the Cr2 horizon fine (total) (ft) and fine (nonmagnetic) (fn) fractions. The decrease in surface area implies that the Fe oxides are small, discrete particles and that they are smaller than the mean size of minerals remaining in the sample after deferration. An increase in specific surface following treatment suggests very intimate association of the Fe oxide with other minerals in the clay fraction.

The negative Fe oxide surface area values of the fine clay (total) (ft) and fine (nonmagnetic) (fn) clay fractions in the Cr2 horizon are, of course, not real and can be attributed to several factors previously cited for increased surface area values upon Fe removal. The generally smaller values of specific surface for the untreated Cr2 clays plus the smaller calculated values for the Fe-oxide removed by treatment also suggest close particle association, i.e., "coatings."

Table 3. Citrate-dithionite-extractable Fe, Al, and Si and external surface area for the natural and CD-extracted clays ($2-0.2 \times 10^{-6}$ m, $< 0.2 \times 10^{-6}$ m, total, magnetic, and nonmagnetic).

Horizon	Depth	Fraction†	CD-extractable				Surface area (BET-N ₂)			mmol Kg ⁻¹ Al in Fe + Al
			Wt. loss	Fe	Al	Si	Natural	CD	Fe-oxides‡	
	10 ⁻³ m		g kg ⁻¹				10 ³ m ² kg ⁻¹			
<u>Enon (metagabbro) profile</u>										
E	10-20	ft	335	152	23	18	113	65	268	239
		fm	519	234	34	10	106	49	159	225
		fn	272	119	21	5	119	61	274	268
		ct	318	146	21	7	51	17	124	229
		cm	397	185	25	7	75	16	165	219
		cn	73	31	6	2	23	7	226	286
Bt1	33-51	ft	138	52	10	5	102	49	433	285
		fm	312	144	21	11	81	26	202	232
		fn	133	50	9	4	98	73	261	271
		ct	131	54	8	4	31	11	164	235
		cm	169	73	9	5	42	8	209	203
		cn	46	11	4	2	24	10	314	429
Cr2	114-147	ft	79	23	8	7	63	82	(-159)	419
		fm	172	71	11	10	41	33	80	243
		fn	74	21	7	6	64	89	(-249)	408
		ct	69	25	4	5	32	27	99	249
		cm	94	43	5	5	34	29	82	194
		cn	12	1	2	3	26	19	602	805
<u>Enon (gabbro) profile</u>										
Bt	18-43	ft	106	45	8	4	114	75	443	269
		fm	169	73	9	5	111	78	273	203
		fn	115	45	8	6	104	95	173	269
		ct	303	145	12	8	67	45	118	146
		cm	312	163	12	8	97	48	205	132
		cn	122	45	9	7	59	13	390	293

† f = fine clay ($< 0.2 \times 10^{-6}$ m; c = coarse clay ($2-0.2 \times 10^{-6}$ m); m = magnetic; n = nonmagnetic; t = total (not magnetically separated).

‡ Calculated surface area of the iron oxides = $[A_N - A_{CD}(1 - W)]/W$

where

A_N = specific surface area of the natural clay;

A_{CD} = specific surface of deferrated clay; and

W = gravimetric weight loss resulting from CD extraction, expressed as a fraction of the clay weight.

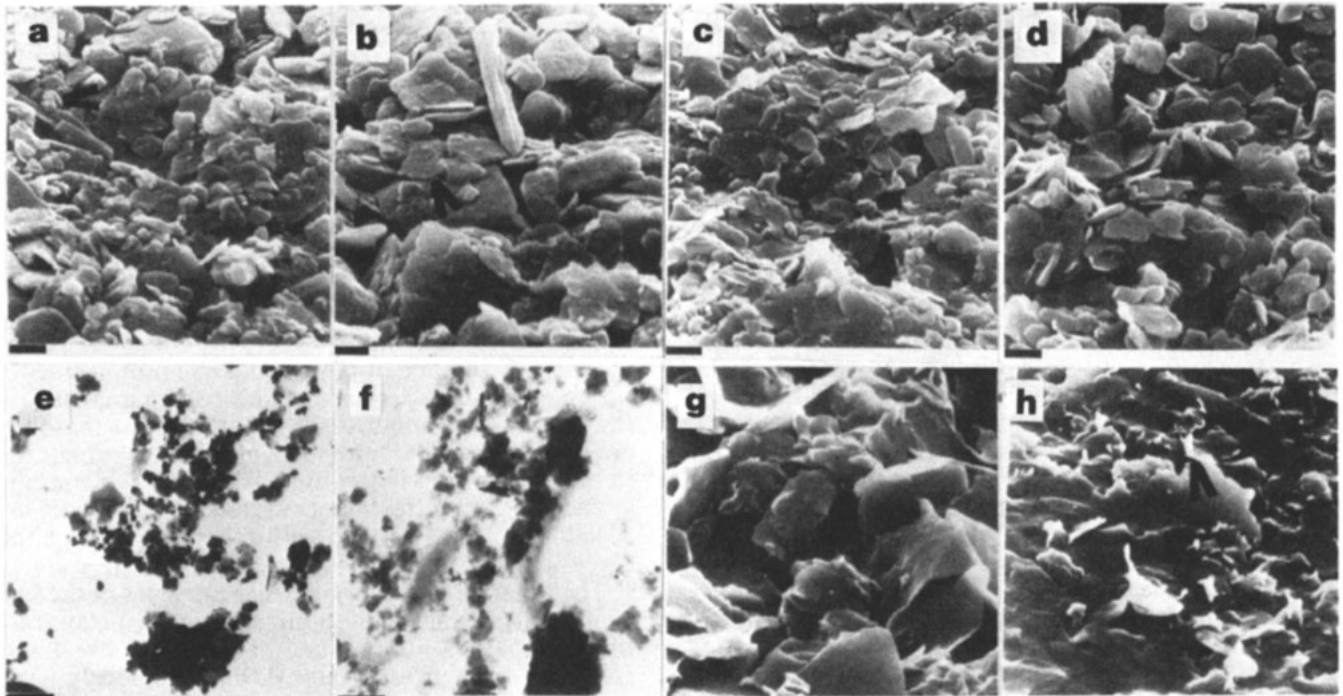


Fig. 1—Electron micrographs from the Enon (metagabbro) profile: (black bar represents 1×10^{-6} m): a) SEM, coarse clay from E horizon, nondeferrated, magnetic fraction: b) SEM, coarse clay from E horizon, deferrated, magnetic fraction: c) SEM, coarse clay from E horizon nondeferrated, nonmagnetic fraction: d) SEM, coarse clay from E horizon deferrated, nonmagnetic fraction: e) TEM, fine clay from E horizon, nondeferrated, magnetic fraction: f) TEM, fine clay from E horizon, deferrated, magnetic fraction: g) SEM, coarse clay from Cr2 horizon, nondeferrated, magnetic fraction: h) SEM, coarse clay from Cr2 horizon, nondeferrated, nonmagnetic fraction.

Table 4. Normalized net intensities of diagnostic XRD peaks for minerals identified in the total, magnetic, and nonmagnetic fractions of the fine and coarse clays from the Enon (metagabbro) profile and Enon (gabbro) profile.

Fraction†	Minerals‡													
	G	H	H _v	K1	K2	M	P	Q	R _g IV	R _d IV	S1	S2	V1	V2
<u>Enon (metagabbro): A horizon</u>														
ct	74	81	36	70			31	43						
All cm	78	100	58	89			0	17						
1st cm	100	82	34	79			0	11						
2nd cm	67	73	98	100			0	19						
3rd cm	44	27	100	100			0	11						
cn	41	0	39	85			100	100						
ft	100			78							36			
fm	100			44							100			
fn	90			100							49			
<u>Enon (metagabbro): Br1 horizon</u>														
ct	86		54		52			68	23					
All cm	64		100		92			0	100					
1st cm	100		89		100			0	50			100	75	
2nd cm	64		88		79			0	11			46	100	
3rd cm	55		80		66			0	4			31	30	
cn	45		64		71			100	0			23	61	
ft	56				100					21		57		
fm	100				60					100		100		
fn	76				97					0		54		
<u>Enon (metagabbro): Cr2 horizon</u>														
ct	81				90	12			60					91
All cm	96				95	13			100					100
1st cm	100				100	2			58			91		93
2nd cm	59				90	20			63			45		81
3rd cm	52				86	100			79			53		80
cn	37				90	6			0			100		18
ft	41				98					50		100		
fm	100				87					100		70		
fn	55				100					30		88		
<u>Enon (gabbro): Bt horizon</u>														
ct	53			15							28			
all cm	94			73							37			
1st cm	100			77							33			
2nd cm	94			69							100			
3rd cm	71			69							79			
cn	59			100							37			
ft	100			100							100			
fm	100			71							67			
fn	57			76							47			

† Fraction legend: c = coarse clay (2–0.2 10⁻⁶ m); f = fine clay (< 0.2 10⁻⁶ m); m = magnetic; n = nonmagnetic; t = combined magnetic and nonmagnetic; 1st = 1st pass; 2nd = 2nd pass; 3rd = 3rd pass; All = combined (1st + 2nd + 3rd).

‡ Mineral legend (the peak measured followed by the treatment are in parentheses): G = goethite (0.418 nm; Na); H = hornblende (0.84 nm; Na); H_v = hydroxy-interlayered smectite or vermiculite (1.4 nm; Na); K1 = kaolinite with some higher order H_v and S effects (0.72 nm; Na); K2 = kaolinite with some higher order H_v, S, V, R_gIV, R_dIV effects (0.72 nm; Na); M = biotite mica (1.0 nm; Na); P = calcic plagioclase feldspar (0.32 nm; Na); Q = quartz (0.334 nm; Na); R_gIV = regularly interstratified chlorite-smectite (3.0 nm; Na); R_dIV = randomly interstratified chlorite-smectite (3.0 nm; Na); S1 = smectite with some V effects (1.5 nm; Na); S2 = smectite (1.8 nm; Na-ethylene glycol for cc; 1.5 nm; Na for fc); V1 = vermiculite with H_v effects (1.4 nm; Na-ethylene glycol); V2 = vermiculite with higher order R_gIV, S effects (1.4 nm; Na).

Scanning electron micrographs of the non-deferrated, E horizon, coarse, magnetic clay fraction (Fig. 1a) show numerous grape-like clusters of small irregular aggregates or "blackberries" believed to be goethite (Greenland et al., 1968). These aggregates are largely removed by the dithionite treatment (Fig. 1b). Also, a general surface etching of the aluminosilicate clays suggests partial destruction of the paramagnetic clays that contain isomorphously substituted Fe in their structures (Coffin, 1963). The E horizon, coarse, non-magnetic clay fraction (Fig. 1c) exhibits fewer of the grape-like clusters. The dithionite extraction appears to remove smaller particles and cause a "smoothing" of particle surfaces (Fig. 1d).

Numerous electron dense particles were seen in the transmission electron micrographs for the E horizon, coarse, magnetic clay fraction. These were generally ill-defined and the clusters seen in the scanning micrographs were not apparent. There was little obvious

change upon deferration. The E horizon, fine, magnetic fraction, (Fig. 1e) showed small electron dense clusters that were likely Fe oxides (Beutelspacher and Van der Marel, 1968). The apparent association of these clusters with other clay surfaces may be partly due to surface tension effects upon sample drying. Deferration caused nearly complete removal of the Fe-oxide clusters (Fig. 1f).

Many "Fe oxide" clusters were also evident in the Bt1 horizon coarse, magnetic clay fraction. The surfaces of the aluminosilicate clays appeared smooth. Deferration removed the clusters and, as in the E horizon, produced a general "roughening" of mineral surfaces believed to be caused by partial destruction. The Bt1 horizon coarse, non-magnetic clay fraction had fewer clusters and there was little change in the appearance of the sample after the dithionite treatment.

Transmission electron micrographs of the Bt1 ho-

Cr2 horizon coarse, magnetic fraction again were non-definitive and showed little difference between the nondeferrated and deferrated samples. Few electron dense particles appeared to have been selectively removed by the CD treatment. The Bt1 horizon fine, magnetic clay fraction contained common small clusters which were removed by deferration.

Scanning electron micrographs of the Cr2 horizon coarse, magnetic clay fraction showed possible smectite minerals as indicated by a "curled edge" on some minerals (Fig. 1g). There were no obvious changes in morphology upon deferration. Some of the Fe removed by dithionite extraction may have come from Fe-bearing aluminosilicate clays. The Cr2 horizon coarse, nonmagnetic clay fraction (Fig. 1h) looked very similar to electron micrographs of montmorillonite (Grim, 1968; p. 176). Treatment for Fe oxide removal (CD) brought very little Fe, Al, or Si into solution (Table 3) though electron micrographs suggested less edge curling and increased surface roughness (data not shown).

Several electron dense particles occurred in transmission micrographs of the Cr2 horizon coarse, magnetic clay fraction. There was no apparent CD treatment effect. Some small irregular-shaped electron dense particles were present in the Cr2 horizon fine, magnetic clay fraction. The electron dense particles were removed by deferration treatment. The Cr2 horizon fine, nonmagnetic clay fraction consisted of "fluffy" material with curled edges resembling smectites (Beutelspacher and Van der Marel, 1968) and a few electron dense particles. Dithionite extraction removed some "curled edges" and all the small electron dense particles (data not shown).

Based on the interpretations of the electron micrographs and comparison with physical, chemical and mineralogical data, most of the Fe oxides present in the clay fractions from the E, Bt1, and Cr2 horizons occur as small, discrete particles with little association with the aluminosilicate clay surfaces. Some aluminosilicate clay destruction as a result of deferration is evident in the magnetic clay fractions from the E and Bt1 horizons. This may imply isomorphously substituted Fe in the mineral structures. Examination of the transmission electron micrographs for the Cr2 horizon fine, nonmagnetic clay fraction revealed some loss of electron dense particles on deferration. However, no obvious dispersion of aggregated particles and no selective removal of larger particles were apparent in the dithionite-treated sample. Therefore, the increase in surface area upon deferration of this fine, nonmagnetic clay fraction appears to be due to dissolution of some aluminosilicate clays and their breakdown into smaller units.

X-ray Diffraction Analyses

The following conclusions can be made about the mineralogical compositions of the HGMS clays for all horizons studied in the Enon (metagabbro) profile.

1. The concentrating of goethite into the magnetic fractions appears to be more effective in the coarse clays than in the fine clays (Tables 3 & 4). This was also reported by Schulze and Dixon (1979) and was attributed to the relationship between the "drag force"

and the magnetic force, which becomes less favorable as particle size decreases, resulting in less trapping of the fine clays. A stronger magnetic field would be necessary to obtain a more effective separation of the Fe oxides and the layer silicates.

2. Quartz and plagioclase are effectively concentrated in the non-magnetic fractions.

3. Hornblende is effectively concentrated in the magnetic fractions.

4. The higher concentration of regularly interstratified chlorite-vermiculite in the magnetic fractions of the coarse clays in the Bt1 (not shown) and Cr2 horizons (Fig. 2) supports earlier observations that Fe-chlorite (penninite) in the metagabbro parent rock is the precursor for this mineral. Regularly interstratified chlorite-vermiculite retains the chlorite's paramagnetic character. Concentration of randomly interstratified chlorite-vermiculite in the magnetic fraction of the clay in the Bt1 horizon again supports the conclusion that an Fe-chlorite intermediate weathering product (regularly interstratified chlorite-vermiculite) is the precursor.

5. The occurrence of smectite in both magnetic and nonmagnetic fractions and the different peak positions in each fraction suggest two possible precursors: i) smectite containing structural Fe, probably forming from chlorite intermediates, and ii) smectite without structural Fe, possibly forming by precipitation from solution.

6. The occurrence of kaolin in the magnetic and nonmagnetic fractions suggests two different types of 1:1 type clay mineral. Several explanations can be made for this phenomenon.

i. Kaolinite is derived from two different precursors; nonmagnetic calcic plagioclase feldspar and ferromagnesian minerals with Fe isomorphously substituted in its structure.

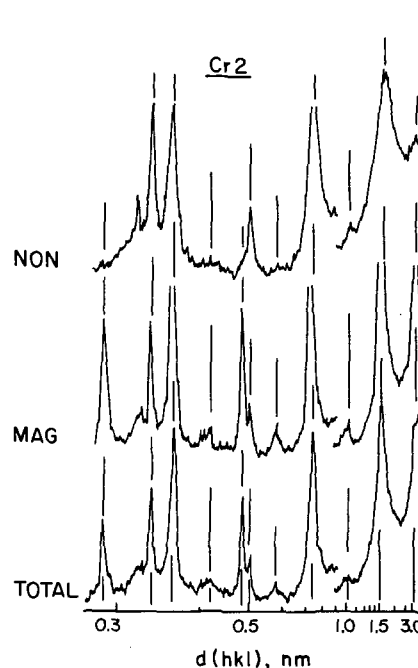


Fig. 2—X-ray diffractograms of Na-saturated total, magnetic, and non-magnetic fractions of coarse clays ($2-0.2 \cdot 10^{-6}m$) from Cr2 horizon, Enon (Metagabbro) profile.

ii. Kaolinite has no structural Fe, but kaolinite in the magnetic fraction is coated with Fe oxides.

iii. Kaolinite is mechanically trapped by the steel wool in the magnetic fraction. However, this effect appears negligible since the packing density of the steel wool was low.

iv. Kaolinite may be bound to some other paramagnetic mineral like regularly interstratified chlorite-vermiculite, causing it to be trapped in the magnetic fraction.

For comparison purposes, high gradient magnetic separation was performed on fine clays and coarse clays from the Bt horizon, Enon (gabbro) profile. The following conclusions are based on the analysis of x-ray diffractograms where the peak intensities were normalized by assigning a value of 100 to the most intense for each specific mineral within each size fraction (Table 4):

i. Smectite and vermiculite are found in all fractions.

ii. Kaolinite is found in all fractions, but appears to be more abundant in the nonmagnetic fractions.

iii. Fe is effectively concentrated in the magnetic fractions with a small amount found in the nonmagnetic fractions.

The following conclusions, based on x-ray diffractograms of the fine clay (Table 4) and calculated normalized peak intensities, can be made.

i. Smectite and kaolinite are found in all fractions.

ii. Goethite is not as effectively concentrated in the magnetic fraction as in the coarse clays.

CONCLUSIONS

The results do not permit a clear definition of mode of occurrence of the Fe-oxides with respect to other clay minerals present. Electron micrographs suggest that oxide particles do occur as discrete entities, separate from other minerals. At the same time, small particles of apparently the same characteristics are observed on the surface of other, larger mineral particles, indicating an intimate association, if not a coating. High gradient magnetic separation (HGMS) resulted in a concentrating of Fe-oxides in the magnetic fractions, but the occurrence of kaolinite in both magnetic and nonmagnetic fractions may be interpreted as indicating Fe-oxide coatings or close association of the oxide and the kaolinite particles. Finally, specific surface determinations of untreated and deferrated clays indicate that Fe-oxides are present primarily as discrete particles in three samples but possibly as coatings or "aggregates" in the fourth [Cr2 of Enon (metagabbro)]. It is tempting to speculate that Fe-oxides initially formed in the saprolite in close association with layer silicates (coatings?) may recrystallize as separate entities with further soil development or be dislodged as the layer silicates, themselves, weather and recrystallize.

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