THE PROBLEM OF EXPRESSING THE SPECIFIC SURFACE AREAS OF CLAY FRACTIONS

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Abstract—Estimations of the external specific surface areas (S.S.A.) by the N_2-BET method of clay separates that were further fractionated by the high gradient magnetic separation technique revealed that the magnetic fractions had consistently lower S.S.A. compared to non-magnetic fractions. This phenomenon has been attributed, in the past, to the intimate association of Fe-oxides with silicate clays. It is the contention of this study that this reasoning is insufficient due to the following reasons. X-ray diffractograms (XRD) confirmed that heavy minerals were abundant in the magnetic fractions of these clays. Total chemical analyses and energy dispersive X-ray analyses showed that these heavy minerals contained Fe and Ti, which were not completely extracted by the dithionite-citrate bicarbonate (DCB) treatments. Crystallinity and quantity of these oxides in the different fractions did not show any relationships with the S.S.A. Lower S.S.A. were found in the magnetic fractions of both coarse and fine clays in the untreated as well as DCB-treated samples. The average particle density of the magnetic fractions was found to be higher than the non-magnetic fractions, resulting in an underestimation of the S.S.A. This underestimation was further proven when clay-sized illmenite (density = 4.79 Mg m^{-3}) was found to have lower S.S.A. than quartz (density = 2.65 Mg m^{-3}) and well-crystallized Georgia kaolinite (density = 2.61 Mg m^{-3}), even though the illmenite particles were smaller in size compared to the kaolinite particles and similar in size compared to the quartz particles. It is, therefore, proposed that the specific surface areas should be expressed either on a volumetric basis or corrected for differences in density to avoid underestimations when heavy minerals are present in the samples.

Key Words—Density, Fe and Ti oxides, Magnetic and non-magnetic fractions, Specific surface area.

INTRODUCTION

Specific surface area (S.S.A.) is one of the most significant characteristics of soils and sediments, which has been related to the type and amount of clay (Tiller and Smith 1990), water content (Newman 1983), clay mineralogy and cation exchange capacity (De Kimpe et al 1979). The S.S.A. also has been used extensively to interpret physical characteristics such as shrink-swell potentials (Dasog et al 1988), frost-heave susceptibility (Rieke et al 1983), stability, dispersibility and erodibility (Churchman and Burke 1991, Barberis et al 1991) as well as the Atterberg limits (Smith et al 1985). Since the S.S.A. determined by the adsorption methods is a function of reactions between surface functional groups and the probe molecules (Sposito 1984), these estimations could be used to evaluate surface chemical properties such as adsorption of chemicals (Peter and Weber 1985), metals and phosphates on oxides and other minerals in soils (Harsh and Doner 1985).

Hillel (1982) stated that the S.S.A. may eventually prove to be a more meaningful and pertinent index for characterizing a soil or sediments than textural analyses. In this context, attempts also have been made to group soils according to their S.S.A. for management purposes (Wann and Juang 1985, Buol 1985). In the tropics, clay fractions of soils and sediments are usually dominated by kaolinite and sesquioxides. The significance of the S.S.A. on the understanding and characterization of these soils has been a subject of widespread interest (Gallez et al 1976, Bigham et al 1978, Borggaard 1982, Buol 1985, Schwertmann and Kämpf 1985, Feller et al 1992).

It is well known that the S.S.A. of soils and sediments is influenced by the mineral type and content, organic matter content, the degree of inter-particle association and also the average size of the particles (Bigham et al 1978, Borggaard 1982, Schulze and Schwertmann 1984, Schwertmann and Kämpf 1985, Feller et al 1992). The common methods used to estimate the total S.S.A. of soils and sediments include the ethylene glycol monoethyl-ether (EGME), ethylene glycol and the water vapor method, whereas, the external S.S.A. is estimated by the N_2-BET method (Feller et al 1992, Churchman and Burke 1992, Gallez et al 1976).

Sposito (1984) had stressed the significance of the density of particles in the estimations of the S.S.A. However, the importance of particle density has been overlooked when using the positive adsorption methods to evaluate soils and sediments that may contain appreciable quantities of heavy minerals. In such situations, expressing the S.S.A. in the conventional manner of m^{2}g^{-1} does not appear to be realistic. It is worth noting that Hillel (1982) pointed out that the S.S.A. also can be expressed as m^{2}cm^{-3}.

Fontes (1992) found that soils with poorly crystalline iron oxides had somewhat a lower surface area than expected when using the N_2-BET method. He suggested that this is likely due to a strong interaction between kaolinite and iron oxides. Although Fontes

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Table 1. General characteristics of Soils 1 and 2.

Depth (cm)	Horizon	Color (moist)	Texture	pH (1:1) (soil : water)	CEC cmol./kg	O.C.	Fe$_d$	Fe$_{tl}$	Ti$_{tl}$
						%			
				Soil 1					
0–12	A	7.5YR 4/3	scl	4.1	8.3	0.83	1.67	3.12	0.55
27–60	BA	7.5YR 4/4	scl	5.0	5.4	0.72	1.75	3.33	0.73
98–150	Bo2	7.5YR 5/6	scl	5.4	3.2	0.35	1.73	3.51	0.74
				Soil 2					
0–12	A	7.5YR 4/4	scl	6.4	5.1	0.85	0.37	0.73	0.28
40–82	Bt1	7.5YR 5/6	scl	4.5	4.5	0.17	0.73	1.53	0.51
135–180	Bt3	7.5YR 5/8	scl	4.4	3.8	0.11	0.80	1.76	0.67

O.C. = organic carbon, Fe$_d$ = DCB-extractable Fe, Fe$_{tl}$ and Ti$_{tl}$ = Total Fe and Ti in the untreated samples, scl = sandy clay loam.

(1992) mentioned the presence of heavy minerals such as anatase and rutile, their influence on the S.S.A. of the clay fractions were not accounted for. As the association of the oxides with clay particles remains a controversial issue (Greenland *et al* 1968, Bigham *et al* 1978, Borggaard 1982, Jones *et al* 1982, Saleh and Jones 1984, Schwertmann and Kämpf 1985, Barberis *et al* 1991, Feller *et al* 1992), the explanation offered by Fontes (1992) appears to be insufficient to explain the lower S.S.A. in the magnetic fractions. As such, the objectives of this study were: a) to determine the influence of heavy minerals on the S.S.A. of clay fractions and, b) to evaluate the validity of expressing the S.S.A. in terms of m^2g^{-1}.

MATERIALS AND METHODS

Two soils, identified as 1 and 2, from the Pernambuco state in Brazil were used for this study. Soil 1 (Haplustox) developed on Cretaceous sandstone while Soil 2 (Paleustult) was derived from Tertiary pediments. Soil 1 is located on a gently sloping to nearly level tableland at elevations of about 900 m above the sea level, whereas, Soil 2 is in the lower landscape position (400 m above sea level) of the toposequence.

The following analyses were done on bulk soil samples. The cation exchange capacity (C.E.C) determined by the BaCl$_2$ method, pH (soil : water, 1:1) and organic carbon (O.C.) content were done according to McKeague (1978). Total iron (Fe$_{tl}$) and titanium (Ti$_{tl}$) contents were analyzed using the method described by Jackson (1969). The Fe-oxides were extracted by dithionite-citrate bicarbonate (DCB) and the contents of Fe in the extracts (Fe$_d$) were determined by atomic absorption spectrometry (Mehra and Jackson 1960).

Following the removal of organic matter (McKeague 1978) particle-size distribution was determined by the pipette method. Particle-size separation of the samples into sand, silt, coarse and fine clays was done according to Jackson (1969). Further fractionation of the clays into coarse clay magnetic (CCM), fine clay magnetic

(FCM), coarse clay non-magnetic (CCNM) and fine clay non-magnetic (FCNM) fractions was carried out at 1.38T, using the method described by Ghabru *et al* (1987). The following analyses were carried out on the coarse and fine clays and their respective magnetic and non-magnetic fractions. Poorly crystalline Fe-oxides (Fe$_o$) were extracted using acid ammonium oxalate (McKeague and Day 1966) and total free Fe-oxides (Fe$_d$) by the DCB treatments (Mehra and Jackson 1960). The total Fe and Ti contents in the untreated (abbreviated as Fe$_{tl}$ and Ti$_{tl}$) and DCB-treated samples (abbreviated as Fe$_{t2}$ and Ti$_{t2}$) were determined according to the method described by Jackson (1969).

External specific surface areas (S.S.A.) were estimated by the N$_2$-BET method using an Autosorb 1 (Quantachrome Corp., NY). Mineral content was determined by X-ray diffraction (XRD) techniques on oriented specimens using a Phillips diffractometer with an Fe tube. Organic Carbon (McKeague 1978) and total elemental analyses on untreated and DCB-treated clays (Jackson 1969) also were carried out. Transmission electron microscopy (TEM) was done using a Zeiss CM10 TEM (Oberkochen, W. Germany) operated at 100 kV. Energy dispersive X-ray spectra (EDS) of selected magnetic coarse clay fractions were studied with a SEM-Microprobe (JEOL JXA-8600 Superprobe, Japan), operated at 15 kV and 10 nA. Density measurements were made using a pycnometer.

RESULTS AND DISCUSSION

General characteristics of the soils

Some properties of the two soils are given in Table 1. Both soils are generally homogenous in color and texture and have low C.E.C., O.C. and pH. Soil 1 has higher amounts of total Fe and Ti compared to Soil 2. In both soils, the contents of these elements increase with depth. Furthermore, the DCB-extractable Fe accounts for only approximately 50% of the total Fe contents.
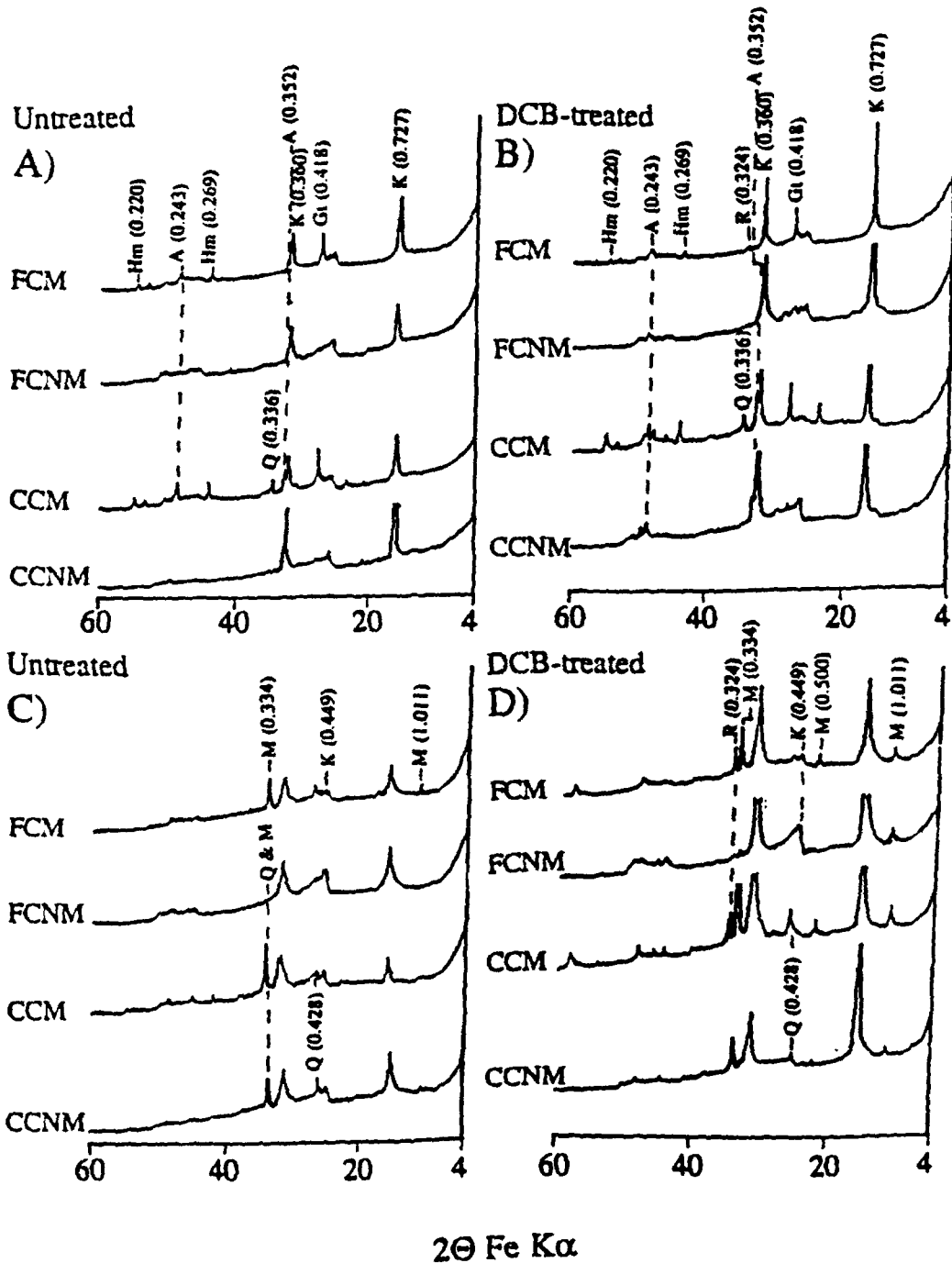
2Θ Fe Kα

Figure 1.   X-ray diffractograms (400 cps) of the various fractions. a) Untreated, and b) DCB-treated fractions from the BA horizon of Soil 1. Similarly, c) untreated, and d) DCB-treated fractions from the Bt1 horizon of Soil 2. Note the presence of heavy minerals after DCB-treatments. (Hm = hematite, A = anatase, K = kaolinite, Gt = goethite, R = rutile, Q = quartz, M = muscovite). d-spacings in nanometres (nm).

Mineralogical and chemical properties of the clay fractions

As shown in Figure 1, muscovite is present only in Soil 2. This soil has higher quartz contents in the coarse clay fractions compared to Soil 1. Both soils comprise anatase, goethite, hematite and rutile as well as kaolinite and minor quantities of halloysite. However, the magnetic fractions in both soils had less intense peaks of kaolinite and minor quantities of halloysite

Table 2. Organic carbon, oxalate-extractable Fe, DCB-extractable Fe, total Fe and Ti before and after DCB extraction, Fe-ratios and specific surface areas of the magnetic and non-magnetic fractions of coarse and fine clays in Soils 1 and 2.

Sample	O.C.	Fe_o	Fe_d	Fe_{t1}	Fe_{t2}	Ti_{t1}	Ti_{t2}	Fe_o/Fe_d	Fe_d/Fe_{t1}	SSA_1	SSA_2
				%						$m^2\ g^{-1}$	
Soil 1											
P6 0-12 CCNM	1.09	0.11	2.02	2.28	0.27	1.14	1.27	0.05	0.88	25	22
P6 0-12 CCM	3.08	0.33	3.11	16.67	13.55	6.13	11.12	0.11	0.19	23	22
P6 0-12 FCNM	0.80	0.18	2.09	5.10	3.02	0.44	0.71	0.08	0.41	47	32
P6 0-12 FCM	3.01	0.33	4.39	10.16	5.77	1.04	1.64	0.07	0.43	37	30
P6 27-60 CCNM	n.d.	0.11	1.26	2.95	1.69	1.87	2.94	0.09	0.42	29	23
P6 27-60 CCM	n.d.	0.47	3.91	17.62	13.71	5.13	9.11	0.12	0.22	22	22
P6 27-60 FCNM	n.d.	0.21	1.93	4.93	3.00	0.56	0.91	0.11	0.39	45	34
P6 27-60 FCM	n.d.	0.38	4.05	12.21	8.16	0.62	1.03	0.09	0.33	36	31
P6 98-150 CCNM	0.29	0.06	1.10	2.44	1.34	1.64	2.54	0.05	0.45	30	23
P6 98-150 CCM	1.12	0.26	2.98	19.19	16.21	4.02	7.42	0.09	0.16	27	20
P6 98-150 FCNM	0.79	0.08	1.89	3.56	1.67	0.51	0.75	0.04	0.53	44	29
P6 98-150 FCM	2.15	0.26	5.57	10.99	5.42	0.61	0.91	0.05	0.51	37	27
Soil 2											
P8 0-12 CCNM	1.23	0.08	1.12	2.28	1.70	1.22	1.84	0.07	0.49	34	23
P8 0-12 CCM	4.21	0.15	2.57	6.14	3.57	4.29	6.78	0.06	0.42	30	19
P8 0-12 FCNM	0.85	0.07	2.47	3.75	2.88	0.75	1.00	0.03	0.66	53	41
P8 0-12 FCM	2.99	0.17	2.65	5.68	3.39	1.56	1.57	0.06	0.47	37	36
P8 40-82 CCNM	n.d.	0.05	1.48	3.59	2.81	2.42	3.83	0.04	0.41	40	26
P8 40-82 CCM	n.d.	0.14	5.45	8.05	4.70	5.53	7.31	0.03	0.68	33	20
P8 40-82 FCNM	n.d.	0.04	1.17	3.53	2.36	0.91	1.52	0.04	0.33	52	35
P8 40-82 FCM	n.d.	0.17	4.96	10.97	6.01	1.98	3.07	0.03	0.45	44	29
P8 135-180 CCNM	0.24	0.04	1.11	3.21	2.10	2.26	3.74	0.02	0.35	34	23
P8 135-180 CCM	1.04	0.16	6.02	8.39	3.58	5.59	7.17	0.02	0.72	33	18
P8 135-180 FCNM	0.85	0.04	1.26	3.60	2.62	1.24	2.05	0.03	0.35	53	36
P8 135-180 FCM	1.91	0.16	6.07	9.72	3.65	2.01	2.76	0.02	0.63	39	31

SSA_1 = specific surface areas of untreated fractions, SSA_2 = specific surface areas of DCB-treated fractions, n.d. = not determined.

and substantially more intense peaks for Fe and Ti oxides compared to the non-magnetic fractions. The XRD of the DCB-treated samples from Soil 1 show that goethite, anatase and rutile still existed in the coarse and fine clay magnetic fractions of Soil 1. Anatase and goethite also could be detected in the DCB-treated non-magnetic fractions. In comparison to Soil 1, the peak intensities for rutile were higher and those for anatase and goethite were lower in the DCB-treated magnetic fractions in Soil 2 (Figure 1).

Total chemical analyses (Table 2) confirmed that in both soils the magnetic fractions have more Fe_o, Fe_d, Fe_{t1} and Ti_{t1} compared to the non-magnetic fractions. The highest contents of Fe and Ti (up to 25%) were found in the coarse clay magnetic fractions. High amounts of Fe and Ti in the DCB treated (Fe_{t2} and Ti_{t2}) coarse clay magnetic fractions correspond well with the presence of high amounts of stable Fe-Ti minerals. The magnetic fractions of the coarse and fine clays in both soils have higher O.C. contents compared to the non-magnetic fractions. In comparing the Fe_o/Fe_d and Fe_d/Fe_{t1} values it is evident that the magnetic fractions in Soil 1 have higher proportions of DCB-resistant Fe-Ti oxides than the non-magnetic fractions.

Submicroscopy and microchemistry

Observations under the TEM (Figure 2) reveal that the coarse-clay fractions of both soils comprise a mixture of well and poorly crystallized oxides of Fe-Ti as well as kaolinite. Spindle-shaped oxides of Fe-Ti are generally concentrated in the coarse-clay magnetic fractions (Figure 2a) whereas the poorly crystallized oxides of Fe and Ti are proportionally more abundant in the coarse-clay non-magnetic fractions. The magnetic separation appears to be somewhat effective in concentrating the Fe-oxides even in the fine clays (Figures 2b–2d). The energy dispersive spectrum (EDS) of electron dense and light areas show some differences in Ti distribution (Figure 3) in the coarse clay magnetic fractions of Soil 1. In comparing the intensities of the $K\alpha$ peaks of Ti and Fe in the two fields it is evident that Ti is concentrated in certain areas, implying the presence of Ti-rich oxides. The similarities of the $K\alpha$ peaks of Al and Si confirm the presence of kaolinite.

Despite the fact that a few well-crystallized kaolinite particles are present in the micrographs, the dominant type of kaolinite in all fractions of both soils is poorly crystallized (Figures 2c and 2d). Halloysite occurs in
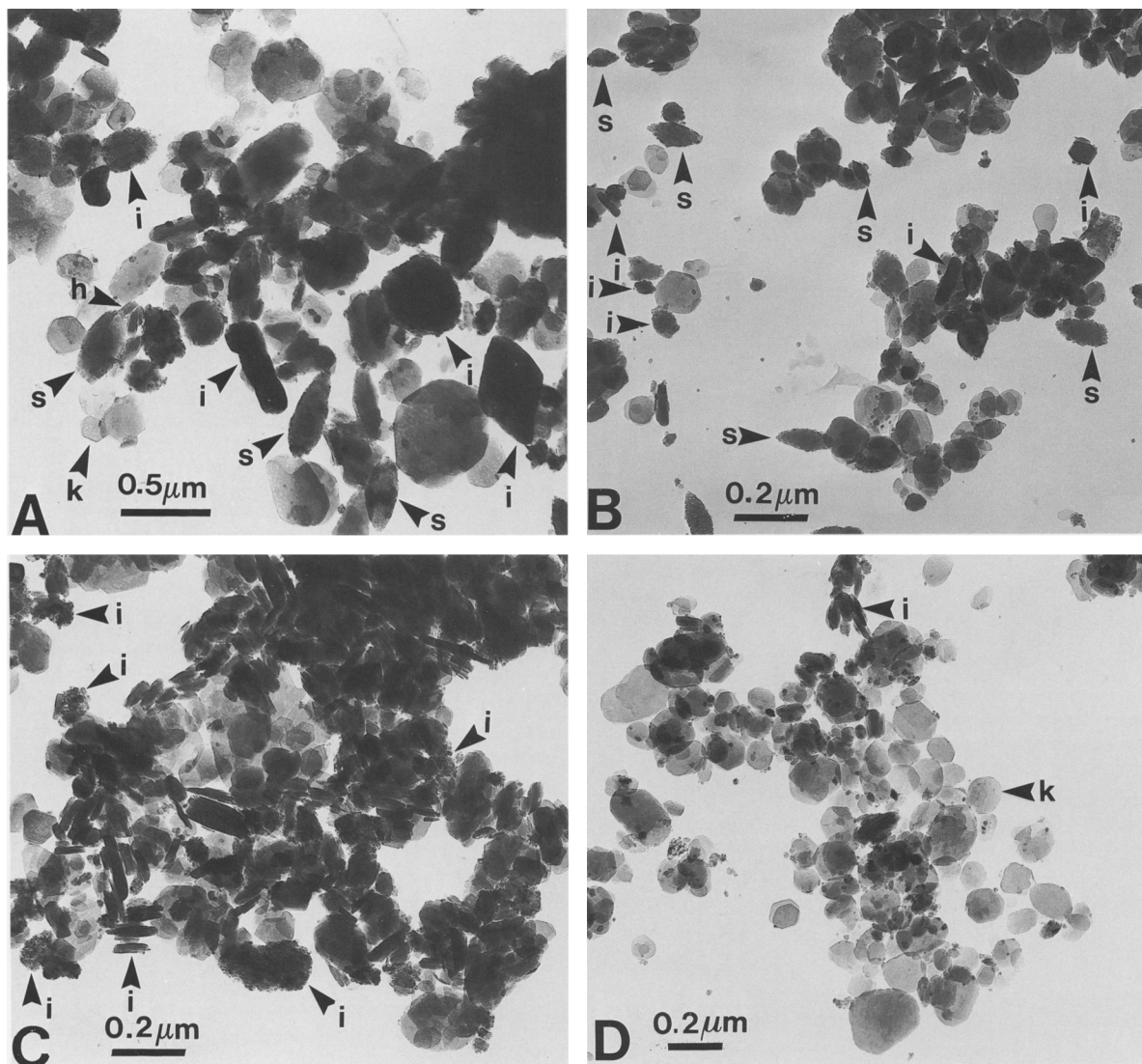
Figure 2.   Transmission electron micrographs of the magnetic and non-magnetic fractions of the BA horizon of Soil 1 and the Bt1 horizon of Soil 2. a) CCM of Soil 1, b) FCM of Soil 1, c) FCM of Soil 2, d) FCNM of Soil 2. Note the concentration of heavy minerals in the magnetic fractions. i = Fe-oxides, s = spindle shaped oxides, k = kaolinite, h = halloysite.

minor amounts in both soils and is generally found as discrete tubes or in association with other particles, especially with kaolinite. A few cubic, electron dense crystals, which are assumed to be magnetite, also were seen in the magnetic fractions of both soils. Furthermore, the coarse-clay fractions in both soils are dominated by non-aggregated kaolinite particles (dimensions greater than 0.2 μm) with subordinate amounts of fine-clay particles. The TEM observations of DCB-treated fractions (Figures 4a and 4b) show that cubic crystals (magnetite) and spindle-shaped Fe-Ti oxides (Fe$_{t2}$ and Ti$_{t2}$) still exist, indicating that the poorly crystallized Fe-oxides have been removed.

Specific surface areas of the clay fractions

The S.S.A. for a given untreated clay fraction appear to be quite similar in all horizons (Table 2). Generally, the clay fractions in Soil 2 have higher S.S.A. compared to Soil 1. As expected, the fine clay fractions have higher S.S.A. compared to the coarse clay fractions. In all cases, the magnetic fractions of both coarse and fine clays had a lower S.S.A. compared to the non-magnetic fractions.

The magnetic fractions have higher O.C. and Fe$_o$ contents compared to the non-magnetic fractions, which is in agreement with the findings of Hughes (1982).
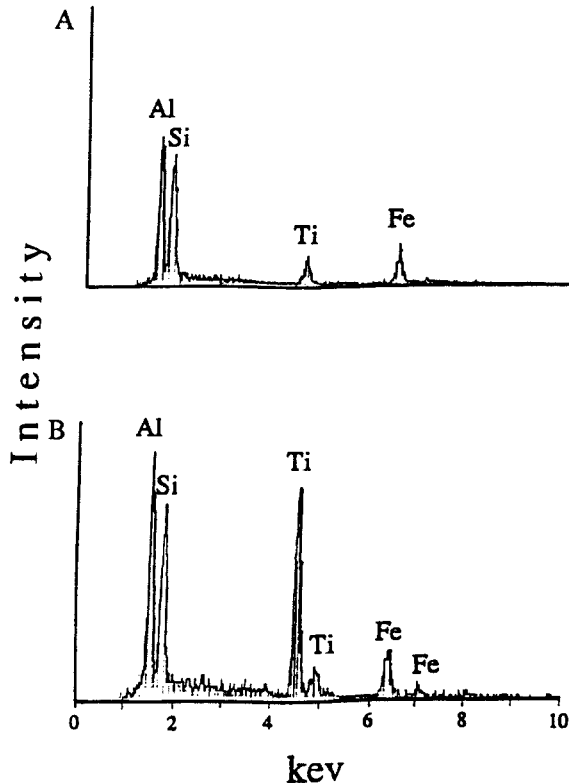
Figure 3. Energy dispersive X-ray spectra of the coarse-clay magnetic fractions from the BA horizon of Soil 1 showing the a) electron light, and b) electron dense areas.

However, the S.S.A. of selected samples (results not presented here) which were treated with acid ammonium oxalate and H_2O_2, did not show any satisfactory relationships with the Fe_o or the O.C. contents. Similarly, relationships could not be observed between Fe_d and the S.S.A. of the untreated clay fractions ($S.S.A._1$) nor between the changes in S.S.A. after the DCB-treatments ($S.S.A._1 - S.S.A._2$, where $S.S.A._2 = $ S.S.A. of the DCB-treated sample) and the Fe_d contents. Considering the type of minerals present in the samples, the higher S.S.A. in Soil 2 compared to 1 could be attributed, in part, to the presence of muscovite (Van Olphen and Fripiat 1979). However, the relative amounts of muscovite were not related to the differences in S.S.A. between the magnetic and non-magnetic fractions of Soil 2.

The S.S.A. of the DCB-treated coarse-clay fractions ($S.S.A._2$) are generally low in both soils and are comparable to those reported for poorly crystallized Georgia kaolinite (20 m^2g^{-1}; Van Olphen and Fripiat 1979). As expected, the DCB-treated fine clays have higher S.S.A. compared to the coarse clays (Table 2). The DCB-treated magnetic fractions with higher Fe and Ti contents (Table 2) tend to have lower S.S.A. compared to the non-magnetic fractions.

In Soils 1 and 2, the coarse clay fractions consist of subordinate amounts of fine clay-sized particles (Figure 2). This implies that there is a minimum influence of the fine-clay particles on the S.S.A. of these coarse clay fractions, which is in agreement with the findings of Feller *et al* (1992). The TEM observations show that the average particle size of kaolinites is quite similar
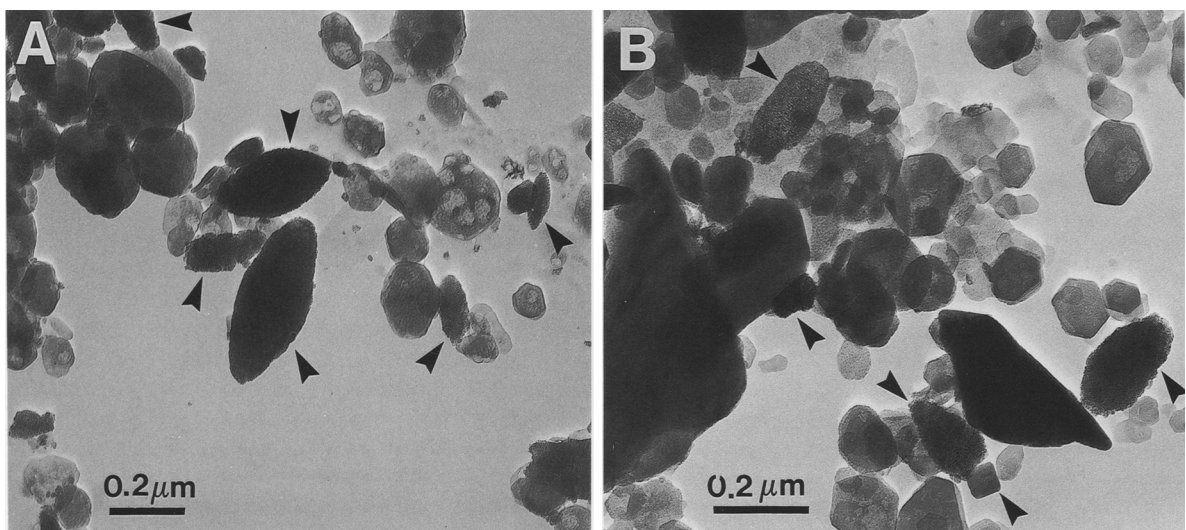

Figure 4. Transmission electron micrographs of DCB-treated coarse-clay magnetic fractions. a) The BA horizon of Soil 1, and b) the Bt1 horizon of Soil 2. The spindle-shaped oxides and presumably cubic magnetite particles are still present and generally occur as discrete particles. Arrows indicate the spindle shaped oxides. Note presence of cubic shaped oxide in (b).
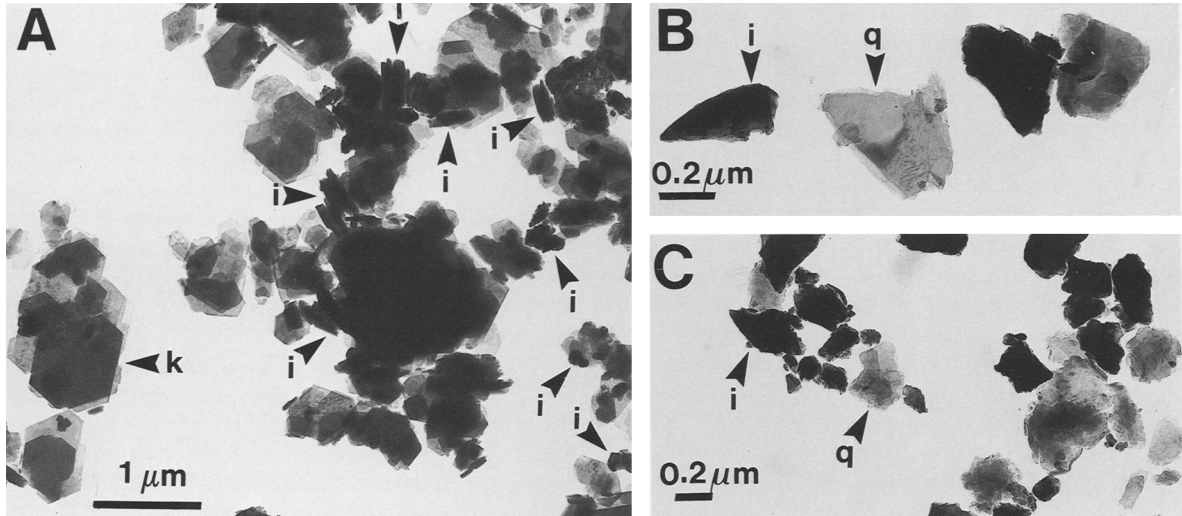
Figure 5.   A mixture of clay-size illmenite (indicated by arrows) and well-crystallized Georgia kaolinite under the TEM. Note that the kaolinite particles are clearly larger than the illmenite. b) and c) show a mixture of the illmenite and clay-size quartz particles.

in both the magnetic and non-magnetic samples for a given size fraction. The Fe-oxides, however, are either similar in size or smaller than the kaolinite particles (Figure 2). If the influence of particle size were to be considered, the presence of smaller particles of Fe-oxides should have resulted in higher S.S.A. values for the magnetic fractions than that observed. Working on similar materials containing rutile, anatase, goethite and hematite, the low S.S.A. of the Fe-oxides were attributed to strong inter-particle association by Fontes (1992), without taking into consideration the influence of heavy minerals on the estimated S.S.A.

Fontes (1992) reported that hematite, with lower Al-substitution, was differentially concentrated in the magnetic fractions. However, Figure 1 shows that for Soils 1 and 2, both hematite and goethite exist in the magnetic fractions without any apparent differential concentrations (in the magnetic fractions) between these two Fe minerals. The majority of Fe and Ti oxides in Soils 1 and 2 are well crystallized and, therefore, their effective contribution to the estimated S.S.A. would be expected to be less compared to poorly crystallized oxides and this would result in lower S.S.A. values. However, variations in the ratios Fe_o/Fe_d and Fe_d/Fe_{t1} could not explain the low S.S.A. in the magnetic fractions. As pointed out by Schulze and Schwertmann (1984), the overall relationship between the property and contents of the different types of Fe-oxides and their S.S.A. is not quite simple. They also have shown that the ionic substitution of Al for Fe does not account for many of the differences in the properties of Fe-oxides and oxyhydroxides especially in the context of S.S.A.

The influence of heavy minerals on the S.S.A. of clay fractions

Differences in S.S.A. between untreated and DCB-treated samples were correlated to the Fe-oxide contents in the past (Desphande *et al* 1968, Gallez *et al* 1976, Bigham *et al* 1978, Borggaard 1982, Feller *et al* 1992) but, as discussed before, it has been shown that this correlation was not valid for the soils used in this study. The lack of correlation between the Fe_d and the S.S.A. could be explained partly by the collective influence of variations in particle size, mineralogy, crystallinity, quantity and distribution of these oxides as well as possible inter-particle association.

The main characteristic of the DCB-treated coarse clay magnetic fractions is the high contents of Fe (Fe_{t2}) and Ti (Ti_{t2}). Despite this, their S.S.A. values are quite close to the non-magnetic fractions (which have much lower Fe_{t2} and Ti_{t2} contents). As the majority of the Fe-oxides are smaller than the kaolinite particles the S.S.A. of the magnetic fractions should be higher than the non-magnetic fractions. Since this is not the case, this implies that the S.S.A. of the magnetic fractions have been underestimated.

In expressing the S.S.A. conventionally as m^2g^{-1}, it is observed that the S.S.A. of the DCB-treated as well as the untreated samples decrease with increasing amounts of Fe and Ti in both coarse and fine clays. This trend suggests a clear relationship between the S.S.A. and the average particle density of the fractions. To confirm this hypothesis, the average particle densities of the magnetic and non-magnetic fractions (coarse-clays) from Soil 1 were determined. The mag-

netic fractions had an average density of 3.45 Mg m^{-3} whereas, the non-magnetic fractions, 2.90 Mg m^{-3}. This proves that the difference in average particle density between these fractions is due to the higher concentrations of Fe and Ti oxides in the magnetic fractions.

The following experiment was carried out to establish the relationship between particle density and S.S.A. Two grams of illmenite (Ward's Natural Science Mineral Collection) were ground and the clay-sized particles separated using the centrifugation method (Jackson 1969). The S.S.A. of clay-sized illmenite was estimated as 9 m^{2}g^{-1} whereas, the well-crystallized Georgia kaolinite (Clay Minerals Society, Source Clay Minerals Repository) had an average S.S.A. value of 10 m^{2}g^{-1}. Observations under the TEM showed that the clay-sized illmenite particles were distinctly smaller than the kaolinite particles (Figure 5), a phenomenon which was similar to those encountered in the magnetic fractions of Soils 1 and 2.

Since the illmenite particles are smaller than the kaolinite particles, the former should then logically have a much higher S.S.A. than observed. This shows quite clearly that the higher density of illmenite (4.79 Mg m^{-3}) has a role in influencing the S.S.A. of the oxide. To further test this hypothesis, the experiment was extended to include quartz as well to consider the shape of particles as one of the factors influencing the S.S.A. The S.S.A. of clay-size quartz grains (density = 2.65 Mg m^{-3}) were estimated as 14 m^{2}g^{-1}. The TEM observations (Figures 5b and 5c) indicate that the quartz grains have similar morphology and particle size compared to the illmenite particles. This shows clearly that regardless of particle size and shape, the higher density of the illmenite particles (approximately 1.8× the density of quartz) has resulted in a reduction of its estimated S.S.A.

As discussed by Sposito (1984), the average particle density has to be taken into consideration during the estimation of S.S.A. For a given mass of sample, when the density is higher, the volume occupied by the material is lower than the sample of lower density. Assuming a monolayer coverage of the N$_2$ molecules, if the results are expressed in the conventional manner of m^{2}g^{-1} this would imply a much lesser extent of coverage of these molecules on the samples of higher densities (smaller sample volumes) amounting to an underestimation of the S.S.A.

Proposals for expressing the S.S.A.

From the foregoing discussion, it is evident that if two particles had equal dimensions and morphology but differed only in density, the particle with higher density and as such, a higher mass, will give a lower S.S.A. While it is true that particles with plate-like morphology might have different S.S.A. compared to more rounded-shaped particles, if two particles were of the same size with similar morphology but differed only in density, then the particles with higher density will have a lower S.S.A. if the estimations were expressed as m^{2}g^{-1}. This further implies that for samples that have high contents of Fe, Ti or other heavy minerals, the S.S.A. will be underestimated. This explains the persistently lower S.S.A. of the magnetic fractions compared to the non-magnetic fractions even after DCB-treatments. Conversely, there will be an overestimation of the S.S.A. of soils or clays that have low particle densities. To solve this problem, two solutions are put forth:

a) Express the surface areas of samples on a volumetric basis by multiplying the measured S.S.A. with the average particle density. This results in the surface area being expressed as m^{2}cm^{-3}. This method has its advantages in that it gives a better perception of the spatial extent of the surface area of any sample, thereby enabling logical and reliable comparisons to be made, regardless of the variations in particle density. Since *Specific* in S.S.A. refers to "per unit mass" (Sposito 1984), expressing surface areas on a volumetric basis would not require the use of the term "Specific".

b) Incorporate a correction factor into the calculations. The correction factor could be calculated as the ratio between the average particle density of the sample and the density of quartz (density = 2.65 Mg m^{-3}, Deer *et al* 1967).

CONCLUSIONS

Studies have shown that untreated and DCB-treated magnetic fractions had consistently lower S.S.A. than the non-magnetic fractions and contained considerable amounts of heavy minerals. This observation proved that particle density is an important criterion that has to be corrected for in the estimations of S.S.A., especially when the soils, clays or sediments are enriched in Fe-Ti oxides, oxyhydroxides, or other heavy minerals. This correction is required because Fe- and Ti-oxides or other heavy minerals increase the average particle density resulting in underestimation of S.S.A. Conversely, the S.S.A. of soils and clays with low density particles will be overestimated. It is, therefore, proposed that the S.S.A. should be expressed either 1) on a volumetric basis, or 2) a correction factor should be incorporated for realistic comparisons of soils, clays and sediments.

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