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Clay mineralogy and cation exchange capacity of Brazilian soils from water contents determined by thermal analysis

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Abstract

The clay size fraction of subtropical soils is dominated by kaolinite, gibbsite, iron oxides, and small amounts of 2:1 clay minerals. Among these minerals, it is more difficult to quantify the presence of the 2:1 clay minerals where kaolinite is the dominant clay mineral present. Thermal analyses of 56 size clay size fractions, free of iron oxides, developed on magmatic rocks, were used to quantify the presence of expandable 2:1 clay minerals. The water content of the samples, measured in three different ranges of temperatures, gave significant ($P < 0.0001$) linear correlations with the percentage of expandable 2:1 clay minerals and the cation exchange capacities of the whole soil materials. Water content can thus be used as a tool to estimate the quantity of 2:1 minerals in lieu of more complicated procedures.

Keywords: Water content; Kaolinite; Gibbsite; 2:1 Clay minerals; CEC

1. Introduction

Kaolinite, gibbsite, iron oxides, and variable amounts of 2:1 clay minerals are the dominant minerals in the clay size fraction ($<2\,\mu$m) of humid tropical and subtropical soils [1]. Gibbsite and kaolinite have very characteristic thermal properties associated with dehydroxylation (T_d) at temperatures of 250–350 °C and 450–550 °C, respectively, [2] and can be quantified from the weight lost or heat consumed by this process [3]. The observed range in temperature of dehydroxylation varies with particle size, degree of crystallinity [4], particle morphology [5], and experimental conditions [6].

Smykatz–Kloss [7] used T_d to classify kaolinites as extremely disordered ($T_d < 530\,°C$), strongly disordered ($T_d = 530–555\,°C$), little disordered ($T_d = 555–575\,°C$) and well-ordered ($T_d > 575\,°C$) and argued that there should be few naturally occurring samples with dehydroxylation temperatures below 530 °C. The T_d of kaolinite overlaps with that of some 2:1 clay minerals [8], such as beidellite [9].

In samples free of iron oxides, gibbsite can be quantified even when present in very small amounts (∼0.1%) because the mineral has a much higher ratio of hydroxyls evolved (34.6%) than kaolinite (13.9%) or smectite/vermiculite (≈5%) [10]. The T_d of gibbsite is unique from those of layer silicate minerals usually found in tropical soils.

The expandable 2:1 clay minerals, mainly smectites and vermiculites, also have characteristic thermal properties [9,12], but are seldom quantified by thermal analysis. Most of the weight loss from heating these minerals occurs in the range of 50–200 °C and is due to dehydration of internal particle surfaces (50–110 °C) and the vaporization of water solvating exchangeable cations in the interlayer spaces [10,11,13]. Speil et al. [11] obtained good statistical correlation between the area of the 100 and 250 °C double endothermic peak of montmorillonite/kaolinite mixtures when montmorillonite percentages were smaller than 60%.

Hydroxyls within the octahedral sheets are lost at much higher temperatures, 500–700 °C, which vary with the crystallographic and chemical characteristics of these minerals [8,9,14]. Comparing different smectites, Earnest [13] observed an average weight loss of 18% due to interlayer water, while between 4 and 5.9% weight loss corresponded to the loss of structural OH.

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In subtropical soils, the expandable 2:1 clay minerals are usually present in concentrations smaller than 10% and are difficult to quantify by standard techniques due to their small particle size, high degree of interstratification with kaolinites [15], and the presence of Al-hydroxy polymers instead of exchangeable cations in their interlayer regions [16,17]. Although not abundant, the expandable 2:1 minerals have high specific surface areas (SSA), high cation exchange capacity (CEC) [18], and layer charge, play a major role in the sorption of water and dissolved cations from the soil solution. Their quantification is thus important for both agricultural and environmental utilization of subtropical soil resources.

There are two major sources of CEC in tropical and subtropical soils: (1) associated with organic matter and (2) derived from inorganic colloids [18]. For most subtropical oxisols there is a close relationship between organic carbon content and CEC [19] because these highly weathered soils have a homogeneous particle size distribution and mineralogy with depth. Average CEC values of pure kaolinites are less than 5 $\mathrm{cmol_c/kg}$ [20,21]. The iron oxides and gibbsite have almost no capacity to retain cations because of their relatively high point of zero charge-PZC values. Other soils are usually shallower, and the intensity of weathering decreases with depth. In these soils, CEC values are less dependent on the organic carbon content.

Gibbs et al. [22] evaluated the water content of whole soil samples from Barbados and observed a good correlation between the cation exchange capacity of the soils and a relative thermal activity index (F) derived by adjusting the weight loss between 50 and 1100 °C to the lowest observed weight loss, which was assigned a value of 1. The objective of the current study was to determine if water contents obtained by thermal analysis of clays from kaolinitic subtropical soils in southern Brazil could be correlated with the abundance of expandable 2:1 clay minerals and the cation exchange capacity of the whole soil materials.

2. Experimental

Samples of 18 A horizons and 28 subsurface horizons (B, BC or C) were collected from 31 soils in the state of Paraná-Brazil (Table 1). The objective was to select soil materials with different degrees of weathering due to the action of various soil forming factors and processes. These soils represent the most important agricultural soils of the state of Paraná [23] and were all developed from magmatic rocks of the Paraná continental flood volcanism [24] that covers about 70% of the Paraná basin. The current climate is subtropical humid mesothermic (Table 1).

2.1. Characterization of the soils

The methods used for basic characterization of the <2 mm soil materials are described by EMBRAPA [25]. Chemical characterization consisted of pH in water, exchangeable cations ($\mathrm{Al^{3+}}$, $\mathrm{Ca^{2+}}$, $\mathrm{Mg^{2+}}$ and $\mathrm{K^+}$) and the exchangeable acidity ($\mathrm{Al^{3+} + H^+}$). With these results, it was possible to calculate the cation exchange capacity (CEC $(\mathrm{cmol}_c/\mathrm{kg}) = \mathrm{Ca^{2+} + Mg^{2+} + K^+ + Al^{3+} + H^+}$), the base saturation (V (%) $= 100{*}(\mathrm{Ca^{2+} + Mg^{2+} + K^+})/\mathrm{CEC}$) and the aluminum saturation (Al(%) $= (100{*}\mathrm{Al^{3+}}/(\mathrm{Ca^{2+} + Mg^{2+} + K^+ + Al^{3+}}))$ of each sample. The organic carbon content of the soils was measured by the Walkley–Black chromic acid wet oxidation method.

The particle size distribution was determined by dispersing 100 g of the <2 mm soil material with 0.1 M NaOH. The sand fraction (2–0.05 mm) was separated by sieving, and the clay (<2 μm) was isolated from the silt (0.05–0.002 mm) by repeated siphoning of the dispersed material. The clay was flocculated with 1 M $\mathrm{MgCl_2}$, transferred to spectrum dialysis tubes, and equilibrated against double-deionized water until the electrical conductivity of the wash water was less than 2 μΩ. The clays were then quick frozen in liquid nitrogen and freeze-dried. All fractions were subsequently dried at 60 °C in a force-draft oven, and the masses were used to calculate the percentage of each fraction.

Iron oxides were selectively dissolved from the clay samples by using the dithionite-citrate-bicarbonate (DCB) procedure of Mehra and Jackson [26].

The residues were dialyzed, freeze-dried, and held for X-ray and thermal analysis. Iron contents of the DCB extracts were determined with a Varian Techtron AA-6 spectrophotometer, and the results were used to calculate the $\mathrm{Fe_2O_3}$ content of the clays.

2.2. X-Ray diffraction

Qualitative mineralogical compositions of the DCB-treated clays were obtained by X-ray diffraction analysis of oriented mounts following procedures given by Brown and Brindley [27]. Diffraction patterns were recorded from 2 to 30° (2θ) using Cu Kα radiation and a Philips Electronics PW 1316/90 wide range goniometer fitted with a theta-compensating slit, a 0.2 mm receiving slit, and a diffracted beam graphite monochromometer. Data were collected in step scan mode (0.02° (2θ) for 5 s) and transferred to a computer using a Databox (Radix Instruments, 1990) interface and software.

2.3. Thermal analysis

Ten to 20 mg of each DCB-treated and Na-saturated clay were heated from 50 to 800 °C using a Seiko 200 instrument fitted with a Pt–Pt Rh (13%) thermocouple. The instrument was controlled by a Seiko SSC-5020 disk station and was capable of simultaneous thermogravimetric (TG) and differential thermal analysis (DTA). Samples were heated under a 200 $\mathrm{ml\,min^{-1}}$ flux of $\mathrm{N_2}$-gas with a heating rate of 20 $\mathrm{^\circ C\,min^{-1}}$ and an empty Pt pan as a thermally inert reference material. The amount of gibbsite was determined using

Table 1
Location, climate, parent rock, soil classification, soil horizon and number of samples

Location	Climatic classification Koeppen[a]	Parent rock	Soil classification[b] soil survey staff	Soil horizon	No. of samples
Campo Mourão	Cfa	Basaltic andesite	Anionic Acrudox	A, Bo	2
		Basaltic andesite	Anionic Acrudox	Bo	1
		Basaltic andesite	Typic Troporthent	A	1
Cambará	Cfa	Basaltic andesite	Rhodic Hapludox.	A, Bo	2
		Basaltic andesite	Rhodic Hapludox	B	1
Cascavel	Cfa	Transitional basalt	Rhodic Hapludox	Bo	1
Cruzmaltina	Cfa	Basaltic andesite	Typic Kandihumult	A, Bt	3
		Basaltic andesite	Typic Troporthent	A, CR	2
		Basaltic andesite	Humic Rhodic Hapludox	A, Bo	2
		Basaltic andesite	Humic Rhodic Hapludox	A, Bo	2
Faxinal	Cfa	Rhyodacite	Humic Hapludox	A, Bo	3
		Rhyodacite	Lithic Troporthent	A	1
		Rhyodacite	Lithic Troporthent	A	1
Faxinal	Cfa	Basaltic andesite	Humic Rhodic Hapludox	A	1
Ibiporã	Cfa	Basaltic andesite	Rhodic Kandiudalf	A, Bt	3
		Basaltic andesite	Lithic Hapludoll	A, C	2
		Basaltic andesite	Lithic Eutrudox	A, Bo	2
Londrina	Cfa	Transitional basalt	Typic Troporthent	A, C	2
			Rhodic Hapludox	Bo	1
Maringá	Cfa	Basaltic andesite	Typic Endoaquerts	A, C	3
		”	Typic Kandiudults	A, Bt, C	3
		”	Rhodic Hapludox	A, B, BC	3
		”	Typic Argiudoll	Bt, BC	2
Palotina	Cfa	Basaltic andesite	Rhodic Hapludox	Bo	1
Pato Branco	Cfa	Basaltic andesite	Typic Hapludox	A, Bo	2
		Basaltic andesite	Typic Hapludox	Bo	1
Tamarana	Cfa	Quartz latite	Oxic Humitropept	(B), C	2
		Quartz latite	Typic Kandihumult	A, Bt, BC	3
		Quartz latite	Typic Kandihumult	A, Bt	2
União da Vitória	Cfb	Quartz latite	Humic Hapludox	Bo	1
Total		Quartz latite			56

[a] Cfa refers to a subtropical humid mesothermic climate with hot summers and a concentration of rain in the summer months. The mean temperature of the hottest month is above 22 °C. Cfb refers to a subtropical humid mesothermic climate with fresh summers and a frequent, severe frost in the winter. The mean temperature of the hottest month is below 22 °C and the coldest month is below 18 °C.

[b] Soil Survey Staff [32].

the weight loss of the sample between 250 and 350 °C as compared to a calculated weight loss corresponding to complete dehydroxylation of a pure sample of gibbsite, i.e.: gibbsite $\% = 100 \times (\mathrm{WL}_s/\mathrm{WL}_{\mathrm{Gib}})$ where WL_s is the percent weight loss of the sample and $\mathrm{WL}_{\mathrm{Gib}}$ is the percent weight loss of pure gibbsite. A similar approach was used for determining the kaolinite (Kao) content based on the pronounced dehydroxylation event occurring between 450 and 550 °C; i.e, kaolinite $\% = 100 \times (\mathrm{WL}_s/\mathrm{WL}_{\mathrm{Kao}})$, where WL_s is the weight loss of the sample and $\mathrm{WL}_{\mathrm{Kao}}$ is the weight loss of pure kaolinite [3,16,17].

2.4. Mass balance of the clay size fraction

The total Fe oxide contents (Fe_2O_3) of the clays, including poorly crystalline materials, were obtained by selective dissolution using the DCB procedure as previously described. Quantitative analysis of kaolinite (Kao) and gibbsite (Gib) were achieved by thermal analysis of the DCB-treated clays with a correction for weight loss due to iron oxide removal. Other trace or minor components included quartz, anatase, and rutile, none of which are subject to dehydroxylation events [23,28]. The only major component left unaccounted for was the expandable 2:1 clay minerals, and the following working equation was used for their "quantitative" analysis: $2{:}1 = 100 - (\mathrm{Kao} + \mathrm{Gib} + \mathrm{Fe_2O_3})$.

2.5. Evaluation of water content

A basic assumption of this analysis was that the only possible dehydration and dehydroxylation events, for the DCB treated clays, within the temperature range of interest

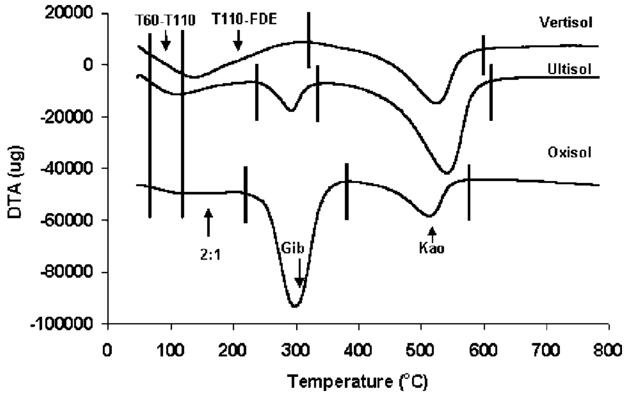

Fig. 1. Differential thermal analysis of selected samples of DCB-treated clays from an oxisol, ultisol, and vertisol. Range of temperatures evaluated included at 60–110 °C, and 110 °C and the temperature of the first dehydroxylation event (FDE). Kao indicates kaolinite; Gib indicates gibbsite; 2:1 indicates expandable clay minerals.

(60–800 °C) were those related to gibbsite, kaolinite, and the expandable 2:1 clay minerals. The thermal patterns were, therefore, divided into three regions, for analysis (Fig. 1). The weight lost by each sample between the temperatures of 60 and 110 °C (T60–T110) was considered to arise from water adsorbed on the surface of the clay particles (i.e., water of hydration). The weight loss between 110 °C and the first dehydroxylation event (FDE); i.e., 250–350 °C for gibbsite or 450–550 °C for kaolinite (no gibbsite present) was considered to be due to water solvating exchangeable Na in the 2:1 clay minerals. A third water content was calculated by summation of the former two measurements, i.e., the water contents between 60 °C and the first dehydroxylation event (T60–FDE).

Simple and multiple regression analysis were obtained using the PROC REG and stepwise procedures of the software SAS [29].

3. Results and discussion

3.1. Characterization of the soils

The average physical and chemical properties of the soils collected in this study shows that they have a high clay content (>50%), acid pH (<5.0), high organic carbon content ($C > 1\%$), low cation exchange capacity ($CEC < 15\,cmol_c/kg$), low base saturation ($V < 50$), and moderate exchangeable aluminum ($Al > 20\%$) (Table 2). However, the data also show the effects of weathering intensity (Table 2). The oxisols are the most weathered soils, and they have the highest average clay contents, are the most acidic, and have the lowest organic carbon content, cation exchange capacity and base saturation. The inceptisols, vertisols, and mollisols are not highly weathered and represent the other extreme.

X-ray diffraction analyses of the DCB-treated clays confirm that the oxisols and ultisols/alfisols are enriched with kaolinite and gibbsite (Fig. 2).

By contrast, the inceptisols, vertisols, and mollisols contain, on average, 18% expandable 2:1 minerals (Table 3). These minerals are not stable under subtropical conditions and ultimately weather to form iron oxides, gibbsite, and 1:1 clay minerals like kaolinite (Table 3). Kaolinite is the most common mineral in the clay fraction of subtropical soils [1,2,23,28]. In areas where the average annual precipitation is above 1500 mm and the average annual temperature

Table 2
Particle size distribution and basic soil chemical characteristics of the different soils

Soil order		Sand (%)	Silt (%)	Clay (%)	pH H_2O	C[a] (g/kg)	CEC[b] ($cmol_c$/kg)	V[c] (%)	Al[d] (%)
Oxisols	Average	13.8	13.0	72.3	4.88	13.70	9.50	27.81	34.26
	S.D.[e]	7.3	4.1	9.6	0.54	10.26	3.33	26.01	30.42
	C.V.[f]	53	32	13	11	75	35	94	89
Alfisols	Average	16.36	20.14	62.14	5.21	13.89	12.93	45.70	21.46
Ultisols	S.D.	9.72	8.11	15.74	0.46	11.14	3.26	26.56	27.97
	C.V.	59	40	25	9	80	25	58	130
Vertisols	Average	25.31	26.06	48.53	5.49	23.22	23.27	64.76	12.74
Inceptsols	S.D.	11.03	6.93	13.91	0.73	12.52	9.48	29.27	24.74
Mollisols	C.V.	44	27	29	13	54	41	45	194
All soils	Average	17.75	18.54	63.02	5.14	16.47	14.29	42.84	24.91
	S.D.	10.19	8.24	15.97	0.63	11.77	8.17	30.93	29.33
	C.V.	57	44	25	12	71	57	72	118

[a] Organic carbon content.

[b] Cation exchange capacity.

[c] Base saturation.

[d] Aluminum saturation.

[e] S.D. indicates standard deviation.

[f] C.V. indicates coefficient of variation.

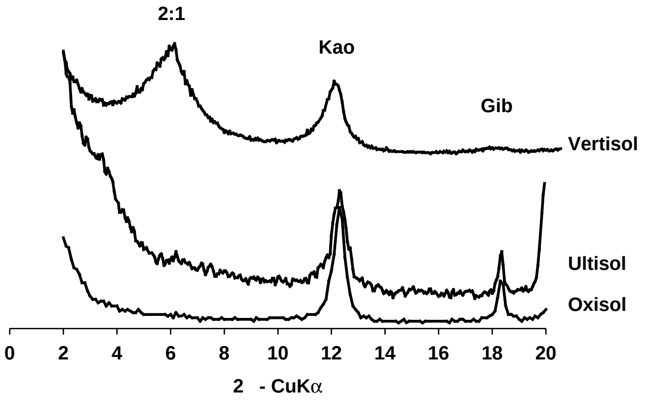

Fig. 2. X-rays diffraction patterns of the DCB-treated clays from selected vertisol, ultisol, and oxisol soils samples.

is above 20 °C, there is an excess of water leaching the soil profiles. Under these conditions, soil kaolinites are also unstable and will ultimately weather to gibbsite as observed in bauxites of the Amazon [30] and in gibbsitic soils of the savannas in Australia [2]. During the weathering process, iron that is released from both primary and secondary minerals is concentrated as iron oxides (mostly goethite, hematite, and maghemite) that also have very low solubility.

Table 3 shows that while the percentage of kaolinite is almost constant throughout all soils (60–70%), the percentage of 2:1 minerals decreases (18–8%) while the amount of iron oxides (12–19%), and gibbsite (3–13 %) increase from the less weathered soils to the oxisols. Gibbsite is sometimes present in the BC and/or C horizons of the vertisols, mollisols, and inceptisols because it can be one of the first minerals formed in the weathering process [31]. When poorly crystalline, however, this gibbsite is usually re-dissolved and combined with silicic acid to form kaolinite. Consequently, the coefficient of variation for gibbsite content is over 100% among the least weathered soils because some horizons had no gibbsite, especially in the vertisols and mollisols that have chemical properties which prevent its stabilization [23,28,31].

3.2. *Relationship between water content and clay mineralogy*

The TG/DTA diagrams were used to define the exact temperature and mass of the sample where dehydration and dehydroxylation events started and ended (Fig. 2). The average T_d for the soil gibbsites, taken as the minima of the DTA endotherms, was 282 °C with a range of 255–312 °C. Variations in the T_d of gibbsite have been attributed to crystallinity of the mineral [4], which in turn, is related to position in the landscape [23] and the local weathering environment [31].

The kaolinites had an average T_d, taken as the minima of the DTA endotherms, of 516 °C with a range of 478–553 °C. These results are in close agreement with the literature for soils [2,28], but are lower than the values found for standard kaolinites. This difference is due to the poor crystallinity, small particle size, and variable chemical composition of soil kaolinites [6].

Following Smykatz–Kloss [7], 70% of the soil kaolinites examined in this study are extremely disordered and come from the least weathered profiles. The remainders are strongly disordered (30%) and were derived mostly from the oxisols where the intense leaching process might ultimately weather releasing silicic acid and form gibbsite.

The correlation coefficients between the percentages of kaolinite, gibbsite, and the water content, independent of the range of temperature evaluated, are negative or approximately, zero (Table 4). Therefore, an increase in the percentages of these minerals results in less water being physically adsorbed.

The average specific surface areas of kaolinite and gibbsite are small compared to the SSA of expandable 2:1 clay minerals (Bohn et al., 1985). The SSA of expandable clay

Table 3
Mineralogy and moisture content among the three ranges of temperature of the clay size fractions of the different soils

Soil order		Gibbsite (%)	Kaolinite (%)	2:1 (%)	Fe_2O_3 (%)	Moisture content (%)		
						T60-T110	T110-FDE	T60-FDE
Oxisols	Average	13.09	60.55	7.80	18.55	0.47	1.25	1.73
	S.D.	9.51	9.55	2.46	3.77	0.24	0.30	0.41
	C.V.	73	16	32	20	51	24	24
Alfisols	Average	3.30	69.75	11.12	15.83	0.68	1.26	1.96
Ultisols	S.D.	3.36	6.92	3.61	4.43	0.32	0.47	0.62
	C.V.	102	10	32	28	47	37	32
Vertisols	Average	3.40	67.20	17.75	11.65	1.43	2.44	3.92
Inceptsols	S.D.	5.59	8.59	7.46	4.02	0.85	1.26	2.00
Mollisols	C.V.	165	13	42	35	59	52	51
All soils	Average	7.87	64.75	11.48	15.90	0.80	1.59	2.41
	S.D.	8.74	9.45	6.23	4.91	0.65	0.91	1.48
	C.V.	111	15	54	31	81	57	62

Table 4
Pearson Linear correlation coefficients (r) and the probability (P) of statistical significance for different minerals and the cation exchange capacity (CEC) as related to moisture content calculated between the temperatures of 60, 110 °C and the temperature of the first dehydroxylation event (FDE)

Variable		Moisture content		
		T60–T110	T110–FDE	T60–FDE
Gibbsite	r	−0.35	−0.20	−0.28
	P	<0.01	n.s.[a]	<0.05
Kaolinite	r	0.01	−0.12	−0.07
	P	n.s.	n.s.	n.s.
2:1	r	0.66	0.76	0.76
	P	<0.0001	<0.0001	<0.0001
CEC	r	0.62	0.70	0.71
	P	<0.0001	<0.0001	<0.0001

[a] n.s. Indicates “statistically non-significant”.

minerals usually exceeds 100 m^2/g [18] and are associated with the presence of internal surfaces not found in kaolinite and gibbsite.

If the average water contents between 110 °C and the FDE (T110-FDE) are assumed to be associated with the expandable 2:1 clay minerals, therefore, the water contents of 22, 18, and 28% can represent the smectites/vermiculites in the highly weathered oxisols, in the moderately weathered ultisols and alfisols and in the least weathered mollisols, inceptisols, and vertisols. These values of water contents are close agreement with those reported for standard smectites and vermiculites [10,13].

The amount of expandable 2:1 clay minerals actually produced positive and highly significant ($P < 0.0001$) correlation with all measures of water content (Table 4). The weakest correlation was with water content between the temperatures of 60 and 110 °C ($r = 0.66$). The correlation improved when the water content between 110 °C and the temperature of the first dehydroxylation event (T110–FDE) was considered ($r = 0.76$) or when the full temperature range (T60–FDE) was evaluated ($r = 0.76$). The quality of the various correlations supports the use of thermal analysis for quantifying expandable 2:1 clay minerals in subtropical soils when more traditional techniques, such as X-ray diffraction, are not available.

3.3. *Water content and the cation exchange capacity (CEC)*

Whole soil CEC values and organic carbon contents show no significant statistical correlation ($r = 0.03$, $P > 5\%$), suggesting that the CEC values are mostly derived from negative charges present in the inorganic fraction (Fig. 3). Pearson linear correlation coefficients for CEC and water content were all highly significant ($P < 0.0001$) and increased with the range of temperature evaluated (0.62–0.71) confirming that the CEC values of the soils are mostly related to the presence of 2:1 clay minerals (Table 4; Fig. 4).

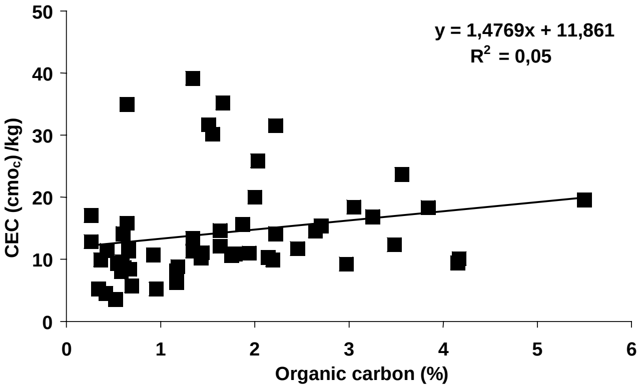

Fig. 3. Organic carbon content (C) and the cation exchange capacity (CEC) of all soil samples.

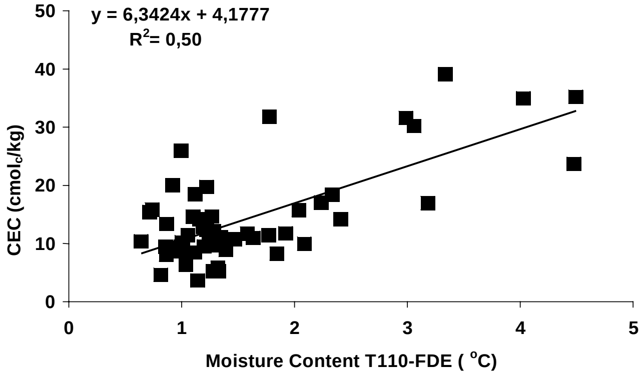

Fig. 4. Relationship between the water content (T110–FDE) and the cation exchange capacity (CEC) of the soils.

Stepwise correlations [29] between CEC values and all the variables of Table 3 show that only the percentages of 2:1 clay minerals and organic carbon content were significantly correlated ($R^2 = 0.5747$, $P < 0.0001$). Between these two variables, the 2:1 clay minerals contributed about 86% of the determination coefficient while the organic carbon content contributed only 14% of the R^2.

Our data are not described by the thermal activity index (F) of Gibbs et al. [22] (Fig. 5), presumably because these

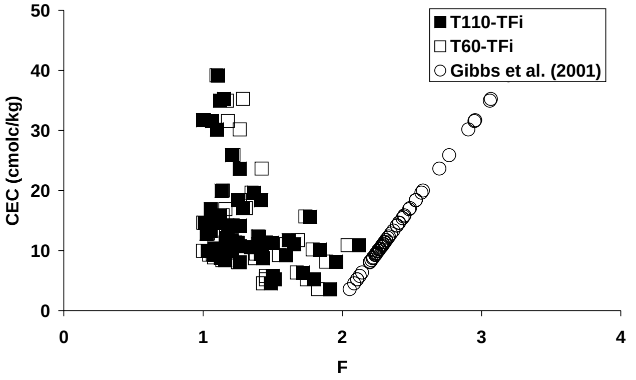

Fig. 5. Cation exchange capacity (CEC) and the relative thermal activity index (F) of the soils.

authors considered a much wider temperature range (up to 1100 °C) and used whole soil material for analysis. The Barbados soils were all developed over coralline limestone or chalks and most of the water was lost above 600 °C.

4. Conclusion

The water content of DCB-treated clay size fraction materials of subtropical soils measured in three different ranges of temperatures, gave significant ($P < 0.0001$) linear correlations with the percentage of expandable 2:1 clay minerals and the cation exchange capacities of the whole soil materials. Kaolinites is main clay size mineral in tropical and subtropical soils and present high degree of disorder evaluated by the temperature of dehydroxylation of the mineral. Cation exchange capacity of soil materials with different degrees of weathering presented high correlation with the percentage of the 2:1 clay minerals and not the organic carbon content.

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References

[1] U. Schwertmann, A.J. Herbillon, Some aspects of fertility associated with the mineralogy of highly weathered tropical soils, in: R. Lal, P.A. Sanchez (Eds.), Myths and Science of Soils of the Tropics, Special Publication No. 29, Soil Science Society of America Inc., Madison, 1992, pp. 47–60.

[2] B. Singh, R.J. Gilkes, J. Soil Sci. 43 (1992) 645–667.

[3] J.B. Dixon, Clays Clay Min. 14 (1966) 83–89.

[4] S.K. Mehta, A. Kalsotra, M. Murat, Thermoch. Acta 205 (1992) 191–203.

[5] F.J. Huertas, S. Fiore, J. Linares, Clays Clay Min. 45 (1997) 587–590.

[6] D. Yeskis, H. Shimazu, K. Nagasawa, A. Masuda, H. Saito, Amer. Miner. 70 (1985) 159–164.

[7] W. Smykatz-Kloss, Differential Thermal Analysis, Applications and Results in Mineralogy, Springer, New York, 1975.

[8] S. Guggenheim, A.F.K. van Groos, Clays Clay Min. 49 (2001) 433–443.

[9] J.L. Post, B.L. Cupp, F.T. Madsen, Clays Clay Min. 45 (1997) 240–250.

[10] I. Barshad, Thermal analysis techniques for mineral identification and mineralogical composition, in: C.A. Black (Eds.), Methods of Soil Analysis, Part 1; Physical and Mineralogical Methods, American Society of Agronomy Inc., Madison, 1965, pp. 699–742.

[11] S. Speil, L.H. Berkelhamer, J.A. Pask, B. Davies, Differential Thermal Analysis, Its Application to Clays and other Aluminous Minerals, Technical Report No. 664, United States Department of Interior, 1945.

[12] J. Cuadros, A. Delgado, A. Cardenete, E. Reyes, J. Linares, Clays Clay Min. 42 (1994) 643–651.

[13] C.M. Earnest, Compositional Analysis by Thermogravimetry, American Society of Testing Materials, Philadelphia, 1988.

[14] Z. Malek, V. Balek, D. Garfinkel-Shweky, S.J. Yariv, Therm. Anal. 48 (1997) 83–92.

[15] B.P.K. Yerima, F.G. Calhoun, A.L. Senkayi, J.B. Dixon, Soil Sci. Soc. Am. 49 (1985) 462–466.

[16] W.G. Harris, K.A. Hollen, S.R. Bates, W.A. Acree, Clays Clay Min. 40 (1992) 335–340.

[17] A.D. Karathanasis, B.F. Hajek, Soil Sci. Soc. Am. J. 46 (1982) 419–425.

[18] H. Bohn, B. McNeal, G. O'Connor, Soil Chemistry, second ed., Wiley, New York, 1985.

[19] A.C.S. da Costa, C.A. Torino, J.G. Rak, Acta Sci. 21 (1999a) 491–496.

[20] C.H. Lim, M.L. Jackson, R.D. Koons, P.A. Helmke, Clays Clay Min. 28 (1980) 223–229.

[21] C. Ma, R.A. Eggleton, Clays Clay Min. 47 (1999) 174–180.

[22] H.A.A. Gibbs, L.W. O'Garro, A.M. Newton, Therm. Acta 374 (2001) 137–143.

[23] A.C.S. da Costa, J. Bigham, F.E. Rhoton, S.J. Traina, Clays Clay Min. 47 (1999) 466–473.

[24] E.M. Piccirillo, A.J. Melfi, P. Comin-Chiaramonti, G. Bellieni, M. Ernesto, L.S. Marques, A.J.R. Nardy, I.G. Pacca, A. Roisember, D. Stolfa, in: J.D. MacDougall (Ed.), Continental Flood Basalts, Kluwer Academic Publishers, Dordrecht, 1988, pp. 218–245.

[25] EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA—EMBRAPA, Sistema Brasileiro de Classificação de Solos, Centro Nacional de Pesquisas de Solo, Brasília, 1999.

[26] O.P. Mehra, M.L. Jackson, Clays Clay Miner. 7 (1960) 317–327.

[27] G. Brown, G.W. Brindley, X-ray Diffraction procedures for clay mineral identification, in: G. Brown (Ed.) Crystal Structure of Clay Minerals and their X-ray Identification, Mineralogical Society, London, 1980.

[28] V.F. Melo, B. Singh, C.E.G.R. Schaefer, R.F. Novais, M.P.F. Fontes, Soil Sci. Soc. Am. J. 65 (2001) 1324–1333.

[29] SAS. STATISTICAL ANALYSIS SYSTEM INSTITUTE, SAS/STAT Procedure Guide for Personal Computers, fifth ed., SAS Institute, Cary, 1999.

[30] B. Hieronymus, B. Kotschoubey, W. Truckenbrodt, J. Boulegue, Sci. Geol. Bull. 42 (1989) 3–14.

[31] B. Mulyanto, G. Van Ranst, E. Stoops, Geoderma 89 (1999) 287–305.

[32] Soil Survey Staff, AID/USDA-SCS/SMSS, Keys to Soil Taxonomy, fifth ed., Pocahontas Press, Blacksburg, 1992.