

## Clay mineralogy effects on sodium fluoride pH of non-allophanic tropical soils

M. E. Alves<sup>A</sup> and A. Lavorenti<sup>B,C</sup>

<sup>A</sup>Departamento de Física e Informática, Instituto de Física de São Carlos – IFSC/USP, Caixa Postal 369, 13560-970, São Carlos (SP), Brazil.

<sup>B</sup>Departamento de Ciências Exatas, Escola Superior de Agricultura ‘Luiz de Queiroz’ – ESALQ/USP, Caixa Postal 09, 13418-900, Piracicaba (SP), Brazil.

<sup>C</sup>Corresponding author. Email: alavoren@esalq.usp.br

**Abstract.** Soil pH measured in 1 M NaF ( $\text{pH}_{\text{NaF}}$ ) can be a useful tool for soil classification and to provide better advice on the chemical management of agricultural soils in the tropics. In this study, we verified the effects of clay mineralogy on  $\text{pH}_{\text{NaF}}$  values of non-allophanic soils of São Paulo State, Brazil. Fourteen subsurface soil samples were characterised for chemical properties, clay content, clay mineralogy, and for  $\text{pH}_{\text{NaF}}$  values, which were measured in the whole soil and in both natural and deferrified (dithionite-treated) clay fractions. Regression and correlation analyses showed that both ammonium-oxalate-extractable Al ( $\text{Al}_o$ ) and gibbsite contents have positive relationships with both clay and soil  $\text{pH}_{\text{NaF}}$  values. On the other hand, kaolinite is inversely related to the  $\text{pH}_{\text{NaF}}$  measured in the clay and has nonsignificant effect on soil  $\text{pH}_{\text{NaF}}$ . X-ray diffraction patterns of dithionite-treated clays did not show disruption of kaolinite or gibbsite after the treatment with 1 M NaF, suggesting that the displacement of surface OH groups by  $\text{F}^-$  seems to be the main mechanism associated with the pH increase verified in the NaF solution after its contact with the deferrified clay fraction. The smaller influence of hematite on  $\text{pH}_{\text{NaF}}$  seems to be due to its correlation to  $\text{Al}_o$ . Goethite and ammonium-oxalate-extractable Fe ( $\text{Fe}_o$ ) exert no effect on  $\text{pH}_{\text{NaF}}$ . Finally, the relationships observed in the present study strongly suggest that  $\text{pH}_{\text{NaF}}$  values  $<10.3$  measured in non-allophanic kaolinitic soils with low levels of non-humified organic matter are essentially due to their smaller  $\text{Al}_o$  and gibbsite contents, which agrees with the direct correlation verified between  $\text{pH}_{\text{NaF}}$  and soil weathering degree.

**Additional keywords:** gibbsite, kaolinite,  $\text{pH}_{\text{NaF}}$ , ammonium-oxalate-extractable Al, weathered soils.

### Introduction

Increase in pH of 1 M NaF solution ( $\text{pH}_{\text{NaF}}$ ) after its contact with soil was recommended by Fieldes and Perrott (1966) as a suitable field or laboratory test to evidence the presence of allophanic material. Subsequently,  $\text{pH}_{\text{NaF}}$  was also used to estimate the phosphate adsorption capacities of both volcanic-ash-derived (Alvarado and Buol 1985) and non-allophanic soils (Singh and Gilkes 1991; Gilkes and Hughes 1994). The use of  $\text{pH}_{\text{NaF}}$  as a P adsorption estimator is based on the premise that  $\text{F}^-$  displaces mineral OH surface groups that are exchanged by P ions during the adsorption process. This also seems to be the reason for the high positive correlation verified by Alves and Lavorenti (2004) between  $\text{pH}_{\text{NaF}}$  and sulfate adsorption on weathered Brazilian subsoils.

Soil  $\text{pH}_{\text{NaF}}$  values can be lowered by acids derived from non-humified organic matter or increased when the NaF solution reacts with soil noncrystalline minerals and/or carbonates (Perrott *et al.* 1976a). Furthermore,  $\text{pH}_{\text{NaF}}$  can

also be increased due to NaF reactions with exchangeable Al, Al-humus complexes, and interlayered hydroxy-Al present in layer silicates (Wada 1980). In this context, the greatest reactivity of noncrystalline minerals towards NaF solution (Perrott *et al.* 1976a) is used in Soil Taxonomy (Soil Survey Staff 1999) as an additional criterion to define the isotic family mineralogy class. Likewise, the soil reaction towards 1 M NaF constitutes a field test adopted by the Australian Soil Classification System (Isbell 1996) to estimate the amount of reactive aluminium aiming at the identification of Podsol diagnostic B-horizons.

Besides its utilisation as an additional criterion for soil classification,  $\text{pH}_{\text{NaF}}$  is potentially useful as an ancillary tool for better advice on the chemical management of weathering tropical soils, including the determination of both fertiliser-P and gypsum requirements (Bolland *et al.* 1996; Alves and Lavorenti 2004).

Most of Brazilian soils were formed under tropical conditions, which promote intense removal of silica and

accumulation of hydrated iron and aluminium oxides. Furthermore, both higher temperature and rainfall do not favour the presence of high amounts of organic matter in such soils. Although high contents of allophane are found in some South American regions (Escudéy and Galindo 1988; Buytaert *et al.* 2002), there is no relation to the presence of this tephra-derived material in soils of São Paulo State, Brazil (de Oliveira 1999), whose clay mineralogy is dominated mainly by kaolinite, gibbsite, hematite, and goethite, with traces of other minerals (Schwertmann and Herbillon 1992). It is probable, as verified by Varajão *et al.* (2002) for a Brazilian hydromorphic lateritic soil, that the small amounts of noncrystalline aluminosilicates present in the São Paulo State soils are derived from kaolinite and/or gibbsite destabilisation.

Considering that most studies on the interactions between F solutions and soil minerals were carried out with either isolated mineral specimens (Huang and Jackson 1965; Bower and Hatcher 1967; Perrott *et al.* 1976a) or employing acid fluoride solutions (Arocena *et al.* 1995), the present study aims to evaluate the effects of clay mineralogy of non-allophanic tropical soils on  $\text{pH}_{\text{NaF}}$ .

### Material and methods

Samples of the subsurface horizons of 8 Oxisols, 4 Ultisols, 1 Alfisol, and 1 Entisol (Soil Survey Staff 1999) were collected from different sites of São Paulo State, Brazil, air-dried, and crushed to pass through a 2-mm sieve. General information on these soils including classification, parent materials, localisation, sampled horizon, and depth of sampling is presented in Table 1.

Clay content was determined by the pipette method (Gee and Bauder 1986), organic carbon by the Walkley and Black method (Nelson and Sommers 1982), exchangeable Al by extraction with 1 M KCl (Bertsch and Bloom 1996), and soil pH by measuring in 0.01 M  $\text{CaCl}_2$  at 1:2.5 soil (g)/solution (mL) ratio (EMBRAPA 1997). The Si, Fe, and Al contents associated to secondary minerals were determined in extracts obtained after boiling both 1 g of soil for 30 min in 20 mL of

9 M  $\text{H}_2\text{SO}_4$  (Fe and Al) and the remaining solid for 1 min in 150 mL of 0.2 M NaOH (Si). The acid extracts were analysed for Al and Fe by atomic absorption spectrometry (AAS), whereas Si was quantified in the alkaline extracts by colourimetry (EMBRAPA 1997). With these data the weathering indices Ki ( $\text{SiO}_2/\text{Al}_2\text{O}_3$ , mol/mol) and Kr ( $\text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ , mol/mol) were calculated (EMBRAPA 1997). Dithionite- and ammonium-oxalate-extractable Fe and ammonium-oxalate-extractable Al were determined by AAS after extractions carried out directly in the clay fraction ( $<2 \mu\text{m}$ ), previously separated by gravity settling (Jackson 1969), following the procedures outlined by Buurman *et al.* (1996) ( $\text{Fe}_d$ ) and McKeague and Day (1966) ( $\text{Fe}_o$  and  $\text{Al}_o$ ). The  $\text{pH}_{\text{NaF}}$  values were measured in the soil, natural clay, and dithionite-treated clay after shaking 0.5 g of each material for 1 h with 20 mL of 1 M NaF (Bolland *et al.* 1996).

The mineralogical composition of the clay fraction was evaluated qualitatively through X-ray diffraction (XRD) analysis. For the dithionite-treated clays, oriented slides of Mg-saturated and K-saturated clay dried at 25°C were analysed in a Phillips PW 1830 diffractometer using monochromated  $\text{CuK}\alpha$  radiation at 40 mA and 40 kV. The scans were obtained between 5 and 30°2 $\theta$  at a speed of 1.2°2 $\theta$ /min. The XRD patterns of the heated K-saturated clays (350°C and 550°C) and Mg-saturated clays treated with ethylene glycol were recorded using the same procedure. In order to evaluate the causes of the relations verified between  $\text{pH}_{\text{NaF}}$  and kaolinite and gibbsite contents in the deferrified clay, we analysed the deferrified clay of Soils 4 and 11, which showed contrastable kaolinite and gibbsite contents, by XRD before and after the reaction with 1 M NaF. Oriented slides of deferrified clay dried at 25°C were analysed by XRD as above described.

XRD analyses were also performed on non-oriented powder samples of the clay fractions after their treatments with boiling 5 M NaOH for concentration of iron oxides (Kämpf and Schwertmann 1982). The patterns were recorded with a Siemens D5000 computer-oriented diffractometer using monochromated  $\text{CoK}\alpha$  radiation at 25 mA and 35 kV. The scans were obtained from 20 to 45°2 $\theta$  at a speed of 0.6°2 $\theta$ /min, and both peak positions and raw areas were determined using the software EVA 3.09.

Kaolinite and gibbsite contents were semiquantified by differential thermal analysis (Tan *et al.* 1986) carried out in the dithionite-treated clay previously mixed with anhydrous  $\text{Al}_2\text{O}_3$  as inert material. The analyses were performed under  $\text{N}_2$  atmosphere in a Shimadzu DSC-50 analyser operated at a heating rate of 10°C/min. The results

**Table 1. Classification, parent materials, localisation in the São Paulo State and sampling depth of the soils**

Soil	Classification	Parent material	Localisation	Horizon	Depth (cm)
1	Rhodic Acrudox	Basalt	Ribeirão Preto	B	100–140
2	Rhodic Eutrudox	Basalt	Iracemápolis	B	100–110
3	Rhodic Hapludox	Basalt	Luís Antonio	B	80–100
4	Rhodic Acrudox	Basalt	Luís Antonio	B	150–170
5	Xanthic Acrustox	Basalt	Guaíra	B	100–130
6	Typic Hapludox	Schist	Piracicaba	B	100–110
7	Typic Hapludox	Sandstone	Piracicaba	B	100–110
8	Typic Hapludox	Sandstone	São Carlos	B	80–100
9	Typic Hapludalf	Diabase	Piracicaba	B	30–40
10	Typic Hapludult	Sandstone	Pindorama	B	100–120
11	Typic Hapludult	Sandstone	Vera Cruz	B	100–120
12	Typic Hapludult	Schist	Rio Claro	B	70–80
13	Typic Hapludult	Basalt	Piracicaba	B	100–110
14	Typic Quartzipsamment	Sandstone	São Pedro	C	80–100

were corrected to the total-clay fraction considering the weight difference of the clay fraction before and after iron oxide removal. Clay contents of hematite (Hm) and goethite (Gt) were semiquantified from the ratio  $Hm/Hm + Gt$  and the difference  $Fe_d - Fe_o$ . The ratio  $Hm/Hm + Gt$  was calculated using the following equation derived by Resende *et al.* (1987):

$$R = \frac{0.708A_{Hm104}}{A_{Gt110} + 0.708A_{Hm104}} \quad (1)$$

where R is  $Hm/Hm + Gt$  and  $A_{Hm104}$  and  $A_{Gt110}$  are the respective areas of the hematite (104) and goethite (110) diffraction peaks in the XRD patterns of the iron-oxide-concentrated clay. The factor 0.708 corresponds to the ratio  $A_{Gt110}/A_{Hm104}$  found by Jones (1981) in a 1 : 1 hematite and goethite mixture.

For clays that had goethite and hematite, the following equations were used:

$$Gt = \frac{Fe_d - Fe_o}{\frac{160(1-x)}{160-58x} \frac{R}{(1-R)} + \frac{80(1-y)}{89-29y}} \quad (2)$$

where Gt is goethite clay content (%),  $Fe_d$  is dithionite-extractable iron (%  $Fe_2O_3$ ),  $Fe_o$  is ammonium oxalate-extractable iron (%  $Fe_2O_3$ ),  $x$  and  $y$  are respective aluminium substitutions in hematite and in goethite (mol/mol), and

$$Hm = \frac{R}{1-R} Gt \quad (3)$$

where Hm is hematite clay content (%).

For clays that did not have hematite, the goethite clay content was determined with the following equation:

$$Gt = (Fe_d - Fe_o) \frac{(89 - 29y)}{80(1 - y)} \quad (4)$$

Equations 2, 3, and 4 were derived considering that the respective unit cells of Al-substituted hematite and goethite are given by  $Fe_{(2-2x)}Al_{2x}O_3$  and  $Fe_{(1-y)}Al_yOOH$  and that the iron content associated to hematite plus goethite corresponds to  $Fe_d - Fe_o$ . The aluminium substitutions were determined from iron-oxide-concentrated XRD data using the equations derived by Schwertmann *et al.* (1979) for hematite and by Schulze (1984) for goethite.

Finally, the experimental data were submitted to correlation and regression analyses, to evaluate the relationships between them, and to the *t*-test for mean comparisons. These analyses were carried out using the Statistical Analysis System (SAS) software, Version 6.11.

## Results and discussion

### Soil and clay properties

The soil and clay properties are summarised in Table 2, where it can be verified that most of the soils were acidic ( $pH_{CaCl_2} \leq 5$ ), clayey (clay >350 g/kg) (EMBRAPA 1999), poor in organic carbon (0.6–7.8 g/kg), and had no exchangeable Al.

The Ki and Kr indexes are used in the Brazilian System of Soil Classification to characterise the soil weathering status. As the weathering increases, there is a progressive silica loss from clay minerals and a concomitant accumulation of iron and aluminium oxides. Therefore, the lower the Ki and Kr values, the more weathered is the soil. The Ki range (0.49–1.81) shows the wide variation in weathering status of the studied soils, whereas the Kr values separate them into

oxidic ( $Kr < 0.75$ ) and kaolinitic ( $Kr > 0.75$ ) (EMBRAPA 1999), which agrees with the clay mineralogy data (Table 2). The correlations between Ki index and both kaolinite ( $r = 0.95$ ,  $P < 0.01$ ) and gibbsite ( $r = -0.99$ ,  $P < 0.01$ ) deferrified clay contents are in line with the above-mentioned weathering trends. A progressive enhancement in the relative intensities of the gibbsite diffraction peaks due to the increase in the soil weathering degree can be noted comparing, for example, the XRD patterns of the deferrified clays of the soils 7 ( $Ki = 1.65$ ), 3 ( $Ki = 0.97$ ), 5 ( $Ki = 0.85$ ), and 4 ( $Ki = 0.49$ ) (Fig. 1). On the other hand, no diffraction peak in the XRD patterns of the iron-oxide-concentrated clays of such soils (Fig. 2) showed a systematic alteration in its relative intensity from the less to the more weathered soil.

The  $pH_{NaF}$  values ranged from 9.0 to 10.7 in the soil, 9.0 to 11.4 in the clay, and 10.6 to 11.9 in the deferrified clay. Application of the *t*-test at  $P = 0.01$  showed that the mean  $pH_{NaF}$  value of the deferrified clay ( $11.1 \pm 0.5$ ) was bigger than that of the natural clay ( $10.2 \pm 0.8$ ).

### Clay mineralogy influence on $pH_{NaF}$

The mineralogy effect on the  $pH_{NaF}$  measured in the clay was initially assessed through regression analysis. From the scatter plots (Fig. 3) and the values of equation slopes, *F*-statistics, and determination coefficients ( $R^2$ ) presented in Table 3, it can be observed that  $Al_o$  exerts the greatest positive impact on clay  $pH_{NaF}$ , whereas kaolinite has a lowering effect. However, the correlations among the clay component contents (Table 4) make it difficult to reach this conclusion, since the kaolinite content decrease is accompanied by an increase in both gibbsite and  $Al_o$  contents.

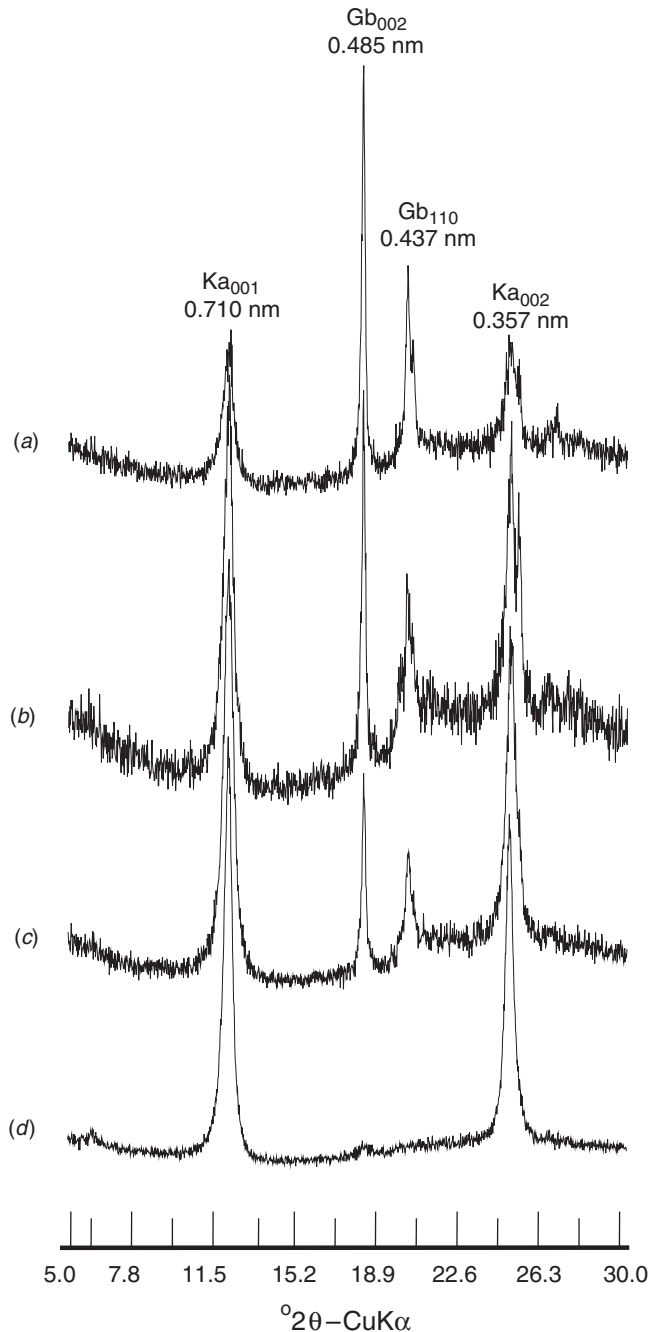
Perrott *et al.* (1976a) verified that the amorphous forms of Al, Si, and Fe were the main OH releasers to the 0.85 M NaF at pH 6.8, whereas kaolinite, gibbsite, hematite, and goethite reacted to a smaller extent. Besides the mineral type, the pH of the NaF solution also accounts for the OH release. Perrott *et al.* (1976b) verified that Si and Fe amorphous oxides reacted with the NaF solution up to pH 7.6 and about 8.5, respectively, and that only the Al amorphous oxide was able to release OH at pH values >8.5. Considering that the initial pH of the 1 M NaF solution used in the present study was ~8.3, the relationships verified in Fig. 3 between clay  $pH_{NaF}$  and both  $Fe_o$  and  $Al_o$  clay contents are in line with the results of Perrott *et al.* (1976b).

The  $pH_{NaF}$  measurement in the deferrified clay allowed better evaluation of the influence of kaolinite and gibbsite, the 2 most abundant minerals found in the clay fraction of weathered Brazilian soils, on  $pH_{NaF}$  without the influence of  $Al_o$ , which was removed during the treatment of clay with dithionite. Regression analysis showed that  $pH_{NaF}$  of the deferrified clay was directly dependent on the gibbsite content and inversely dependent on that of kaolinite (Fig. 4). These results show that gibbsite was the main OH source to the NaF solution even at pH values >8.3. The

**Table 2. Soil and clay properties**  
 C, Organic carbon; Al<sup>3+</sup>, exchangeable Al; Ki, weathering index given by 1.7 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) (EMBRAPA 1997); Kr, weathering index given by 1.7 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) (EMBRAPA 1997); Ka, kaolinite; Gib, gibbsite; Hm, hematite; Gt, goethite; Fe<sub>0</sub>, ammonium-oxalate-extractable Fe; Al<sub>0</sub>, ammonium-oxalate-extractable Al

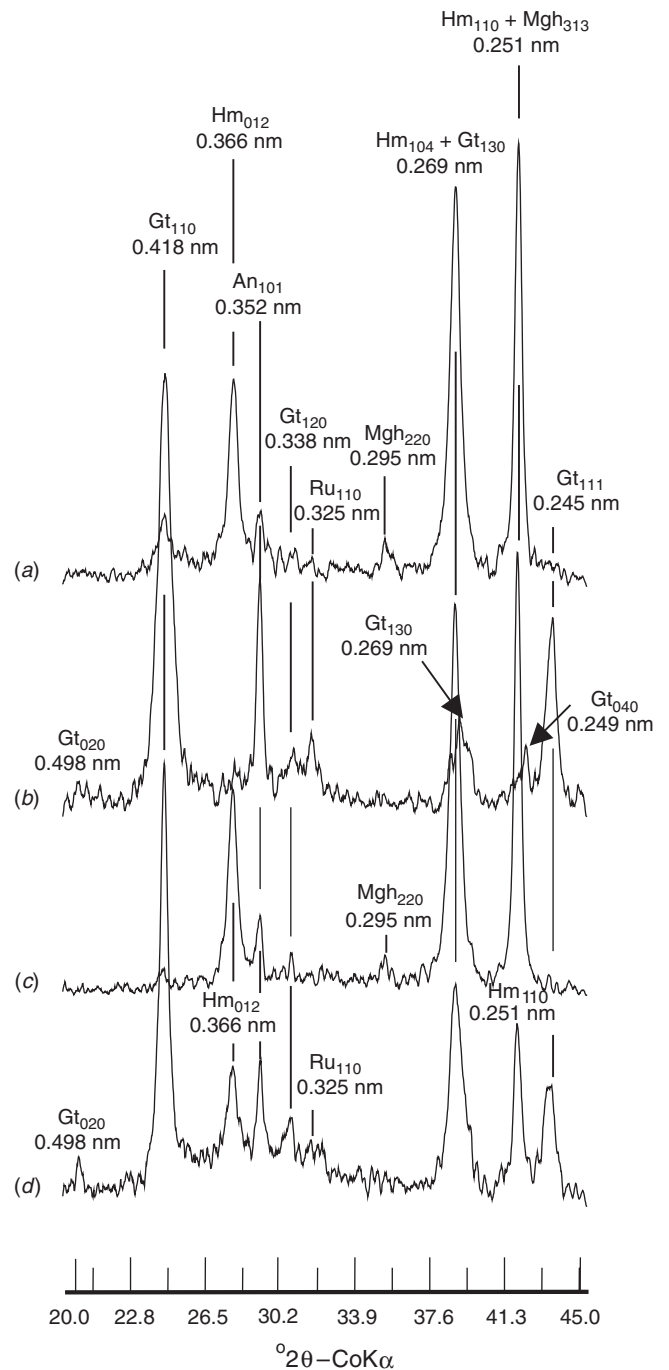
Soil	Whole soil										Clay fraction						Deferrified clay				
	C (g/kg)	Al <sup>3+</sup> (cmol <sub>c</sub> /dm <sup>3</sup> )	Clay (g/kg)	CaCl <sub>2</sub>	pH	pH NaF	Fe <sub>2</sub> O <sub>3</sub> (H <sub>2</sub> SO <sub>4</sub> digestion)	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Ki	Kr	pH <sub>NaF</sub>	Ka (%)	Gib (%)	Hm (%)	Gt (%)	Fe <sub>0</sub> (g/kg)	Al <sub>0</sub> (g/kg)	pH <sub>NaF</sub>	Ka (%)	Gib (%)
1	6.0	0	529	5.0	10.4	10.4	310	284	120	0.72	0.42	11.0	23.40	45.88	22.61	3.34	15	13	11.7	33.17	65.03
2	7.8	0	481	5.5	10.3	10.3	235	252	169	1.14	0.71	10.6	40.50	24.47	20.48	3.72	12	11	11.2	55.70	33.67
3	4.5	0.7	543	4.3	10.3	10.3	209	223	127	0.97	0.61	10.8	40.75	33.70	21.27	0.89	11	10	11.5	54.20	44.83
4	4.9	0	647	5.4	10.7	10.7	324	314	91	0.49	0.30	11.4	14.99	54.30	22.55	4.04	14	16	11.9	21.57	78.07
5	2.0	0	324	5.6	10.4	10.4	122	182	91	0.85	0.60	11.1	29.69	35.67	0	20.77	4	12	11.6	38.53	46.30
6	7.4	0.1	774	4.9	10.3	10.3	101	291	246	1.44	1.18	10.4	52.21	11.93	2.30	11.04	5	8	10.9	61.57	14.07
7	2.1	0	244	4.8	9.3	9.3	39	87	85	1.65	1.29	9.7	63.15	1.03	2.03	8.33	6	6	10.7	71.80	1.17
8	2.4	0	421	4.8	10.3	10.3	69	200	81	0.69	0.56	10.9	25.61	55.26	0.19	15.98	3	11	11.7	31.27	67.47
9	1.8	0	597	5.0	9.8	9.8	202	229	210	1.56	1.00	9.6	53.42	2.32	12.76	8.37	17	7	10.9	70.47	3.07
10	1.5	8.2	347	4.0	9.5	9.5	33	117	120	1.75	1.48	9.4	60.05	0.24	0.26	8.34	5	7	10.5	67.07	0.27
11	2.1	6.6	205	3.7	8.8	8.8	18	5	79	1.81	1.56	9.2	77.31	0	1.40	5.56	5	6	10.5	84.37	0
12	3.0	0	475	5.2	9.7	9.7	162	229	220	1.63	1.12	9.2	53.02	0	2.34	12.43	14	9	10.5	64.47	0
13	2.4	25.4	632	3.8	10.0	10.0	86	234	228	1.66	1.34	10.0	51.32	0.86	2.59	8.97	9	9	10.7	59.60	1.00
14	0.6	0.9	11	4.0	9.0	9.0	8	5	24	1.66	1.39	9.0	68.26	1.59	0.57	6.66	14	8	10.6	75.83	1.77

negative impact of kaolinite on  $\text{pH}_{\text{NaF}}$  may be ascribed to an inhibitory effect on the OH release by this mineral exerted by both high initial pH of the NaF solution and its progressive increase, which takes place after the contact of this solution with the clay sample. Therefore, the increase in kaolinite clay content, which is accompanied by a concomitant decrease in gibbsite ( $r = -0.94$ ,  $P < 0.01$ ), lowers the  $\text{pH}_{\text{NaF}}$ .

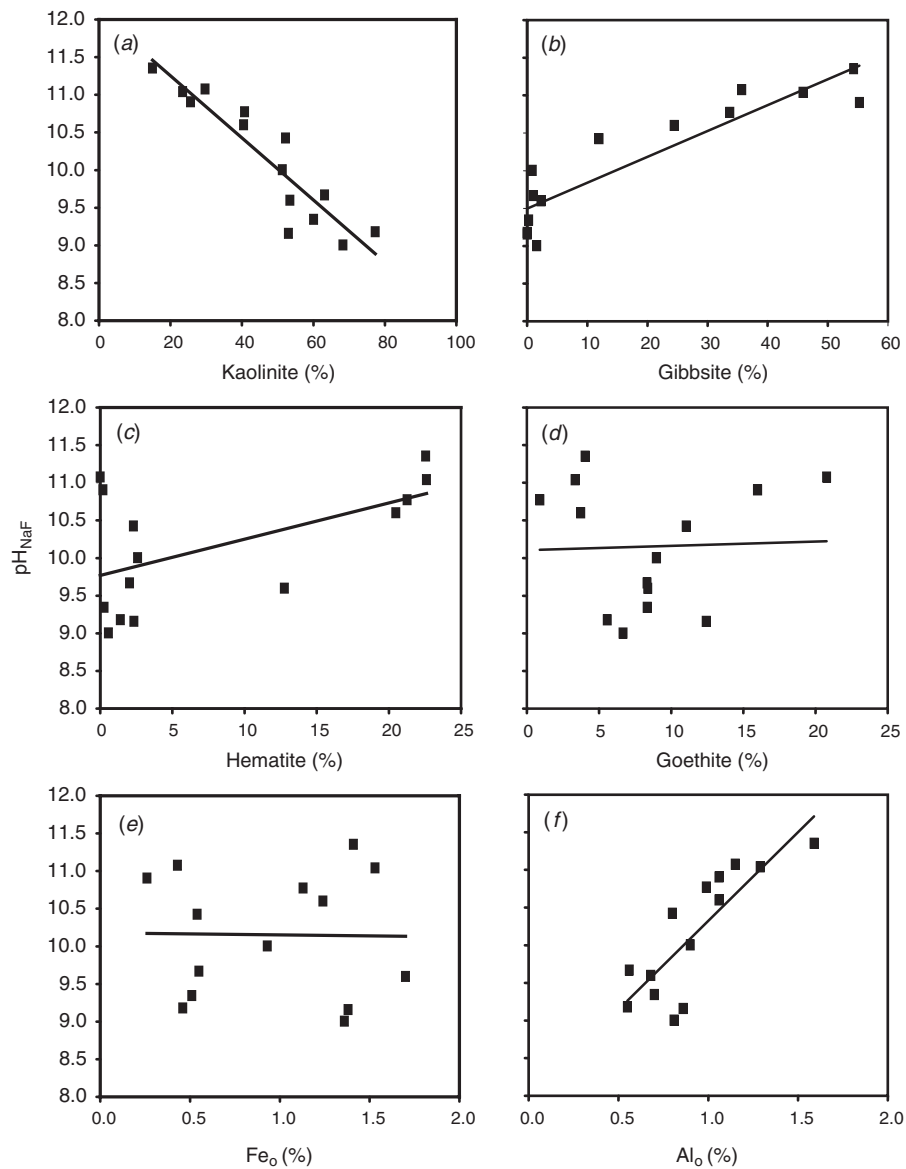


**Fig. 1.** X-ray diffraction patterns of the deferrified clays of Soils (a) 4, (b) 5, (c) 3, and (d) 7. Ka, Kaolinite; Gb, gibbsite.

The higher pH values normally measured in clay–NaF suspensions can be due to the release of OH surface groups displaced by  $\text{F}^-$  (Bower and Hatcher 1967) or to the disruption of minerals (Huang and Jackson 1965). The similarity of the diffraction peak intensities verified for both kaolinite and gibbsite before and after the NaF treatment



**Fig. 2.** X-ray diffraction patterns of the iron-oxide-concentrated clays of Soils (a) 4, (b) 5, (c) 3, and (d) 7. An, Anatase; Gt, goethite; Hm, hematite; Mgh, maghemite; Ru, rutile.



**Fig. 3.** Scatter plots relating  $\text{pH}_{\text{NaF}}$  values measured in the natural clay to (a) kaolinite, (b) gibbsite, (c) hematite, (d) goethite, (e) ammonium-oxalate-extractable Fe ( $\text{Fe}_o$ ), and (f) ammonium-oxalate-extractable Al ( $\text{Al}_o$ ) clay contents (% clay).

**Table 3.** Results of linear regression analyses relating  $\text{pH}_{\text{NaF}}$  values measured in the natural clay to clay component contents (% clay) ( $n = 14$ )

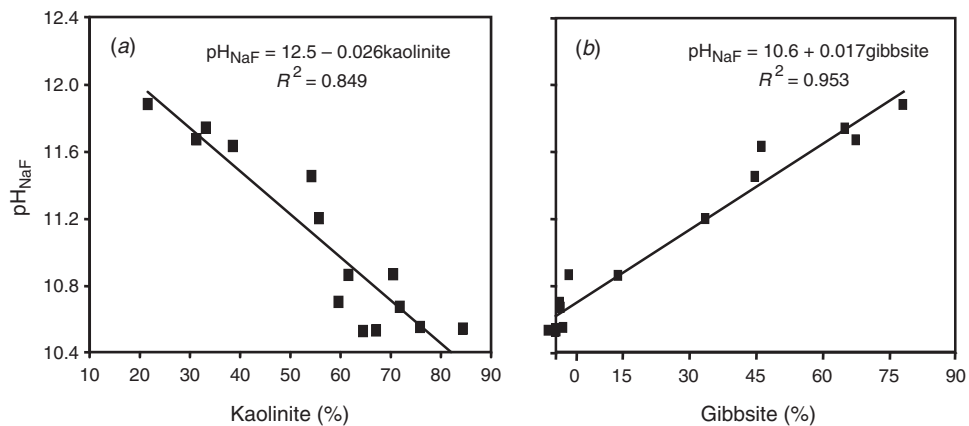
Regression equation	$R^2$	$F$ -value	$P > F$
$\text{pH}_{\text{NaF}} = 12.1 - 0.040 \text{ kaolinite}$	0.846	66.130	0.0001*
$\text{pH}_{\text{NaF}} = 9.5 + 0.030 \text{ gibbsite}$	0.830	58.599	0.0001*
$\text{pH}_{\text{NaF}} = 9.8 + 0.040 \text{ hematite}$	0.311	5.427	0.0381*
$\text{pH}_{\text{NaF}} = 10.1 + 0.004 \text{ goethite}$	0.001	0.013	0.9120n.s.
$\text{pH}_{\text{NaF}} = 10.3 - 0.103 \text{ Fe}_o$	0.004	0.045	0.8359n.s.
$\text{pH}_{\text{NaF}} = 7.9 + 2.386 \text{ Al}_o$	0.707	29.006	0.0002*

\* $P < 0.05$ ; n.s., not significant.

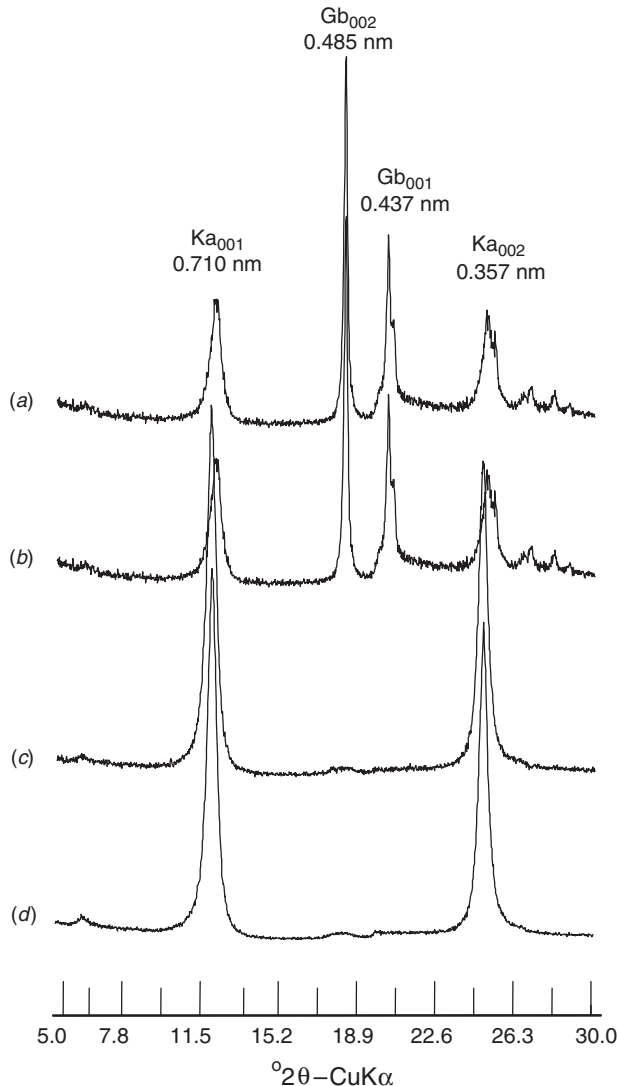
**Table 4.** Correlation matrix of clay component contents (% clay) ( $n = 14$ )

	Kaolinite	Gibbsite	Hematite	Goethite	$\text{Fe}_o$	$\text{Al}_o$
Kaolinite	1					
Gibbsite	-0.92**	1				
Hematite	-0.56*	0.52*	1			
Goethite	-0.10n.s.	0.01n.s.	-0.70*	1		
$\text{Fe}_o$	-0.15n.s.	0.00	0.64*	-0.53*	1	
$\text{Al}_o$	-0.93**	0.87**	0.60*	-0.04n.s.	0.27n.s.	1

\* $P < 0.05$ ; \*\* $P < 0.01$ ; n.s., not significant ( $t$ -test).



**Fig. 4.** Relationships between  $\text{pH}_{\text{NaF}}$  values measured in the deferrified clay and its (a) kaolinite and (b) gibbsite contents.



**Fig. 5.** X-ray diffraction patterns of the deferrified clays of soils 4 and 11 before and after 1 M NaF treatment. (a) Soil 4, (b) soil 4 + NaF, (c) soil 11, (d) soil 11 + NaF. Ka, Kaolinite; Gb, gibbsite.

**Table 5.** Results of linear regression analyses relating  $\text{pH}_{\text{NaF}}$  values measured in the soil to clay component contents (% whole soil) ( $n = 14$ )

$\text{Fe}_o$ , Ammonium-oxalate-extractable Fe;  $\text{Al}_o$ , ammonium-oxalate-extractable Al

Regression equation	$R^2$	$F$ -value	$P > F$
$\text{pH}_{\text{NaF}} = 9.7 + 0.008 \text{ kaolinite}$	0.025	0.301	0.5933n.s.
$\text{pH}_{\text{NaF}} = 9.5 + 0.039 \text{ gibbsite}$	0.629	20.068	0.0008*
$\text{pH}_{\text{NaF}} = 9.6 + 0.064 \text{ hematite}$	0.366	6.931	0.0219*
$\text{pH}_{\text{NaF}} = 9.6 + 0.082 \text{ goethite}$	0.149	2.099	0.1730n.s.
$\text{pH}_{\text{NaF}} = 9.5 + 0.941 \text{ Fe}_o$	0.307	5.305	0.0400*
$\text{pH}_{\text{NaF}} = 9.1 + 1.924 \text{ Al}_o$	0.781	42.744	0.0001*

\* $P < 0.05$ ; n.s., not significant.

of deferrified clay (Fig. 5) shows that the NaF solution did not cause appreciable structural changes in these minerals. Therefore, at least for them, the surface OH displacement by  $\text{F}^-$  seems the main mechanism responsible for the pH increase of the NaF solution after its contact with the deferrified clay. The differences between our results and those of Huang and Jackson (1965), who verified the disruption of clay minerals after a contact period of 24 h with 1 M  $\text{NH}_4\text{F}$  at a solid/solution ratio of 1 : 500, may be due to the smaller shaking time (1 h) and solid/solution ratio (1 : 40) employed in the present study.

#### Soil $\text{pH}_{\text{NaF}}$

The soil  $\text{pH}_{\text{NaF}}$  was better correlated to  $\text{pH}_{\text{NaF}}$  measured in the natural clay ( $r = 0.91$ ,  $P < 0.01$ ) than to  $\text{pH}_{\text{NaF}}$  measured in the deferrified clay ( $r = 0.83$ ,  $P < 0.01$ ), probably due to the removal in the latter of the compounds that contribute to  $\text{Al}_o$ . There was no relation between  $\text{pH}_{\text{NaF}}$  and exchangeable Al, and the positive impact of organic carbon (OC) on  $\text{pH}_{\text{NaF}}$  ( $\text{pH}_{\text{NaF}} = 9.4 + 0.161\text{OC}$ ,  $R^2 = 0.40$ ) may be due to either the NaF reaction with Al-humus (Wada 1980) or the delaying effect of organic matter on crystallisation of Al oxides (Huang and Violante 1986).

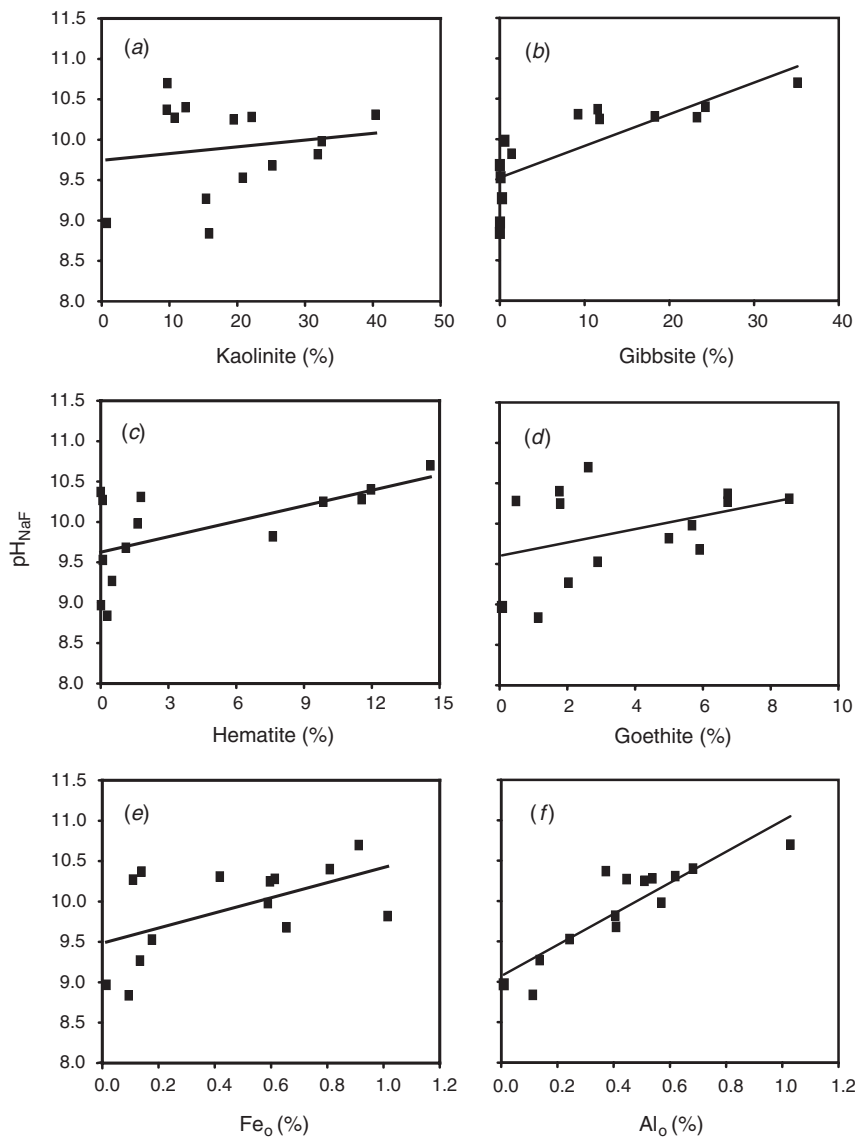
**Table 6. Correlation matrix of clay component contents (% whole soil) ( $n = 14$ )**

	Kaolinite	Gibbsite	Hematite	Goethite	Fe <sub>o</sub>	Al <sub>o</sub>
Kaolinite	1					
Gibbsite	-0.31n.s.	1				
Hematite	-0.01n.s.	0.69**	1			
Goethite	0.53*	-0.03n.s.	-0.37n.s.	1		
Fe <sub>o</sub>	0.39n.s.	0.37n.s.	0.79**	0.04n.s.	1	
Al <sub>o</sub>	0.22n.s.	0.78**	0.73**	0.25n.s.	0.72**	1

\* $P < 0.05$ ; \*\* $P < 0.01$ ; n.s., not significant ( $t$ -test).

The influence of clay composition on soil pH<sub>NaF</sub> values was also evaluated by fitting regression equations whose independent variables consisted of the clay component contents corrected for the whole soil from the soil clay content. Thus, the clay content effect on soil pH<sub>NaF</sub> was also taken into consideration and new correlations among the clay component contents were observed.

It can be verified in the new set of regression equations (Table 5) that only gibbsite, hematite, Fe<sub>o</sub>, and Al<sub>o</sub> exerted significant effect ( $P < 0.05$ ) on soil pH<sub>NaF</sub> values. The greatest slope,  $R^2$ , and  $F$ -value verified for the Al<sub>o</sub> equation



**Fig. 6.** Scatter plots relating pH<sub>NaF</sub> values measured in the soil to (a) kaolinite, (b) gibbsite, (c) hematite, (d) goethite, (e) ammonium-oxalate-extractable Fe (Fe<sub>o</sub>), and (f) ammonium-oxalate-extractable Al (Al<sub>o</sub>) soil contents (% whole soil).

indicate the greatest impact of the oxalate-extractable Al forms on soil  $\text{pH}_{\text{NaF}}$ .

The nonsignificant effect of kaolinite on soil  $\text{pH}_{\text{NaF}}$ , the lack of correlation between the kaolinite and  $\text{Al}_0$  soil contents (Table 6), and the negative impact of the kaolinite deferrified clay content on  $\text{pH}_{\text{NaF}}$  (Fig. 4) strongly suggest that the lower  $\text{pH}_{\text{NaF}}$  values of non-allophanic kaolinitic soils presenting low levels of non-humified organic matter are essentially due to their smaller  $\text{Al}_0$  and gibbsite contents.

In spite of the low significance (low  $F$ -value) of the  $\text{Fe}_0$  effect on soil  $\text{pH}_{\text{NaF}}$ , the  $\text{Fe}_0$  slope is smaller only than that of  $\text{Al}_0$ . This can lead to the misinterpretation that the soil  $\text{pH}_{\text{NaF}}$  is quite sensitive to  $\text{Fe}_0$  contents, when, as verified in the clay measurements, the  $\text{Fe}_0$  is not related to  $\text{pH}_{\text{NaF}}$ . The correlation between  $\text{Fe}_0$  and  $\text{Al}_0$  soil contents (Table 6) is responsible for the apparent influence of the former on soil  $\text{pH}_{\text{NaF}}$  (Table 5).

The nonsignificant effect of goethite (Tables 3 and 5) indicates that this mineral is irrelevant to the soil  $\text{pH}_{\text{NaF}}$  values. The lack of correlation between the goethite content and both gibbsite and  $\text{Al}_0$  contents in both clay and soil (Tables 4 and 6) and its very limited capacity to adsorb  $\text{F}^-$  (Bower and Hatcher 1967) may explain the non-influence of this iron hydroxide on  $\text{pH}_{\text{NaF}}$ .

Although the hematite slopes calculated for both clay and soil were greater than the gibbsite slopes, in both cases the  $F$ -values associated to the hematite equations were lower than those calculated for the equations in which gibbsite was the  $\text{pH}_{\text{NaF}}$  predictor (Tables 3 and 5). This lower significance and the scatter plots relating hematite contents to  $\text{pH}_{\text{NaF}}$  measured in both natural clay and soil (Figs 3 and 6) suggest that the influence of hematite on  $\text{pH}_{\text{NaF}}$  in both clay and soil may also be a result of its positive correlations with both gibbsite and  $\text{Al}_0$  contents (Tables 4 and 6).

The negative correlations of soil  $\text{pH}_{\text{NaF}}$  with  $\text{K}_i$  ( $r = -0.83$ ,  $P < 0.01$ ) and  $\text{K}_r$  ( $r = -0.85$ ,  $P < 0.01$ ) indices show that the clay mineral weathering and the consequent oxide and hydroxide accumulation promote an increase in the  $\text{pH}_{\text{NaF}}$  values, which is in line with the relationships verified in the present study between  $\text{pH}_{\text{NaF}}$  and clay mineralogy.

## Conclusions

Low  $\text{pH}_{\text{NaF}}$  values are indicative of higher kaolinite contents in acidic non-allophanic tropical soils presenting low levels of non-humified organic matter. As these soils become more weathered, their  $\text{pH}_{\text{NaF}}$  values increase mainly due to the accumulation of gibbsite and oxalate-extractable Al forms in their clay fractions. The influences of hematite, goethite, and ammonium-oxalate-extractable Fe on  $\text{pH}_{\text{NaF}}$  are irrelevant.

The main dependence of  $\text{pH}_{\text{NaF}}$  on  $\text{Al}_0$  and the greater influence of the latter on soil anionic retention indicate that  $\text{pH}_{\text{NaF}}$  can be used as a suitable indicator of the

weathering-increased anion adsorption capacities of non-allophanic acidic soils. Thus, also taking into consideration its cheap and quick determination,  $\text{pH}_{\text{NaF}}$  should be included as an additional determination in the Brazilian System of Soil Classification.

## Acknowledgments

We thank FAPESP for the financial support to this research.

## References

- Alvarado A, Buol SW (1985) Field estimation of phosphate retention by Andepts. *Soil Science Society of America Journal* **49**, 911–914.
- Alves ME, Lavorenti A (2004) Sulfate adsorption and its relationships with properties of representative soils of the São Paulo State, Brazil. *Geoderma* **118**, 89–99. doi: 10.1016/S0016-7061(03)00186-1
- Arocena JM, Dudas MJ, Poulsen L, Rutherford PM (1995) Weathering of clay minerals induced by fluoride-containing solutions from phosphogypsum by-product. *Canadian Journal of Soil Science* **75**, 219–226.
- Bertsch PM, Bloom PR (1996) Aluminum. In 'Methods of soil analysis: Part 3. Chemical methods'. (Ed. DL Sparks) pp. 517–550. (ASA and SSSA: Madison, WI)
- Bolland MDA, Gilkes RJ, Brennan RF, Allen DG (1996) Comparison of seven phosphorus sorption indices. *Australian Journal of Soil Research* **34**, 81–89.
- Bower CA, Hatcher JJ (1967) Adsorption of fluoride by soils and minerals. *Soil Science* **103**, 151–154.
- Buurman P, van Lagen B, Velthorst EJ (1996) 'Manual for soil and water analysis.' (Backhuys Publishers Leiden: Wageningen)
- Buytaert W, Deckers J, Dercon G, De Bievre B, Pesen J, Govers G (2002) Impact of land use changes on the hydrological properties of volcanic ash soils in South Ecuador. *Soil Use and Management* **18**, 94–100.
- EMBRAPA (1997) 'Manual de métodos de análise do solo.' (Ministério da Agricultura: Rio de Janeiro)
- EMBRAPA (1999) 'Sistema brasileiro de classificação de solos.' (Ministério da Agricultura: Rio de Janeiro)
- Escudey M, Galindo G (1988) Potassium–calcium exchange on inorganic clay fractions of Chilean andepts. *Geoderma* **41**, 275–285. doi: 10.1016/0016-7061(88)90065-1
- Fieldes M, Perrott KW (1966) The nature of allophane in soils: part 3. Rapid field and laboratory test for allophane. *New Zealand Journal of Science* **9**, 623–629.
- Gee GW, Bauder JW (1986) Particle size analysis. In 'Methods of soil analysis: Part 1. Physical and mineralogical methods'. (Ed. A Klute) pp. 383–409. (ASA and SSSA: Madison, WI)
- Gilkes RJ, Hughes JC (1994) Sodium fluoride pH of south-western Australian soils as indicator of P-sorption. *Australian Journal of Soil Research* **32**, 755–766.
- Huang PM, Jackson ML (1965) Mechanism of reaction of neutral fluoride solution with layer silicates and oxides. *Soil Science Society of America Proceedings* **29**, 661–665.
- Huang PM, Violante A (1986) Influence of organic acids on crystallization and surface properties of precipitation products of aluminum. In 'Interactions of soil minerals with natural organics and microbes'. (Eds PM Huang, M Schnitzer) pp. 159–221. (SSSA: Madison, WI)
- Isbell RF (1996) 'The Australian Soil Classification.' (CSIRO Publishing: Collingwood, Vic.)
- Jackson ML (1969) 'Soil chemical analysis – advanced course.' (University of Wisconsin: Madison, WI)

- Jones RC (1981) X-ray diffraction line profile analysis vs. phosphorus sorption by 11 Puerto Rican soils. *Soil Science Society of America Journal* **45**, 818–825.
- Kämpf N, Schwertmann U (1982) The 5 M-NaOH concentration treatment for iron oxides in soils. *Clays and Clay Minerals* **30**, 401–408.
- McKeague JA, Day JH (1966) Dithionite and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Canadian Journal of Soil Science* **46**, 13–22.
- Nelson OW, Sommers LE (1982) Total carbon, organic carbon, and organic matter. In 'Methods of soil analysis: Part 2. Chemical and microbiological properties'. (Eds AL Page, RH Miller, DZ Keeney) pp. 539–577. (ASA and SSSA: Madison, WI)
- de Oliveira JB (1999) 'Solos do Estado de São Paulo: descrição das classes registradas no mapa pedológico.' (Instituto Agrônomo: Campinas)
- Perrott KW, Smith BFL, Inkson RHE (1976a) The reaction of fluoride with soils and soil minerals. *Journal of Soil Science* **27**, 58–67.
- Perrott KW, Smith BFL, Mitchell BD (1976b) Effect of pH on the reaction of sodium fluoride with hydrous oxides of silicon, aluminium, and iron, and with poorly-ordered aluminosilicates. *Journal of Soil Science* **27**, 348–356.
- Resende M, Bahia Filho AFC, Braga JM (1987) Clay mineralogy of Latosols estimated by chemical allocation of total oxides content by H<sub>2</sub>SO<sub>4</sub> digestion. *Brazilian Journal of Soil Science* **11**, 17–23.
- Schulze DG (1984) The influence of aluminum on iron oxides. VIII. Unit-cell dimensions of Al-substituted goethites and estimation of Al from them. *Clays and Clay Minerals* **32**, 36–44.
- Schwertmann U, Fitzpatrick RW, Taylor RM, Lewis DG (1979) The influence of aluminum on iron oxides Part II. Preparation and properties of Al-substituted hematites. *Clays and Clay Minerals* **27**, 105–112.
- Schwertmann U, Herbillon AJ (1992) Some aspects of fertility associated with the mineralogy of highly weathered tropical soils. In 'Myths and science of soils of the tropics'. (Eds R Lal, PA Sanches, DZ Keeney) pp. 47–59. (SSSA: Madison, WI)
- Singh B, Gilkes RJ (1991) Phosphorus sorption in relation to soil properties for the major soil types of South-Western Australia. *Australian Journal of Soil Research* **29**, 603–618.
- Soil Survey Staff (1999) 'Soil Taxonomy: a basic system of soil classification for making and interpreting soil surveys.' (USDA-SCS: Washington, DC)
- Tan KR, Hajek BF, Barshad I (1986) Thermal analysis techniques. In 'Methods of soil analysis: Part 1. Physical and mineralogical methods'. (Ed. A Klute) pp. 151–183. (ASA and SSSA: Madison, WI)
- Varajão AFDC, Gilkes RG, Hart RD (2002) Amorphous aluminosilicate materials in a Brazilian hydromorphic lateritic soil. *Australian Journal of Soil Research* **40**, 465–481.
- Wada K (1980) Mineralogical characteristics of Andisols. In 'Soils with variable charge'. (Ed. BKG Theng) pp. 87–107. (NZSSS: Lower Hutt)

Manuscript received 14 April 2004, accepted 4 August 2004