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Mineralogical analysis of clays in hardsetting soil horizons, by X-ray fluorescence and X-ray diffraction using Rietveld method

L.V. Prandel [a,*], S.C. Saab [a], A.M. Brinatti [a], N.F.B. Giarola [b], W.C. Leite [a], F.A.M. Cassaro [a]

[a] Laboratory of Soil Physics and Environmental Sciences, Department of Physics, State University of Ponta Grossa (UEPG), Av. Carlos Cavalcanti 4748, 84030-900 Ponta Grossa, PR, Brazil

[b] Department of Soil Science and Agricultural Engineering, State University of Ponta Grossa (UEPG); Av. Gal. Carlos Cavalcanti, 4748, 84030-900 Ponta Grossa, PR, Brazil

HIGHLIGHTS

- Elemental composition of soil samples through X-Ray fluorescence.
- Mineralogical quantification through X-ray diffraction and Rietveld method.
- Oxisol and Ultisol, Brazil 'Barreiras' formation.
- High amounts of Si and Al oxides and low amounts of Fe and Ti oxides.
- Predominance of kaolinite in the clay fraction.

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ABSTRACT

Diffraction and spectroscopic techniques have been shown to be suitable for obtaining physical and mineralogical properties in polycrystalline soil samples, and also in their precursor compounds. For instance, the X-ray fluorescence (XRF) spectroscopy allows obtaining the elemental composition of an investigated sample, while the X-ray diffraction (XRD) technique permits obtaining qualitative and quantitative composition of the soil minerals through the Rietveld method (RM). In this study Yellow Latosol (Oxisol), Yellow Argisol (Ultisol) and Gray Argisol (Ultisol) soil samples, classified as "hardsetting soils", extracted from areas located at Northeast and Southeast of Brazilian coast were investigated. The soils and their fractions were analyzed in an EDX-700 and an XRD-6000 (Cu K_α radiation). XRF results indicate high percentages of Si and Al, and small percentage of Fe and Ti in the investigated samples. The DRX data and RM indicate that there was a predominance of kaolinite and halloysite minerals (kaolin group minerals) in the clay fractions, which are presumably responsible for the formation of kaolinitic plasma in these soils. Also, the obtained results showed that the XRF, XRD techniques and RM were very helpful for investigating the mineralogical composition of a hardsetting soil.

1. Introduction

According to Du et al. (2008), soil is a complex mixture of several compounds, and due to this complexity in its composition, for the study of physical, chemical and mineralogical properties of the soil, which are of great importance for agriculture and environment, the use of spectroscopic and diffraction techniques is very relevant.

Currently, X-ray diffraction (XRD) and the Rietveld method (RM) (Rietveld, 1967, 1969) data is used in the mineral characterization and quantification of Brazilian soils (Brinatti et al., 2010; Alves et al., 2007). These results, together with X-ray fluorescence data (XRF), provide information on the mineral and chemical composition of complex mixtures found in soils (Pantenburg et al., 1992).

The soils to be analyzed are of a hardsetting character, a term which is used in Brazil to describe sub-superficial mineral horizons (B) of soils which present significant increase in cohesion amongst its particles, becoming hard when dry and friable when humid (Lima Neto et al., 2009). Such soils were incorporated to the current Brazilian System of Soil Classification as Yellow Latosol (Oxisol), Yellow Argisol (Ultisol) and Gray Argisol (Ultisol) (Embrapa, 1999), and are part of the advanced process of weathering of tertiary sediments in the Barreiras formation (Lima Neto et al., 2009), which comprises the whole Southeastern and Northeastern coast of Brazil.

* Corresponding author. Tel.: +55 42 3220 3044; fax: +55 42 3220 3042.
E-mail address: luisprandel@hotmail.com (L.V. Prandel).

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These soil compact horizons, when dry, hamper the plant root development, regarding water and air content available; they are physical inhibitors, associated to high aluminum saturation (Lima Neto et al., 2009), they also present low iron content, and quartz grains surrounded mainly by a dense and continuous kaolinitic plasma (Giarola et al., 2009; Melo et al., 2002).

Studies carried out on the hardsetting character of soils are still rudimentary due to lack of defined parameters which might indicate the different cohesion degrees (Giarola et al., 2009). It is believed that some cohesion parameters will be explained through physic-chemical and mineralogical analyses of these soils and their fractions.

2. Experimental methods

Five samples of soils considered to be of a hardsetting character were collected and classified (Table 1). Around 20 g of each sample with average density (2.60 ± 0.03) g/cm^3 were mashed, submitted to a dispersion and sedimentation physical fractioning process, and the fractions coarse sand (cs: 53–1000 μm), fine sand (fs: 20–53 μm), silt (sl: 2–20 μm), and clay (cl: ≤ 2 μm) were extracted.

All samples were reduced to diameters lower than 53 μm and analyzed in a dispersive energy XRF spectrometer (EDX-700) Shimadzu, with an Rh source. The spectra were obtained at 300 s time intervals [in Na–Sc (15 kV) and Ti–U (50 kV) energy bands], in vacuum, semi-quantitative mode. The samples were also examined by XRD, in an XRD-6000 diffractometer Rigaku (model Ultima IV), with Cu K_α radiation, as a function of the 2θ angle (8 to 80°, with 0.02° step, and 5 s time per step).

The RM refinement was carried out in the general structure analysis system (GSAS) software, developed by Larson and Von Dreele (2004), accessed through the EXPGUI interface, developed by Toby (2001). The GSAS uses the RM as a refining tool based on the calculation of square minimums until it reaches the best adjustment between the intensity of the diffraction pattern observed, y_{obs}, and the calculated pattern, y_{calc}:

$$S_y = \sum_i w_i (y_{obs} - y_{calc})^2, \quad (1)$$

where $w_i (= 1/\sqrt{y_{obs}})$ is the function weight in the ith step (Young, 2002; Rietveld, 1967, 1969).

Intensities calculated for each phase (p), with starting crystalline structures obtained from Downs and Hall-Wallace (1993) data basis, are represented through Eq. (2).

$$y_{calc} = A_b S_R \sum_p S_p \sum_K [L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) A_S P_K]_P + y_{bi}, \quad (2)$$

where A_b is the absorption factor; S_R a function which models the surface roughness effect; S_p the scale factor; K is Miller index to each Bragg reflection; L_K contains the Lorentz, polarization and multiplicity factors; ϕ is the diffraction profile function given by the Pseudo-Voigt function; θ_i is the scattering angle; θ_K is the diffraction angle in the Bragg reflecting lattice plane; A_S is the asymmetry function; P_K is the preferential orientation function; $|F_K|^2$ is the square of the structure factor and y_{bi} is the background radiation intensity (Young, 2002).

The refinement quality is indicated through the minimization and convergence of terms R-pattern (R_p), R-weighted pattern (R_{wp}), R-expected (R_e), goodness-of-fit ($S = R_{wp}/R_e$) and R-structure factor (R_F^2) (Young, 2002; Larson and Von Dreele, 2004).

The procedure adopted for the soil samples RM refinement was: (i) simultaneous and individual adjustment of S_p; (ii) individual refinement of each S_p, $|F_K|^2$ and function y_{bi}; (iii) individual refinement of some ϕ parameters of each phase (U, V and W of FWHM), (iv) adjustment of P_K by March–Dollase function for kaolinite, in (0 0 1) and (0 0 2) planes, and quartz, in (0 1 0) and (0 0 1) planes; (v) simultaneous adjustments of S_p, A_b, S_r and peak anisotropy terms (S_{ijk}); (vi) P_K refinement through spherical harmonics; and (vii) finalization with adjustment of S_p,

Table 1
Samples of Brazilian hardsetting soils and their fractions [coarse sand (cs), fine sand (fs), silt (sl), and clay (cl)]: percentage, texture and XRF semiquantitative results.

Sample	Collect place	Frac.	Percentage (%)	Texture	Oxide (g/kg)*			
					SiO_2	Al_2O_3	Fe_2O_3	TiO_2
(1) Yellow argisol	Coruripe/Alagoas	cs	61.53 ± 1.33	Sandy clay loam	973.6 ± 1.2	–	3.4 ± 0.1	7.5 ± 0.1
	(10°07′ 33″S 36° 10′33″W)	fs	2.39 ± 0.08		926.6 ± 1.9	–	15.1 ± 1.2	28.1 ± 0.3
		sl	2.24 ± 0.55		582.6 ± 8.3	317.2 ± 5.7	35.4 ± 2.7	48.1 ± 0.4
		cl	33.70 ± 0.25		388.8 ± 1.8	533.3 ± 3.5	32.5 ± 0.8	22.1 ± 0.4
		Whole soil			444.1 ± 4.4	492.3 ± 7.0	28.9 ± 0.6	22.6 ± 0.4
(2) Yellow latosol	Cruz das Almas/Bahia	cs	64.17 ± 0.33	Sandy clay loam	969.9 ± 1.2	–	5.7 ± 0.1	7.1 ± 0.1
	(12°40′12″S 39°06′07″W)	fs	2.88 ± 0.42		924.1 ± 2.6	–	20.5 ± 0.5	30.8 ± 0.9
		sl	0.89 ± 0.07		884.2 ± 5.1	–	45.9 ± 2.5	49.3 ± 3.8
		cl	32.09 ± 0.31		373.4 ± 3.4	507.9 ± 0.2	76.7 ± 1.3	16.2 ± 0.1
		Whole soil			427.8 ± 3.9	466.1 ± 6.5	74.3 ± 1.5	18.7 ± 0.5
(3) Yellow argisol	Porto Seguro/Bahia	cs	52.28 ± 0.49	Sandy clay	981.3 ± 1.3	–	2.2 ± 0.1	4.4 ± 0.1
	(16°27′00″S 39°03′54″W)	fs	2.35 ± 0.15		915.7 ± 4.0	–	8.8 ± 0.5	33.1 ± 1.3
		sl	1.64 ± 0.23		615.8 ± 1.9	277.9 ± 2.9	29.8 ± 2.0	51.4 ± 6.7
		cl	43.88 ± 0.32		361.1 ± 5.2	543.7 ± 6.2	36.5 ± 1.2	24.0 ± 0.7
		Soil whole			403.0 ± 5.3	524.9 ± 6.2	34.8 ± 0.7	26.1 ± 0.5
(4) Yellow argisol	Aracruz/Espírito Santo	cs	52.88 ± 0.30	Sandy clay	95.6 ± 1.2	–	2.2 ± 0.1	–
	(19°49′12″S 40°16′22″W)	fs	2.21 ± 0.06		914.3 ± 5.1	–	17.8 ± 2.8	33.9 ± 2.0
		sl	1.55 ± 0.09		752.5 ± 2.8	121.8 ± 2.9	42.7 ± 1.5	59.0 ± 2.7
		cl	43.86 ± 0.08		378.3 ± 2.0	514.2 ± 4.7	54.3 ± 1.7	24.9 ± 0.6
		Soil whole			414.4 ± 2.6	489.4 ± 3.0	54.8 ± 0.3	27.4 ± 0.5
(5) Gray argisol	Pacajus/Ceará	cs	67.19 ± 0.80	Sandy clay loam	98.1 ± 1.2	–	–	–
	(04°10′22″S 38°27′39″W)	fs	3.84 ± 0.09		951.8 ± 2.8	–	7.6 ± 0.8	11.9 ± 0.6
		sl	0.60 ± 0.18		937.6 ± 9.3	–	15.6 ± 5.8	18.0 ± 3.2
		cl	28.37 ± 0.31		403.8 ± 3.0	506.8 ± 6.6	25.1 ± 0.4	11.8 ± 0.2
		Soil whole			471.8 ± 3.2	477.8 ± 4.0	22.1 ± 0.6	11.3 ± 0.3

* Ca oxide was found only in the clay fraction: (1) 12.9 ± 2.1; (2) 15.7 ± 2.0; (3) 14.6 ± 0.5; (4) 17.7 ± 2.5; (5) 27.9 ± 6.2.