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Mineralogical characterization of iron-rich clayey soils from the middle plateau in the southern region of Brazil[☆]

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ABSTRACT

We report mineralogical studies of clayey soils collected in various sites of the middle plateau in Rio Grande do Sul in the southern region of Brazil. The analysis of the XRD patterns indicated quartz, rutile, goethite, hematite and kaolinite in the samples. Mössbauer spectroscopy has been used to study the Fe-bearing species. The Mössbauer spectra of all the samples at room temperature consist of a large paramagnetic doublet, in some cases superimposed on a small sextet, whereas at 77 K a prominent sextet appears, which is associated with goethite and/or a hematite substituted structure. The results indicate that the studied soils have iron oxides with high contents of aluminum.

1. Introduction

Iron oxides or hydroxides are often identified in kaolin raw materials. In kaolinites Al can be partially substituted by structural Fe which occupy tetrahedral (Fe^{+3}) and/or octahedral sites (Fe^{+3} and Fe^{+2}) (Malden and Meads, 1967; Fysh and Clark, 1982; Petit and Decarreau, 1990; Bowen and De Grave, 1995; Murad and Wagner, 1998; Castelein et al., 2002; Lombardi et al., 2002). The iron site geometry as well as its valence state can be detected by means of Mössbauer spectroscopy. Measured quantities such as the isomer shift (δ), the electric quadrupolar splitting (2) and the hyperfine magnetic field can be used to distinguish between the different oxidation states of iron in various structural sites and to detect iron oxides of different particle sizes in the sample. The relative amount of each state or phase can be obtained with this technique. Since the first investigations of clays minerals with Mössbauer spectroscopy a large amount of data have been collected regarding the variety of content of iron-bearing species in the samples (Silver et al., 1980; Murad and Wagner, 1998). In some cases the nature of the color in the materials is related to the type and amount of the iron species which are present in the samples, as for instance in colored marbles (Calogero et al., 2000). The present investigation was undertaken to study iron-bearing particulate species in soils from several sites located in the central region of the state of Rio Grande do Sul, in the south of Brazil. The samples collected are representative of raw materials used for the production of clay based structural ceramics applications, as filled and hollow floor bricks, facing bricks, roofing tiles and quality ceramic products.

2. Materials and methods

The soils investigated in this work consist of six samples of clayey surface soil horizons collected from deposits from three localities. All were chemically untreated. The only procedure adopted was a fine screening through 75 μm mesh. Particle size analysis of the samples was determined by a combination of sieving and sedimentation procedures according to NBR 7181-84. The Atterberg limits were determined according to the NBR 6459-84 and NBR 7180-84 standardized procedures. The percentage of the

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Table 1
Geographic data, provenance, appearance and iron minerals identified in the soil samples

Indigenous site	Provenance (RS)	Sample	Appearance	Iron minerals
Carreteiro	Água Santa	S1A	Reddish mid-brown, fine	K, H
Guarita	Redentora	S2A	Yellowish light brown, fine	K, H, M
		S2B	Reddish mid-brown, fine	K, H
Inhacora	São Valério do Sul	S3A	Yellowish light brown, fine	K, H, M
		S3B	Reddish mid-brown, fine	K, H
		S3C	Dark brown, fine	K, H

Table 3
Atterberg limits and size distribution of particles in the soils

Sample	Atterberg limits (%)			Granulometry (%)		
	L.L.	P.L.	P.I.	<2 mm	2– 20 mm	>20 mm
S1A	44.8	24.5	20.3	40	32	28
S2A	51.6	34.6	17.0	34	34	32
S2B	53.3	35.2	18.1	29	43	28
S3A	50.8	29.9	20.9	42	33	25
S3B	52.5	25.4	27.1	28	40	32
S3C	57.8	43.8	13.7	18	46	36

oxides containing Al, Fe, Mn, Na, Mg, K, Ca, Zn and Cu were determined by means of atomic absorption spectrophotometry and the SiO_2 content was determined by weight difference. Powder X-ray diffraction (XRD) patterns were obtained with CuKα radiation. The Mössbauer spectra were collected in the transmission geometry with a 50 mCi ^{57}Co source in rhodium matrix with a multiscaler of 512 channels. The spectrometer was operated with a triangular velocity waveform in constant acceleration mode. The spectra were collected at room temperature (300 K) and at liquid nitrogen temperature (77 K). All quoted isomer shifts (δ) are referred to natural alpha iron at ambient temperature.

3. Results and discussion

The striking feature observed first in the samples is the gradation of colors which ranges from light yellowish brown to dark brown. In order to verify the chemical composition of the soils a careful chemical analysis of the clayey powders has been carried out. The results of the particle size distribution analysis revealed that all studied soils consist of a finely grained material. The analysis of the XRD patterns indicated the presence of quartz, rutile, goethite or hematite and kaolinite in all the samples. Traces of montmorillonite were detected in only two samples, namely, S2A and S3A. Hence, all the soil samples studied here are mainly constituted by clay minerals and quartz. Iron was detected in the minerals kaolinite, montmorillonite, goethite, hematite or mixtures thereof, with the predominant clay mineral being kaolinite. The mineral contents and their appearance are given in Table 1. The light red hue imparted to some of them reflects the presence of hematite which has a very strong pigment. Results of chemical analysis for the oxides in these samples are shown in Table 2, where it can be seen that the SiO_2 content is about the same in all of them. The $Al_2\ O_3$ component, which yields refractoriness to materials, varies from 8.59 to 19.12%. The K_2O and Na_2O components, which give softness, are very low, and the low concentrations of MgO and CaO indicate that these soils contain little or no carbonate. In Table 3 are shown the Atterberg limits for these soils and the size distribution of particles in the samples. As it can be noticed from these data the plastic limit (P.L.) varies from 24.5 to 43.8%. The liquid limit (L.L.) of most (except for S1A) is above 50%, which indicates that these soils have a large compressibility.

The Mössbauer spectra collected at 300 K are shown in Fig. 1. Mostly the spectra consist of a large paramagnetic doublet. However, in the spectra for samples S2A and S3B is also observed the superposition of a broadened sextet, a signature characteristic of the existence of a hyperfine magnetic interaction. For sample S1A, the fitting procedure has been performed by considering the paramagnetic doublet as being composed by the superposition of three doublets, which are thought to be associated with the presence of both Fe^{+3} and Fe^{+2} sites in the mineral and a paramagnetic phase. For Al partially substituted by structural Fe in kaolinite, typical Mössbauer parameters for octahedrally co-ordinated Fe^{+3} are δ=0.37 mm/s (Isomer shift) and 2 =0.58 mm/s (quadrupolar splitting). On the other hand, for Fe^{+3} in kaolinite tetrahedral sites, reported results yield δ=0.2 mm/s and 2 =1 mm/s, whereas for Fe^{+2} substituted trioctahedrally in the structure, δ=1.00 mm/s and 2 =2.39 mm/s (Malden and Meads, 1967; Petit and Decarreau, 1990). The most prominent doublet which is seen in Fig. 1 is then ascribed to a Fe^{+3} site. The δ and 2 values obtained from the fitting procedure for all the samples are close to those obtained at room temperature for Fe^{+3} in kaolinite (Bio kaolin) (Castelein et al., 2002). Hence, the smallest doublet in the spectra might be associated with an Fe^{+2} environment. In addition, the third intermediate doublet can be attributed to the presence of superparamagnetic particles (goethite and/or hematite) in these soils. Natural hematite, for example, exhibits a Mössbauer spectrum at 300 K which consists of a sextet with parameters δ=0.37 mm/s, 2 =−0.20 mm/s, with a hyperfine magnetic field

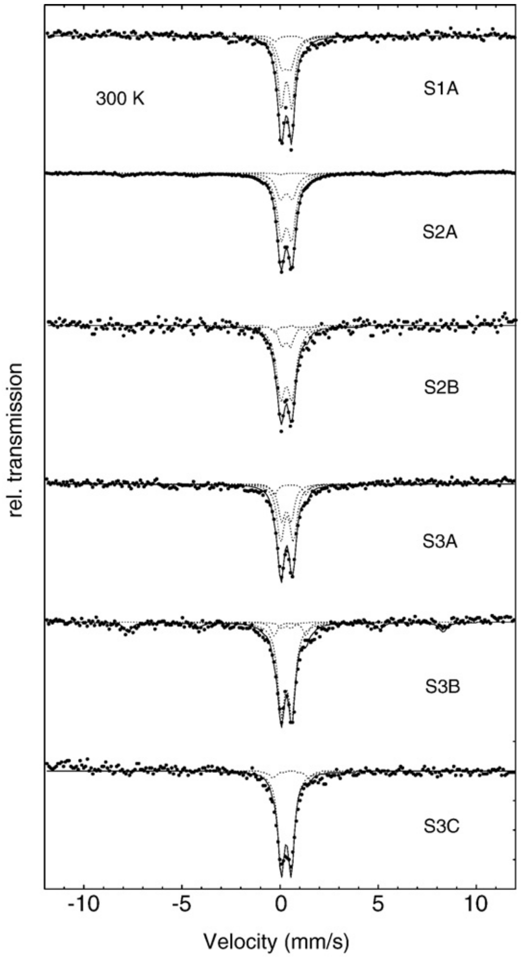

Fig. 1. Mössbauer spectra at room temperature (300 K). The solid line is the result of the fitting procedure for the total spectrum. Dotted lines indicate the subspectra contribution.

Table 2
Chemical composition (in %) of the soil samples

Sample	SiO_2	Al_2O_3	Fe_2O_3	MnO_2	Na_2O	MgO	K_2O	CaO	ZnO	CuO
S1A	57.84	16.32	6.80	0.05	0.02	0.21	0.09	0.04	0.01	0.02
S2A	52.88	8.79	11.20	0.23	0.02	0.22	0.06	0.04	0.01	0.03
S2B	53.27	19.12	4.00	0.04	0.04	0.14	0.07	0.05	0.01	0.03
S3A	58.03	13.86	7.54	0.05	0.02	0.21	0.07	0.04	0.01	0.02
S3B	59.28	8.59	11.50	0.23	0.01	0.13	0.08	0.01	0.01	0.02
S3C	55.10	18.36	5.47	0.05	0.00	0.13	0.02	0.04	0.01	0.02