

# Spectroscopic studies of kaolin from different Brazilian regions

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(Received 29 March 2007; revised 13 August 2007)

**ABSTRACT:** Over the past several decades, kaolin has been intensively used in the paper industry as a coating and filler material. These applications require kaolin of a high brightness grade, which strongly depends on the level of impurities (mainly Fe-bearing minerals such as Fe oxides and hydroxides) and may be improved by beneficiation processes involving grain size classification, magnetic separation and chemical treatments. This investigation was carried out on five Brazilian kaolin samples of different geographical and geological origins. Granulometric, mineralogical, chemical and physical characterizations were performed on all samples before and after the beneficiation process.

Chemical compositions were determined by X-ray fluorescence and the most important crystalline phases were identified using X-ray diffraction. Kaolinite is the dominant mineralogical phase with minor amounts of muscovite and quartz. The nature of Fe impurities was investigated by electron spin resonance and <sup>57</sup>Fe Mössbauer spectroscopy. For all studied kaolin samples, Fe ions (Fe<sup>3+</sup> and Fe<sup>2+</sup>) are present in variable amounts, in the kaolinite structure and also in Fe oxides (magnetite, hematite and goethite). The beneficiation procedure aims to remove these Fe oxides and was found to be most efficient for the Mogi das Cruzes kaolin. The Seridó kaolin had the highest whiteness index observed among the analysed samples.

**KEYWORDS:** kaolinite, Fe impurities, <sup>57</sup>Fe Mössbauer spectroscopy, electron spin resonance.

Kaolin, or China clay, is a fine clay mineral coloured cream to dark brown by its Fe oxide/hydroxide (and/or rutile/anatase) content. Its main constituent is kaolinite, a hydrous aluminosilicate with a single layer of silica tetrahedra linked by O atoms to a single sheet of alumina octahedra. Kaolin may also contain muscovite, feldspar, quartz and Fe or Ti oxides as ancillary minerals. Mainly produced by hydrothermal alteration or residual weathering of feldspar-bearing rocks, it occurs as residual (primary) or sedimentary (secondary)

deposits. The so-called residual kaolin originates from *in situ* alteration of rocks by hot fluids, which percolate mainly in pegmatites. The secondary deposits are formed after deposition of particles transported by water flows. During transportation, particles are sorted by size and composition and become rounded; therefore sedimentary kaolin is generally formed of more fine-grained and aggregated particles than that of its residual equivalent.

Brazil has the second largest international reserve of kaolin (28%), (add reference to Wilson 2005 – referenced in Wilson 2006, see below) with the main deposits occurring in the states of Pará, Amapá, Amazonas, São Paulo, Minas Gerais and Bahia. Large quantities of kaolin are used in paper

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DOI: 10.1180/claymin.2008.043.1.03

TABLE 1. Location and geological origin of the studied kaolin samples. In the case of Rio Capim, samples 2 and 3 were collected from two different deposits.

Kaolin	Location in Brazil (State)	Geological origin
Sample 1	Mogi das Cruzes – SP	Primary – alteration of granites
Sample 2	Rio Capim A – PA	Secondary – Tertiary sediments
Sample 3	Rio Capim B – PA	Secondary – Tertiary sediments
Sample 4	Rio Jari – AP	Secondary – Tertiary sediments
Sample 5	Seridó – RN	Primary – alteration of pegmatites

SP: São Paulo; PA: Pará; AP: Amapá; RN: Rio Grande do Norte

industries as coating and filler materials (45%) and in the production of refractory materials (16%) (Murray, 2002; add reference to Wilson *et al* Clay Min 41(2006) 697; Murray *et al.*, 2007). Other applications include the production of ceramics, fiberglass, cements, rubber tires, latex paints, printing inks, catalysts for petroleum refinement, medicines and cosmetics.

To achieve the specification required by the paper industry, kaolin has to be processed. The procedure aims primarily at improving whiteness (the most important physical property for this type of application). Wet or dry beneficiation processes can be used to achieve this goal, depending on the use of the final product. The wet beneficiation process as applied to kaolin consists mainly of degrading, fractionation by centrifuging, high gradient magnetic separation, selective flocculation, chemical bleaching, filtering and drying (Murray, 2002; Wilson *et al.*, 2006). All these steps are used to remove mineral impurities such as Fe or Ti

oxides, mica and quartz. Chlorination may also be used for Fe and Ti removal (González & Ruiz, 2006). To improve kaolin whiteness, the beneficiation has to take into account the geological origin of the sample (primary or secondary) and most of all the nature of its Fe impurities.

The aim of the present study is to characterize kaolin from different Brazilian deposits, focusing on the influence of Fe impurities on its whiteness and in this way, identifying the most suitable Brazilian kaolin for application as a paper filler and coater.

## SAMPLES AND METHODS

The kaolin samples were collected in primary and/or secondary deposits in different Brazilian regions (São Paulo: SP (1 sample), Pará: PA (2), Amapá: AP (1) and Rio Grande do Norte: RN (1)) (Table 1).

The first step in sample preparation consisted of degrading and fractionation by centrifuging, followed by a granulometric classification using

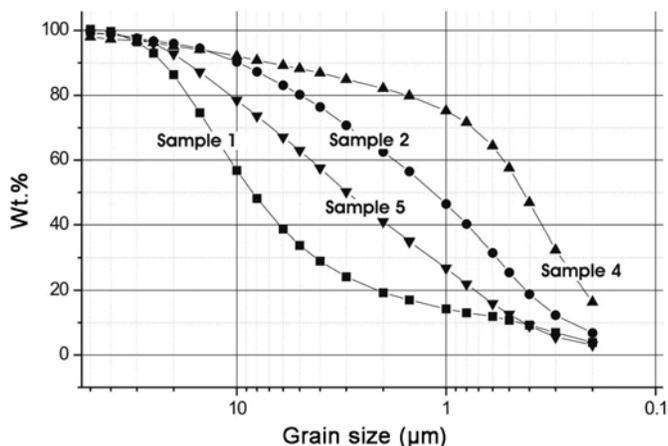


FIG. 1. Grain-size distribution of the studied kaolin samples (wt.% represents the cumulative weight percentage of the samples that passed through the 37 µm sieve).

TABLE 2. Whiteness indexes of kaolin samples after different steps of the beneficiation process.

Sample	Whiteness index (%ISO)		
	Initial	After magnetic separation	After bleaching
1	55.81	63.25	63.34
2	80.51	82.05	82.16
3	78.11	83.61	84.01
4	78.34	79.64	80.57
5	85.96	86.40	87.72

sieves with openings ranging from 3.35 mm to 37  $\mu\text{m}$  (6 to 400 mesh). The fraction  $<37 \mu\text{m}$  was passed through a wet high field magnetic separator (14,000 gauss) and finally the non-magnetic part of the sample was chemically treated with sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ).

A granulometric study was undertaken using a particle size analyser (Micromeritic Sedigraph 5100) and the Micromeritic v1.02 software. Measurements of the whiteness index and opacity were performed with a commercial colourimeter (Tecnidyne Color Touch 2).

Electron spin resonance (ESR) spectra were recorded at room temperature with a commercial spectrometer (Brüker ESP300E) operating at X-band frequency (9.45 GHz). The main spectroscopic parameters were: microwave power 10 mW; magnetic field range 0–8000 gauss; modulation amplitude 10 gauss; and modulation frequency 100 kHz.

The  $^{57}\text{Fe}$  Mössbauer Spectroscopy ( $^{57}\text{Fe}$ -MS) experiments were performed at room temperature in standard transmission geometry using a 25 mCi  $^{57}\text{Co}$ :Rh radioactive source in sinusoidal mode. The isomer shift values (IS) given in the present work are relative to  $\alpha$ -Fe at room temperature. The NORMOS code (Brand, 1992) was used for the spectrum analysis.

Recent studies have shown the potential of ESR and  $^{57}\text{Fe}$ -MS for the characterization of Indian and African kaolin (e.g. Sei *et al.*, 2004; Chandrasekhar & Ramaswamy, 2006).

## RESULTS AND DISCUSSION

The grain-size distribution of kaolin is of great interest for industrial applications. Hence granulometric analyses were carried out on all samples.

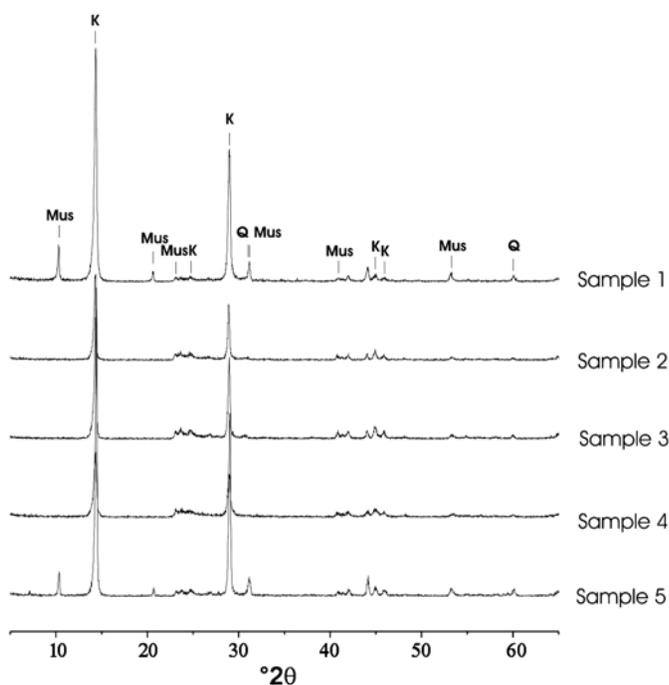


FIG. 2. XRD patterns of kaolin samples ( $V = 35 \text{ kV}$ ,  $I = 40 \text{ mA}$ ,  $\lambda \text{ Co-}K\alpha$ ). K = kaolinite, Mus = muscovite, Q = quartz.

Figure 1 represents the cumulative weight percentage of the samples that passed through the 37  $\mu\text{m}$  sieve vs. particle size. Among the analysed kaolin, samples 2 and 4 from the secondary deposits contain the greatest proportion of fine grains (Fig. 1).

Whiteness indexes of kaolin samples before the beneficiation process and after magnetic separation and chemical bleaching, respectively, are shown in Table 2. The greatest whiteness index (87.72%) was observed for sample 5 (Seridó deposit) and the greatest improvement (+7.53%) after beneficiation was obtained for sample 1 from the Mogi das Cruzes deposit.

X-ray diffraction (XRD) analysis of the untreated kaolin (<37  $\mu\text{m}$  fraction) showed that kaolinite is the dominant mineral phase in all samples (Fig. 2). Muscovite and quartz were detected as ancillary minerals in samples 1 and 5, both of which come from primary clay deposits (Mogi das Cruzes and Seridó, respectively). These last two minerals are mainly present in the coarser fractions and were removed during the beneficiation process.

Chemical composition of the samples was determined by X-ray fluorescence (XRF). The total Fe content decreased after each sequential step of the beneficiation process, after which the remaining amount of Fe was: 0.54 wt.% (sample 1);

TABLE 3. Hyperfine parameters (at room temperature) of kaolin samples before and after the beneficiation process.

		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Before beneficiation						
Fe <sup>3+</sup>	IS*	0.31	0.35	0.36	0.26	0.31
	QS*	0.69	0.65	0.64	0.59	0.72
	W*	0.55	0.47	0.46	0.38	0.58
	A(%)	30	62	56	30	47
Fe <sup>2+</sup>	IS	1.25	1.23	—	—	1.14
	QS	2.13	2.16	—	—	2.42
	W	0.45	0.55	—	—	0.58
	A(%)	8	8	—	—	16
Magnetic	IS	0.29	0.37	0.37	0.37	0.35
	QS	-0.28	-0.22	-0.21	-0.21	-0.19
	B <sub>hf</sub> **	23.9	51.1	50.5	51.1	29.5
	W	0.30	0.44	0.46	0.37	0.35
A(%)	62	30	44	70	37	
After beneficiation						
Fe <sup>3+(a)</sup>	IS	0.34	0.33	0.33	0.35	0.33
	QS	0.45	0.47	0.49	0.47	0.43
	W	0.35	0.40	0.47	0.35	0.40
	A(%)	50	79	86	85	60
Fe <sup>3+(b)</sup>	IS	0.33	0.32	0.33	0.32	0.30
	QS	1.30	1.33	1.32	1.33	1.32
	W	0.40	0.45	0.45	0.35	0.45
	A(%)	25	21	14	15	30
Fe <sup>2+</sup>	IS	1.19	—	—	—	1.21
	QS	2.89	—	—	—	2.79
	W	0.35	—	—	—	0.40
	A(%)	25	—	—	—	10

IS = isomer shift  $\pm 0.02$  mm/s, QS = quadrupole splitting  $\pm 0.01$  mm/s, W = width line  $\pm 0.02$  mm/s, A = relative area  $\pm 3\%$ , B<sub>hf</sub> = hyperfine field  $\pm 0.2$  T

\* in mm/s

\*\* in Tesla

0.44 wt.% (sample 3); 2.0 wt.% (sample 4); and 0.48 wt.% (sample 5). The chemical composition of sample 2 has not been analysed post-beneficiation. As can be seen (Table 3), significant amounts of Fe still remain in the samples. This led us to investigate the nature and distribution of the Fe impurities using  $^{57}\text{Fe}$ -MS and ESR.

### Electron spin resonance (ESR)

Electron spin resonance spectra of Brazilian kaolin before beneficiation (Fig. 3a) are mainly composed of broad and intense lines (line width ranging from 550–2500 gauss) due to Fe and/or Fe-Ti oxides. Samples 2, 3 and 4 present an intense hematite signal centered at 2500–2900 gauss, whereas the ESR spectrum of sample 5 is dominated by the magnetite signal (maximum at ~350 gauss), which covers almost the entire analysed magnetic domain. At low fields, two

superposed signals are associated with  $\text{Fe}^{3+}$  ions (substitution for  $\text{Al}^{3+}$ ) in two types of site with different degrees of distortion (Brindley *et al.*, 1986; Balan *et al.*, 1999). These signals are referred to as  $\text{Fe}_{(I)}$  and  $\text{Fe}_{(II)}$  with  $g$ -values:  $g_{\text{eff}} \approx 4.3$  with a shoulder at  $g_{\text{eff}} \approx 9.8$  and  $g_1 = 3.5135$ ,  $g_2 = 5.0020$  and  $g_3 = 9.1180$ , respectively. In addition, an axial signal with  $g_{\parallel} = 2.0525$  and  $g_{\perp} = 2.0085$ , attributed to radiation-induced defects (RID) (Clozel *et al.*, 1994), was also observed for all samples and the characteristic sextet of  $\text{Mn}^{2+}$  ions was detected for sample 1 (Fig. 3a).

After beneficiation (magnetic separation and chemical treatment), the ESR spectra of all the studied samples still presented structural  $\text{Fe}^{3+}$  (in the  $g \approx 4.3$  region) and RID signals (Fig. 3b). The treated samples did not exhibit signals associated to Fe oxides, except for sample 4, whose spectrum shows a broad signal (line width ~2400 Gauss) centered at  $g \approx 2.75$  due to some magnetic

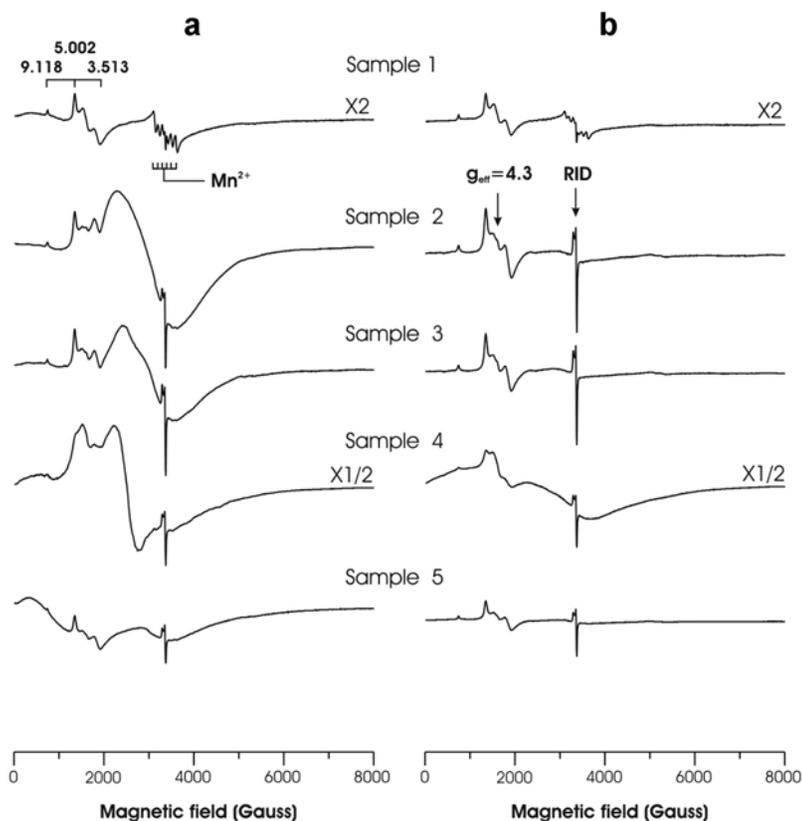


FIG. 3. X-band ESR spectra (at room temperature) of Brazilian kaolin samples (a) before and (b) after the beneficiation process, (RID: Radiation-Induced Defect).

compounds which were not removed by the beneficiation process (Fig. 3*b*). Fine particles of Fe oxides may still be trapped in the lamellar structure of the kaolinite (sample 4).

### <sup>57</sup>Fe Mössbauer spectroscopy

The <sup>57</sup>Fe-MS of different kaolin samples (at room temperature) before the beneficiation process are shown in Fig. 4*a*. All <sup>57</sup>Fe-MS results exhibit magnetic components; the hyperfine parameters (Table 3) are characteristic of hematite (samples 2, 3 and 4) (Murad & Cashion, 2004). In the case of

samples 1 and 5, it was difficult at room temperature to identify the magnetic components observed by ESR. After the beneficiation process, the spectra shown in Fig. 4*b* (hyperfine parameters in table 3) only exhibit two quadrupole doublets related to Fe<sup>3+</sup> (all samples) and Fe<sup>2+</sup> (samples 1 and 5). Mössbauer spectra in high velocity (not shown here) indicated that magnetic components were removed from all samples except for sample 3 and 4, whose spectra contain a weak magnetic sextet due to Fe oxides (goethite and/or hematite). Mössbauer measurements at low temperature are necessary to identify the Fe oxide species more

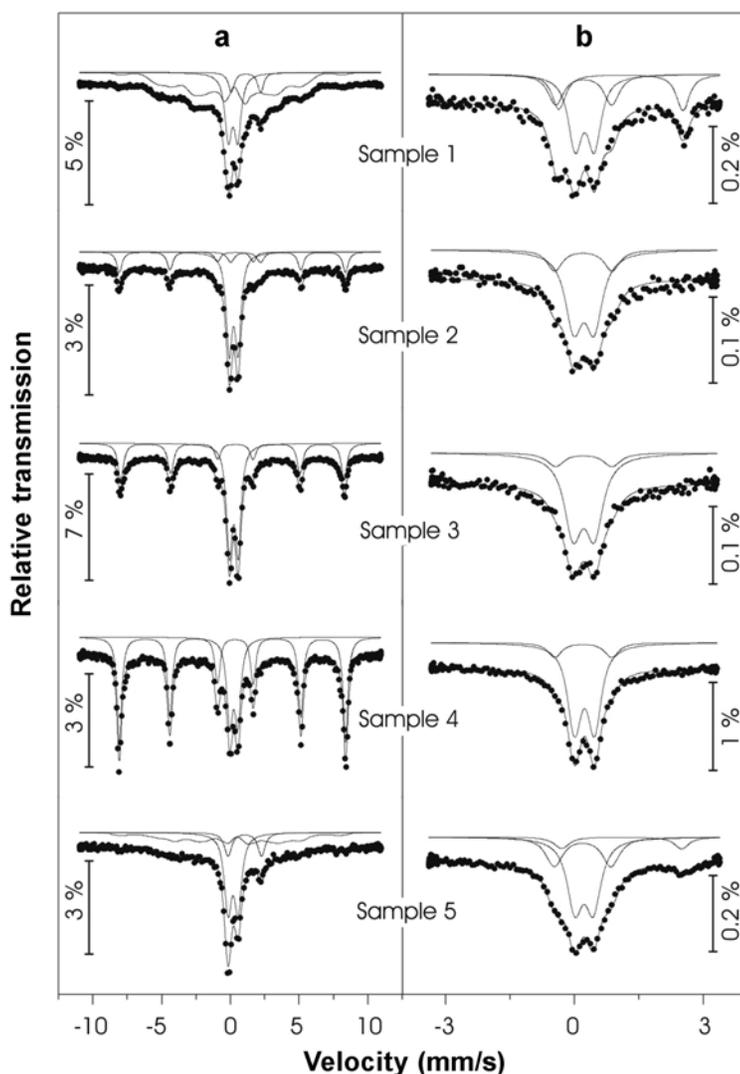


FIG. 4. <sup>57</sup>Fe-MS of kaolin samples at room temperature (a) before and (b) after the beneficiation process.

clearly, before and after the beneficiation process. For sample 3, goethite was not detected by ESR (Fig. 3b) due to its antiferromagnetic nature at room temperature (Guskos *et al.*, 2002).

## CONCLUSION

The granulometric study documented here showed that kaolin grains from primary deposits (Mogi das Cruzes, SP and Seridó, RN) are coarser than those of secondary deposits. After the beneficiation process (involving magnetic separation and chemical bleaching with sodium dithionite), the greatest whiteness index was obtained for sample 5 (87.72%) from the Seridó primary deposit and the most improved sample (from 55.81% to 63.34%), was from Mogi das Cruzes (sample 1), also a primary deposit. For all samples, a significant increase in the whiteness index occurred after magnetic separation, related to the removal of Fe oxides from crude kaolin. However, a non-negligible amount of Fe was still detected by XRF after the chemical bleaching. This Fe may be present as Fe<sup>3+</sup> or Fe<sup>2+</sup> in the kaolinite structure and/or in fine particles of Fe oxides or hydroxides trapped between the kaolinite lamellae. The ESR and <sup>57</sup>Fe-MS investigation confirmed this hypothesis.

Room temperature ESR experiments allowed us to detect two signals in all samples at low field, attributed to structural Fe<sup>3+</sup> in two different sites. Moreover, it was confirmed that Fe oxides (magnetite and hematite) were removed by the beneficiation process except for sample 4 (Rio Jari) which still presents a broad and intense signal, probably due to fine particles of hematite.

The <sup>57</sup>Fe-MS results are consistent with ESR and provide important supplementary information. In addition to structural Fe<sup>3+</sup> doublets (observed in all samples), Fe<sup>2+</sup> doublets were detected for samples 1, 2 and 5. Before beneficiation Mössbauer spectra show the presence of hematite (samples 2, 3 and 4 from secondary deposits) and goethite (samples 1 and 5 from primary deposits), although these minerals were not detected by XRD. These oxides are removed by the beneficiation process (see samples 1, 2 and 5, table 3). However, remaining weak magnetic components of Fe oxide could not be identified at room temperature.

In this study, ESR and <sup>57</sup>Fe-MS provided valuable information on the nature of Fe impurities and the efficiency of the beneficiation process.

## ACKNOWLEDGMENTS

The authors are grateful to the Centro de Tecnologia Mineral (CETEM/MCT) for its support during the beneficiation process of the samples, to the CNPq/MCT for its financial support of the 'Kaolin' project. P. Munayco and M. Duttine are indebted to CLAF/CNPq, and CBPF/CNPq, respectively, for granting their post-doctoral fellowships.

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