Mg-BENTONITE IN THE PARNAÍBA PALEOZOIC BASIN, NORTHERN BRAZIL

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Abstract—Bentonite deposits are rare in Brazil and most of their production comes from a single region. A new bentonite occurrence, the Formosa bentonite from northern Brazil, is described here. The occurrence is associated with altered Mesozoic volcanic rocks of the Parnaíba Sedimentary Basin, one of the largest continental flood basalt (CFB) provinces on Earth. The purpose of the present study was to evaluate the physical and chemical properties of a new smectite-bearing deposit in Brazil. Analysis has shown that the major mineral present in the Formosa bentonite is a dioctahedral smectite along with minor amounts of hematite, K-feldspar, and kaolinite. Quartz is absent. A Li^+-saturation test (Hofmann-Klemen treatment) revealed a montmorillonite smectite; large interlayer-Mg^{2+} contents revealed by N_2 adsorption/desorption and cation exchange capacity results suggested a Mg-bentonite. This characterization helped to explore the structure-functionality (reactivity) relationship and to develop index tests for industrial applications and the research of new materials.

Use of this material as a desiccant-grade bentonite is envisaged (desiccant-grade bentonites contain Mg^{2+} and/or Ca^{2+} as the dominant exchangeable cations), or it could be activated with Na^+ for use in many industrial applications (*e.g.* as a drilling fluid or for pelletizing iron ore). The large areal occurrence of the flood basalts suggests the possibility of very large deposits of these bentonites, a promising new exploration target for this class of industrial minerals in northern Brazil.

Key Words—Bentonite, Brazil, Desiccant, Industrial Mineral, Montmorillonite, Smectite.

INTRODUCTION

Bentonite deposits are rare in Brazil, a country which imports ~60% of the bentonite which it consumes. More than 80% of Brazilian bentonite comes from a single region: the Boa Vista district, State of Paraíba in northeastern Brazil (Beurlen, 1995). Exploration in this region is decreasing due to the exhaustion of its reserves. The mineralogical composition of these deposits is mainly represented by montmorillonite, illite, kaolinite, and mixed layers of illite-montmorillonite and quartz (Gopinath *et al.*, 1981; Amorim *et al.*, 2004). These are classified commercially as Ca-bentonites and must be activated with sodium carbonate to be transformed into Na-bentonites to meet commercial and industrial interests, which are mainly in drilling fluids and iron ore pelletizing. Two main types of bentonites are mined in the Boa Vista region: Chocolate (so called due to its brown color) and Bofe (which has a pale green-yellow color) (Amorim *et al*., 2004). Many Brazilian studies concerning modifications and applications for adsorption and catalysis have used these two types of bentonites as starting materials (Pereira *et al.*, 2005; Paiva *et al.*, 2008; Vieira *et al.*, 2010; Villalba *et al.*, 2010; Cótica *et al.*, 2011; and others).

Recently, a new bentonite occurrence was discovered in northern Brazil (Moraes *et al.*, 2010) that is related to beds of green shales associated with clays and siltstones of the Eopermian Pedra de Fogo Formation, Parnaíba Paleozoic Basin (State of Maranhão, northeast Brazil). The deposit was referred to as the 'Balsas bentonite' after the main city in the area. Although it is not mined, application-based work was carried out by Moraes *et al*. (2011) to modify the Balsas bentonite (functionalization with propyl sulfonic groups) so that it could be used as a catalyst in esterification and other organic reactions.

In the present study, a new bentonite occurrence from the Parnaíba Basin is described. This bentonite, which extends over several km^2 in area, is associated with thick clayey layers that are related to altered basalts. Although these basalts have been described and mapped for many years, no detailed chemical or mineralogical studies of these clays have been carried out.

Thus, the purpose of the present study was to evaluate the physical and chemical properties of such smectite-bearing deposits. The area in question might well become a new exploration target for bentonite deposits in Brazil. Potential industrial applications of this type of bentonite are also discussed here.

GEOLOGICAL SETTING

The Parnaíba Sedimentary Basin, also known as Maranhão Basin, is located in the northeastern part of Brazil and covers an area of ~600,000 km^2 with an

elongated NE−SW polygonal shape (Figure 1). The basin encompasses almost all of the States of Maranhão and Piauí, and some of Tocantins and Ceará. This basin consists of a sedimentary column ~4000 m thick, which is divided into five depositional sequences that are separated by unconformities and orogenic events of global character. The sedimentary fill of the basin is the result of prolonged sediment accumulation that has been occurring since the Silurian−Late Permian period (conglomerates and sandstones) with a few Mesozoic sediments (fine-grained sandstones and clays). Triassic and Early Jurassic eolian sandstones are interlayered with tholeiitic basalts, which are covered locally by Middle−Late Jurassic sediments (Góes and Feijó, 1994; Milani and Zalán, 1999; Vaz *et al.*, 2007).

According to Merle *et al.* (2011), during Mesozoic times the Parnaíba Basin underwent widespread basaltic magmatic activity that was associated with the two-stage opening of the Atlantic Ocean adjacent to South America. This continental flood basalt (CFB) volcanism is considered one of the largest provinces on Earth and is identified as the Central Atlantic Magmatic Province (CAMP) (Marzoli *et al.*, 1999). Two main lithostratigraphic units are related to this magmatism: (1) the Mosquito Formation (~199 Ma), which crops out in the western part of the basin as lava flows of low-Ti tholeiite and is related to the opening of the Central Atlantic Ocean; and (2) the Sardinha Formation, which is related to distinct pulses of volcanic activity that took place until ~190 Ma, mainly as dikes and up to 400 m-thick sills which crop out in the eastern part of the Maranhão Basin.

The first study of the area, including regional geological mapping and the evaluation of industrial minerals in the Parnaíba basin, was conducted by the Geological Survey of Brazil (Lima and Leite, 1978). Those authors mentioned the occurrence of thick clayey deposits overlying the volcanic rocks and interpreted them to be a weathering product of underlying basalts. In the 1990s, the Geological Survey again conducted geological mapping on a 1:2,500,000 scale in the Parnaíba Basin with a special focus on bentonite prospecting (Rezende, 1997). More than 200 clay occurrences were sampled and characterized, mainly by X-ray diffraction (XRD) analysis. Samples from the clayey deposits over the basalts were also characterized, confirming the dominance of smectite. The geological origin (weathering *vs.* hydrothermal alteration) will not be discussed further here.

MATERIALS AND METHODS

Materials

The smectitic deposits extend over large areas and are >10 m thick in places (Rezende, 1997). Several occurrences were observed at various locations along the road between Belém and Brasília (BR-010), in the

area near the border between Maranhão and Tocantins, and on several stretches of State roads that intersect, in particular, south of Maranhão where the Formosa bentonite occurrence is located (Figure 1).

The studied clay was collected from an outcrop of altered basalt of the Mosquito Formation (coordinates 06º25′12′′S, 46º10′52′′ W), which is located in the vicinity of State Road MA-006 in Formosa da Serra Negra County in southern Maranhão (Figure 1). The outcrop is a road cut that is ~2 m thick. Drill cores were performed at the base of the profile and the clayey material was found to extend down to a depth of 5 m. Preliminary XRD analysis of the material revealed that the mineralogical composition is dominated by dioctahedral smectite. The material was given the name 'Formosa Bentonite' because of the nearby location of a city with the same name. The name is used throughout the present study in the comparison of the Formosa Bentonite with two commercial Brazilian bentonites (Chocolate and Bofe, as described above) and with the well known SAz-1 and SWy-2 smectites from the Source Clays Repository of The Clay Minerals Society.

The material collected in the field was taken from different parts of the outcrop and comprised ~40 kg in total. In the laboratory, the sample was crushed and milled using a Jaw Crusher (Retsch, BB200, Hann, Germany), and Planetary Ball Mill (HERZOG, HSM100, Osnabrück, Germany) to a size of <0.15 mm (ASTM 100) with manual sieving. The material retained was milled again until it all passed through the sieve. The sample was homogenized and quartered to ensure a representative sample. The reference samples (Chocolate, Bofe, SWy-2, and SAz-1) were subjected to the same preparation procedure as that described for the investigated clay.

The clay fraction (<2 μm) of the Formosa sample was obtained according to the following procedure: 15 g of the sample was dispersed in 100 mL of distilled water in ultrasonic immersion for 5 min. The suspension was centrifuged for 2 min at $114 \times g$ in a Hitachi HIMAC CR21GII centrifuge to separate the sedimented silt fraction from the overflow (suspended clay fraction). The overflow was further centrifuged for 10 min at $456 \times g$ to concentrate the clay fraction and was finally dried at 60ºC.

Analysis

Chemical analysis (XRF). The X-ray fluorescence (XRF) spectrometer employed was a wavelength dispersive (WDS) sequential Axios-Minerals model from PANalytical, with ceramic X-ray tube and rhodium anode of maximum 2.4 kW power level. The specimens were prepared as glass discs (1 g of sample plus 8 g of lithium metaborate), using the *IQ+* program of PANalytical's *SuperQ Manager*. The measurement of loss on ignition (LOI) was taken on an independent test portion by heating for 1 h at 1000ºC in a muffle furnace.
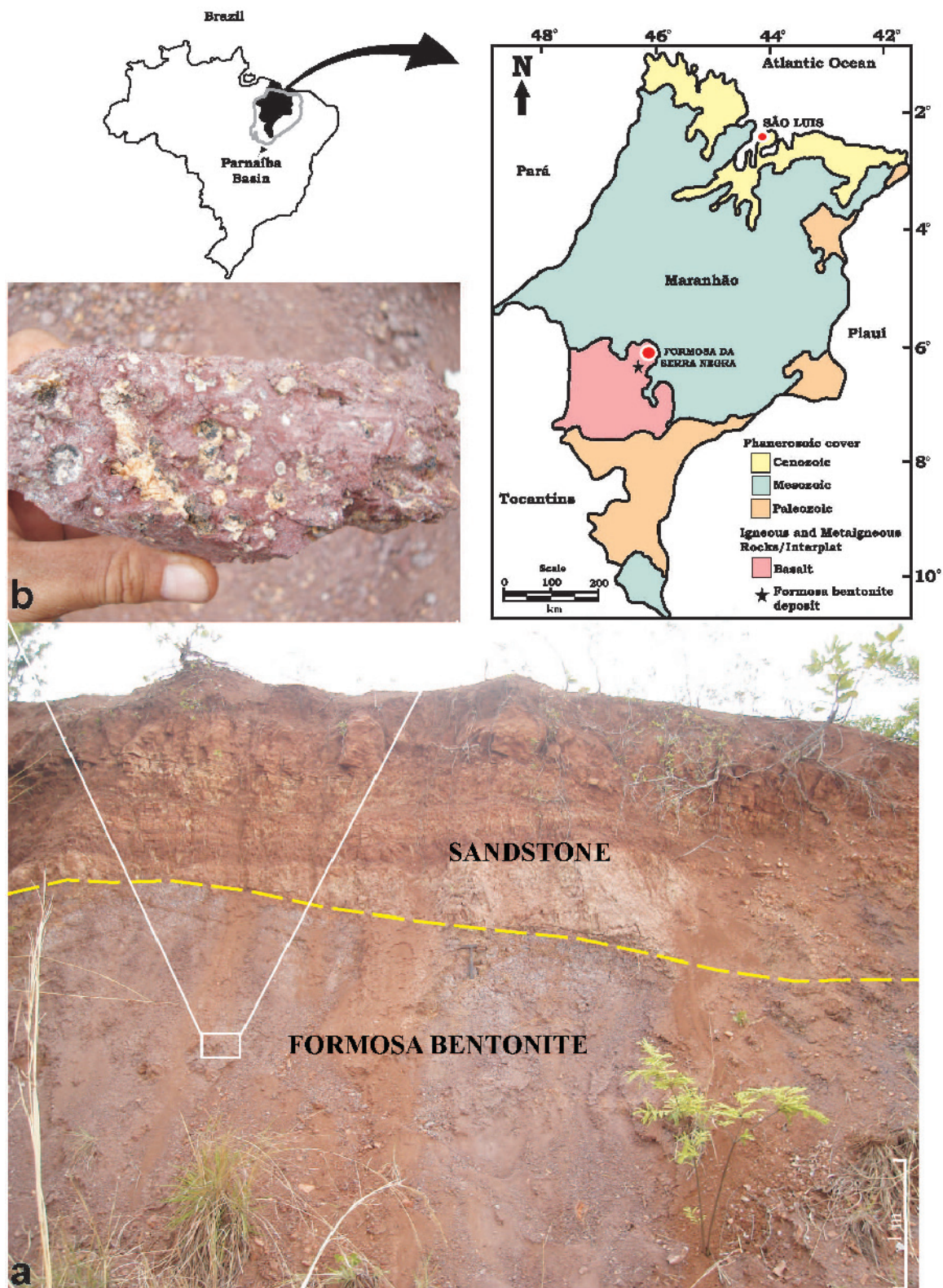
Figure 1. Geological map of the State of Maranhão and the location of the sampled area. (a) Geological outcrop (profile) showing the layers of sandstone and Formosa bentonite; (b) hand sample showing the typical texture of this bentonite: white and dark-green amygdales with a dark-red clayey matrix.

X-ray diffraction. The mineralogical composition of the bulk materials (randomly oriented samples) and the clay fractions (oriented samples) was determined by powder XRD, using a PANalytical X'Pert PRO MPD (PW3040/60) diffractometer with a ceramic X-ray tube (λ CuKα_1 = 0.1540598 nm), Kβ Ni filter, and an X'celerator PSD (Position-Sensitive Detector). For randomly oriented samples, the operating conditions were: scan range from 2 to 52º2θ, tube power of 40 kV and 30 mA, step size of 0.02º, time/step of 60 s, divergence slit of 1/8º, anti scattering slit of 1/4º, mask of 10 mm, and sample spinning with a rotation time of 1.0 s. For oriented samples the operating conditions were: scan range from 3 to 35º2θ, tube power of 40 kV and 30 mA, step size of 0.02º, time/step of 30 s; divergence slit of 1/8º, anti scattering slit of 1/4º, mask of 10 mm, and no sample spinning. Four sample treatments were used for XRD analysis. The first was air-dried; second, ethylene glycolated (without cation saturation); third, heating at 550ºC for 2 h; and fourth, Hofmann and Klemen (1950) treatment − Li saturation, heating at 300ºC for 12 h, and ethylene glycol adsorption.

Thermal analysis (TG/DTA). The measurements were carried out on ~17 mg of sample in a Thermal Science Thermoanalyzer model PL-STA. The experiments used alumina crucibles and N_2 atmosphere with a flow rate of 50 cm^3 min^{-1} with a heating time of 20ºC min^{-1} to 1100ºC.

Infrared spectroscopy (FTIR). The data analysis was conducted using a Perkin Elmer model 1760X FTIR spectrometer. For each sample, 100 scans were recorded with a resolution of 4 cm^{-1} and a range of 4000−400 cm^{-1}. The samples were prepared as pressed discs (1 mg of sample plus 200 mg of KBr).

Specific surface area (BET SSA) and pore volume (BJH PV). The total specific surface area (SSA) and total pore volume (PV) were determined by nitrogen adsorption/desorption analysis at 77 K using a Quantachrome Analyzer, model NOVA 1200. The results were plotted using the BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner- Helenda) methods. Before N_2 adsorption/desorption measurements, the samples were heated for 2 h at 250ºC.

Cation exchange capacity (CEC). The methylene blue adsorption method (Hang and Brindley, 1970) was used to determine the CEC of the five samples (Formosa, Chocolate, Bofe, SWy-2, and SAz-1). Another method was used for only the clay fraction of the Formosa bentonite (ammonium acetate method, Salerno and Mendioroz, 2002) to determine the exchangeable cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) and total CEC, as sum of
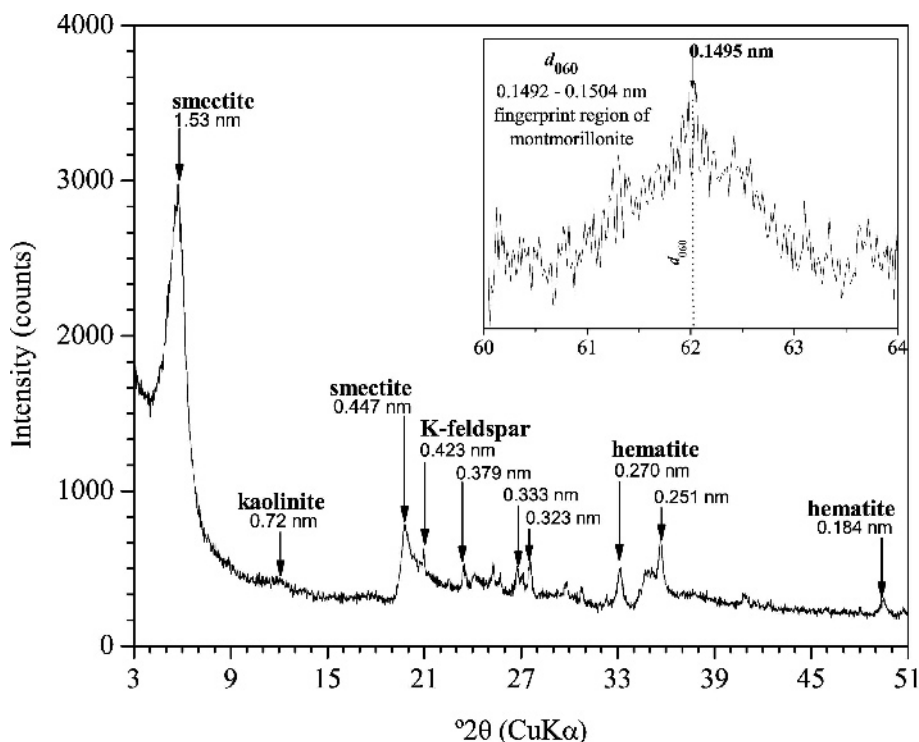

Figure 2. XRD patterns of Formosa bentonite: bulk sample and unoriented clay fraction in the 'fingerprint' region of montmorillonite.

exchangeable Na^+, K^+, Mg^{2+}, and Ca^{2+}, measured using a Perkin Elmer 3300 Atomic Absorption Spectrometer.

RESULTS

The XRD pattern of the Formosa bentonite in a randomly oriented bulk sample (Figure 2) revealed that the major mineral present is smectite (peaks at 1.53, 0.447, and 0.149 nm) along with minor amounts of hematite (0.270, 0.251, and 0.184 nm), K-feldspar (0.423, 0.333, and 0.323 nm), and kaolinite (0.72 nm).

The XRD analysis of the clay fraction, as analyzed on randomly oriented mounts (Figure 2), revealed a d_{060} value of 0.149 nm, which indicates a dioctahedral smectite. The expandability of the smectite in which the octahedral charge was neutralized (Hofmann-Klemen treatment) was investigated in the clay fraction on oriented mounts (Figure 3), which revealed the 0.99 nm peak that is typical of montmorillonite. The oriented-mount XRD pattern in the air-dried state (Figure 3) showed the typical shift of the d_{001} peak from 1.53 to 1.73 nm in the ethylene glycol state. After heating, the typical collapse to 0.99 nm was observed, which overlaps with a small illite peak that was not detected in the bulk sample. The result for the d_{002} peak (ethylene glycol slide) was 0.85 nm, i.e. a regular smectite (rational harmonic); the possible presence of an I-S R0

(non-rational harmonic, d_{002} between 0.85 and 1.00) can be dismissed.

The XRD pattern of the Formosa sample was compared with those of the Brazilian bentonites (Chocolate and Bofe) (Figure 4). These comparisons revealed that smectite is the dominant mineral in all samples, with very similar d_{001} values for the main peak. The kaolinite contents were apparently greater in the Bofe material than in the Formosa sample and were almost absent from the Chocolate bentonite. The quartz content was greater in Chocolate than in Bofe and absent from the Formosa bentonite. Cristobalite and goethite were only found in the Chocolate and Bofe samples, respectively.

The XRD pattern of the Formosa sample was also compared with SWy-2 and SAz-1 (Figure 5). The comparison shows a marked difference in terms of the d_{001} spacing of SWy-2 (1.2 nm), in comparison with the other four samples (close to 1.5 nm). According to Grim (1968) and Yildiz and Kuscu (2007), d_{001} values ranging from 1.489 to 1.55 nm indicate the presence of Ca,Mg-smectite, as observed in the Formosa, Chocolate, Bofe, and SAz-1 samples, and $d_{001} \approx 1.2$ nm indicates a Na-smectite, as observed in SWy-2, which is the best known Na-bentonite in the world. Calcite is only present in SWy-2.

The chemical compositions of the bulk samples (Table 1) revealed that SiO_2 and Al_2O_3 are the major components
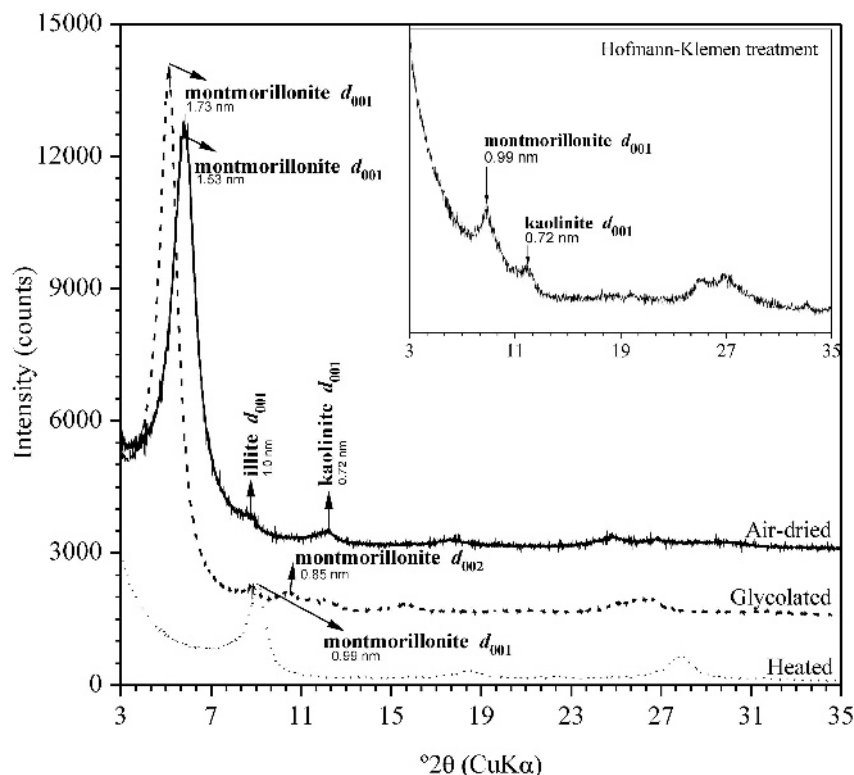

Figure 3. XRD patterns of the oriented <2 μm fraction of the Formosa bentonite: air-dried, glycolated, heated at 550°C, and after Hofmann-Klemen treatment.
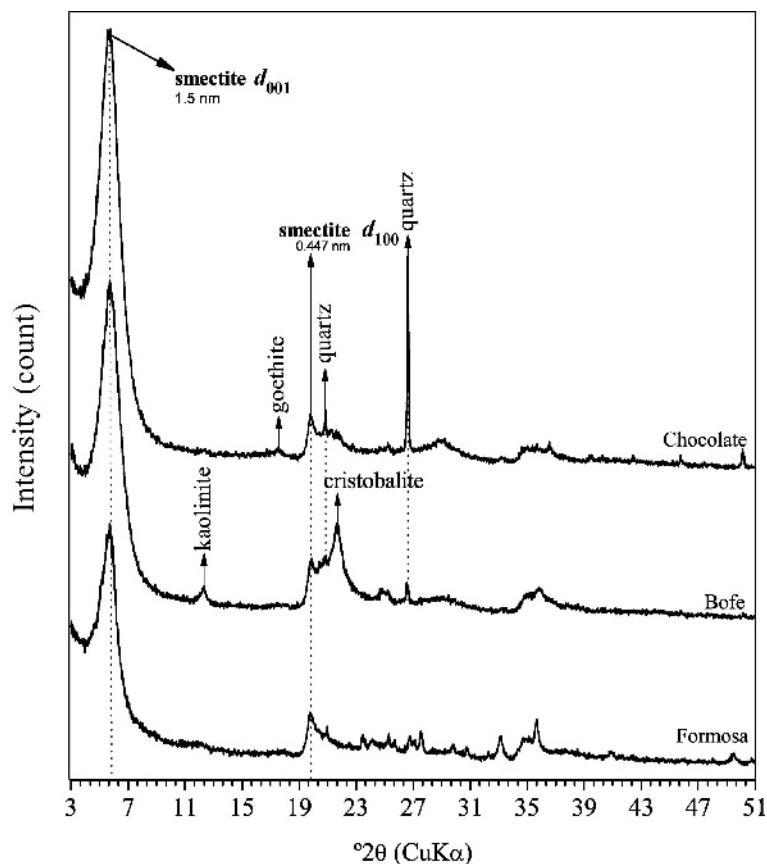
Figure 4. Comparison of the XRD patterns of the Formosa, Bofe, and Chocolate bentonites (bulk samples).

found in all of the samples because their mineralogy is dominated by smectite. The Formosa bentonite exhibited greater Al_2O_3 contents than Chocolate, Bofe, and SAz-1, even though the SiO_2 contents were the smallest of all of the samples (quartz and/or cristobalite were absent).

The clay fraction of the Formosa bentonite exhibited greater SiO_2 and Al_2O_3 contents and smaller Fe_2O_3 and K_2O contents in comparison with the bulk sample (Table 1), because of the greater concentration of smectite in the fine fraction and the smaller amounts of hematite and K-feldspar. The MgO and CaO contents were almost the same in the two fractions.

The Formosa contained the most Fe_2O_3 (14.08%), followed by Chocolate (10.19%) and Bofe (6.87%). These three samples also had relatively small Na_2O and CaO contents in comparison with the SWy-2 and SAz-1 samples. This is a typical chemical characteristic of the Brazilian bentonites. The Formosa sample contained the second largest amount of MgO (3.63%), just less than that of the SAz-1 sample (5.95%). The LOI results were very close among the samples analyzed, except for SWy-2, which exhibited a smaller value (7.36%).

The DTA curves of the samples studied (Figures 6, 7) revealed closer similarities between Formosa and the

Table 1. Chemical compositions (wt.%) of the samples studied.

Bentonites	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	MnO	TiO_2	P_2O_5	LOI
Formosa bulk	48.13	17.40	14.08	3.63	0.27	1.59	–	0.17	1.49	0.05	13.08
Formosa (<2 μm)	51.65	21.58	8.51	3.87	0.29	0.90	–	–	0.47	–	12.70
Chocolate bulk	56.76	15.37	10.19	2.76	0.53	0.29	0.86	–	0.70	0.19	12.12
Bofe bulk	64.07	14.63	6.87	1.91	0.44	0.19	0.61	–	0.70	0.03	10.53
SWy-2 bulk	63.77	18.53	3.89	2.46	1.50	0.48	1.66	–	0.15	0.08	7.36
SAz-1 bulk	60.12	16.77	1.45	5.95	2.68	0.17	–	0.08	0.25	0.03	12.41

LOI: Loss on ignition as determined by heating at 1000ºC after drying at 105ºC; –: below the detection limit
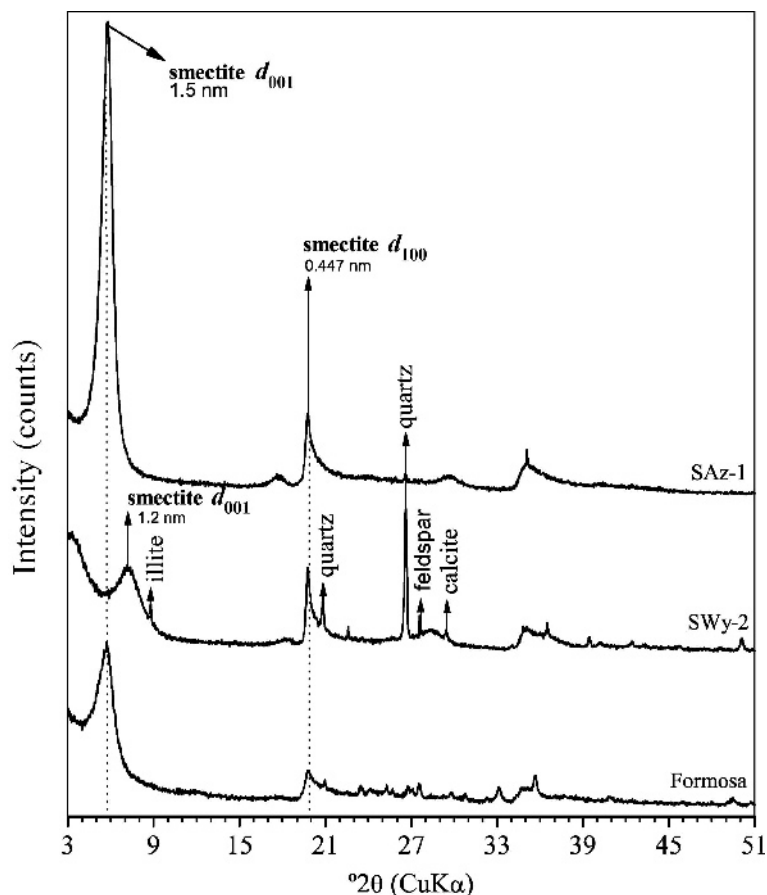
Figure 5. Comparison of the XRD patterns of the Formosa, SWy-2, and SAz-1 bulk samples.

two other Brazilian bentonites than with the two smectites. In all of the curves, two main features were observed: (1) a characteristic H_2O desorption-dehydration endothermic peak ranging from 96 (SWy-2) to 124ºC (Formosa); and (2) a second endothermic peak, ranging from 506 (Chocolate) to 702ºC (SWy-2), caused by dehydroxylation. This lower dehydroxylation temperature for the Chocolate sample (region a, Figure 6) may be due to a larger Fe content in the octahedral site in its smectite, while the Formosa sample had larger Fe_2O_3 contents, which are more related to hematite. On the other hand, the Formosa sample exhibited a lower dehydroxylation temperature (512ºC) than the SWy-2 sample (702ºC) (region a, Figure 7). The greater dehydroxylation temperature observed for SWy-2 is the

normal temperature for a smectite with low Fe-for-Al isomorphic substitution in the octahedral sheet (Todor, 1976; Souza Santos, 1989). A final double peak (endothermic-exothermic) corresponds to destruction of the structure and is followed by recrystallization of α-quartz and/or β-mullite between 850 and 1050ºC (region b, Figures 6 and 7).

The main mass losses during thermal treatments of the materials studied (Table 2) are suggested to be related to the following effects: loss of water molecules (Δwt.H_2O) in the form of free water, hydration water, and hydroxyl groups (Δwt.OH^-) (Guggenheim and Koster van Groos, 2001; Pansu and Gautheyrou, 2006). Mass loss due to desorption-dehydration (ambient up to 300ºC) is quite variable among the different samples

Table 2. Main thermogravimetric data of the bulk samples studied.

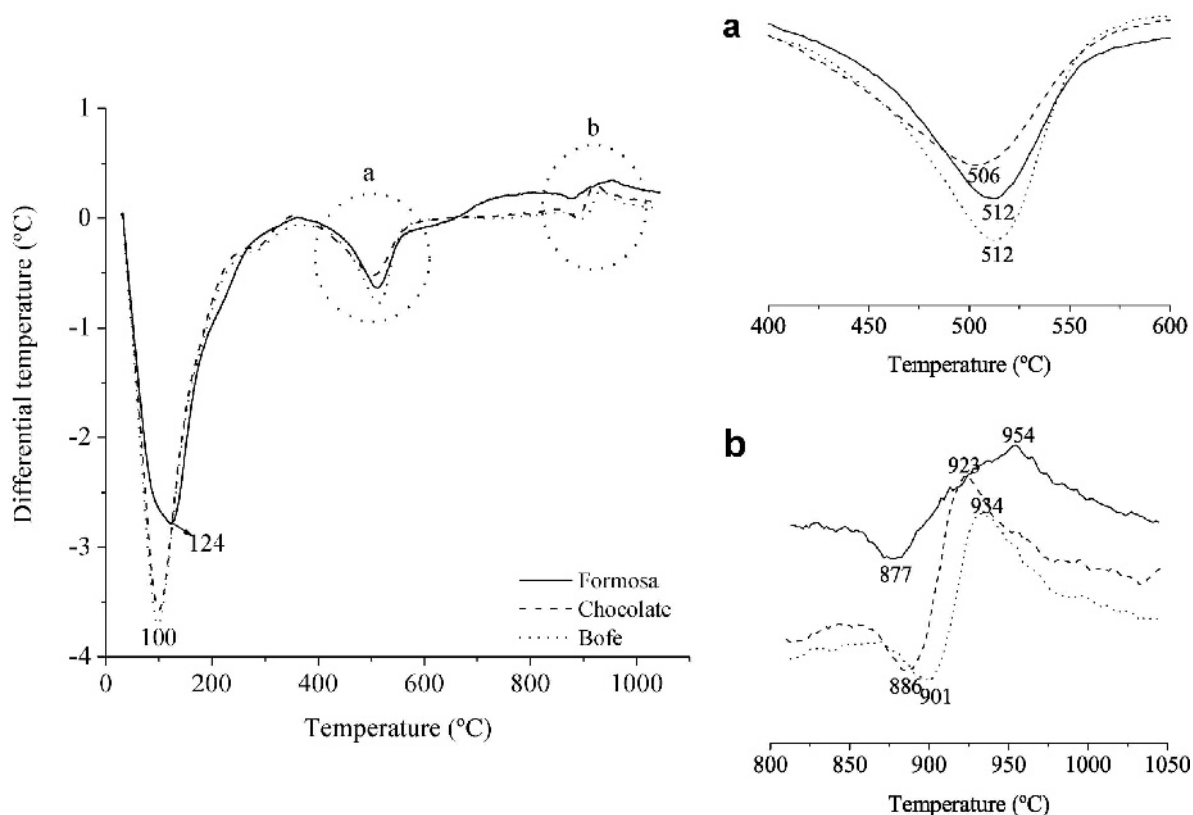| Mass loss (%)	Formosa	Chocolate	Bofe	SWy-2	SAz-1
Δwt.H_2O (temperature; ambient up to 300ºC)	9.86	14.78	11.81	4.48	15.77
Δwt.OH^- (400−750ºC)	3.74	4.19	2.94	3.70	3.20
Δwt.Total (temperature: ambient up to 1050ºC)	13.52	20.33	15.56	7.94	18.42

Figure 6. DTA curves of the Formosa, Chocolate, and Bofe bentonites (bulk samples).

studied and is mainly related to the chemical composition of the smectites, though a small contribution from the accessory minerals is also possible. Mass losses due to dehydroxylation (400−750°C) did not vary dramatically; this mass loss (*i.e.* the difference between Chocolate and Bofe) had a greater Δ value of 1.25%. The differences due to H_2O loss may reach 11.3%, when one compares the Δwt.H_2O of the Ca-Mg samples (Formosa, Chocolate, and SAz-1) with Na-montmorillonite (SWy-2).

The FTIR spectrum of the Formosa sample was similar to that of the reference samples (Figures 8, 9). The typical bands assigned for smectite (Van der Marel and Beutelspacher, 1976) are as follows: ~3622 cm^{-1} (OH-stretching of structural hydroxyl groups); ~3422 cm^{-1} (OH-stretching of water); ~1030 cm^{-1} (Si−O stretching); ~915 cm^{-1} (Al−Al−OH deformation); ~528 cm^{-1} (Al−O−Si deformation); and ~466 cm^{-1} (Si−O−Si deformation).

The bands at 3700 (OH stretching), 752, and 700 cm^{-1} (perpendicular vibration of the Si−O bond) are related to kaolinite, identified in the Formosa and Bofe spectra and confirming the XRD results. The bands at 800 and 770 cm^{-1} are due to Si−O stretching, and may be related to other SiO_2-bearing phases that are present in small amounts in the samples. Thus, the 798/787 cm^{-1} doublet in the SWy-2 and Chocolate

samples may be related to quartz, while the single band at 792 cm^{-1} (Bofe, SAz-1, and Formosa) may be related to a mixture of quartz and low-crystallinity silica (Madejová and Komadel, 2001). In the case of the Formosa sample, it must be related to low-crystallinity silica (opal) which was originally associated with vesicles in the amydaloidal basalts.

The band at 885 cm^{-1}, is related to Al-Fe-OH deformation (it can also be related to carbonates if no other absorption band at 1400−1440 cm^{-1} is found.) Note that this region was excluded because no other band was detected in the samples, except for SWy-2 which contains a small amount of calcite. The IR spectrum of SAz-1 lacks a deformation band at 885 cm^{-1}. All samples have a deformation band at 842 cm^{-1} which is attributed to Al-Mg-OH. This band is very strong in SAz-1 and very weak in SWy-2. At 620 cm^{-1}, the Al−O and Si−O out-of-plane bending modes are very strong in SWy-2 and SAz-1, weak in Formosa, and not observed in either Bofe or Chocolate.

Finally, note that the bands related to the groups linked directly to the smectite tetrahedral and octahedral sites undergo frequency and intensity changes depending on small chemical variations in the dioctahedral smectites, *e.g.* the bands at ~885, 842, and 620 cm^{-1}.

The SSA and PV results (Table 3) revealed that the Bofe bentonite has the largest values and SWy-2, the
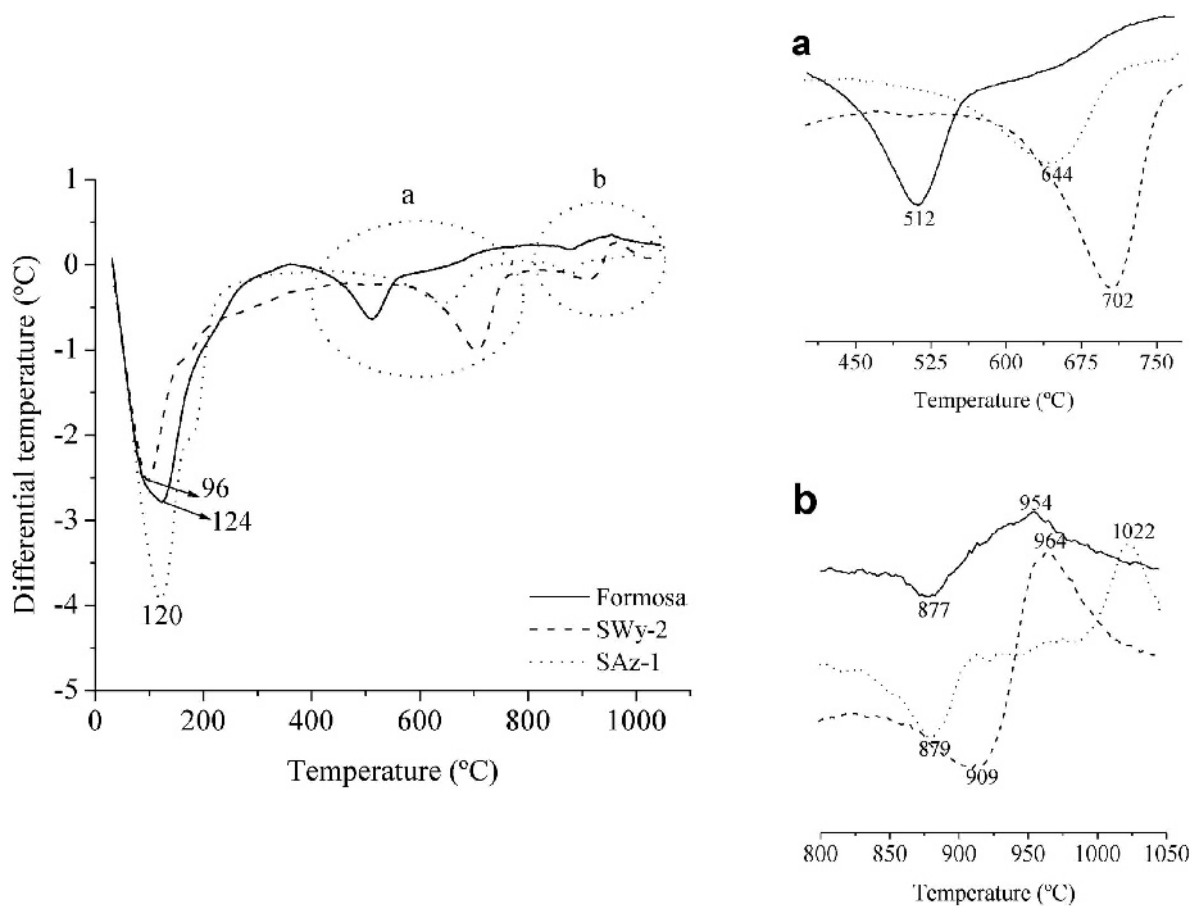
Figure 7. DTA curves of the Formosa, SWy-2, and SAz-1 bulk samples.

smallest. The isotherms of N_2 adsorption/desorption (Figure 10) of all of the samples belong to type IV with hysteresis loop of type H3, which is typical of solids containing clusters of particles with slit-shaped pores and no uniformity in terms of size and/or shape (Leofanti *et al.*, 1998). The hysteresis loop of type H3 corresponds to capillary condensation of liquid N_2 in mesopores. Thus, the hysteresis loop of the Ca-rich samples (Chocolate, Bofe, and SAz-1), which have more mesopores, are more open than the Na-montmorillonite

(SWy-2), which has fewer mesopores (Neaman *et al.*, 2003). The Formosa clay (Mg-bentonite, discussed below), exhibits an intermediate opening of the hysteresis loop in comparison with the Ca and Na samples. The SSA and PV results were also intermediate for this sample.

The CEC results obtained using the methylene blue adsorption method (Table 3) revealed that SAz-1 had the largest value (93.7 meq/100 g of dry clay) among all samples and that Chocolate had the largest value among

Table 3. Main physical and chemical properties of the bulk samples studied.

Bentonites	SSA ($m^2 g^{-1}$)	PV ($cm^3 g^{-1}$)	CEC (meq/100 g of dry clay) (this analysis, MBA method*)	CEC (meq/100 g of dry clay)
Formosa	55.9	0.06	50.5	
Chocolate	101.4	0.09	68.1	106[a]
Bofe	115.6	0.19	49.2	74[a]
SWy-2	23.3	0.04	58.8	85[b]
SAz-1	74.8	0.09	93.7	123[b]

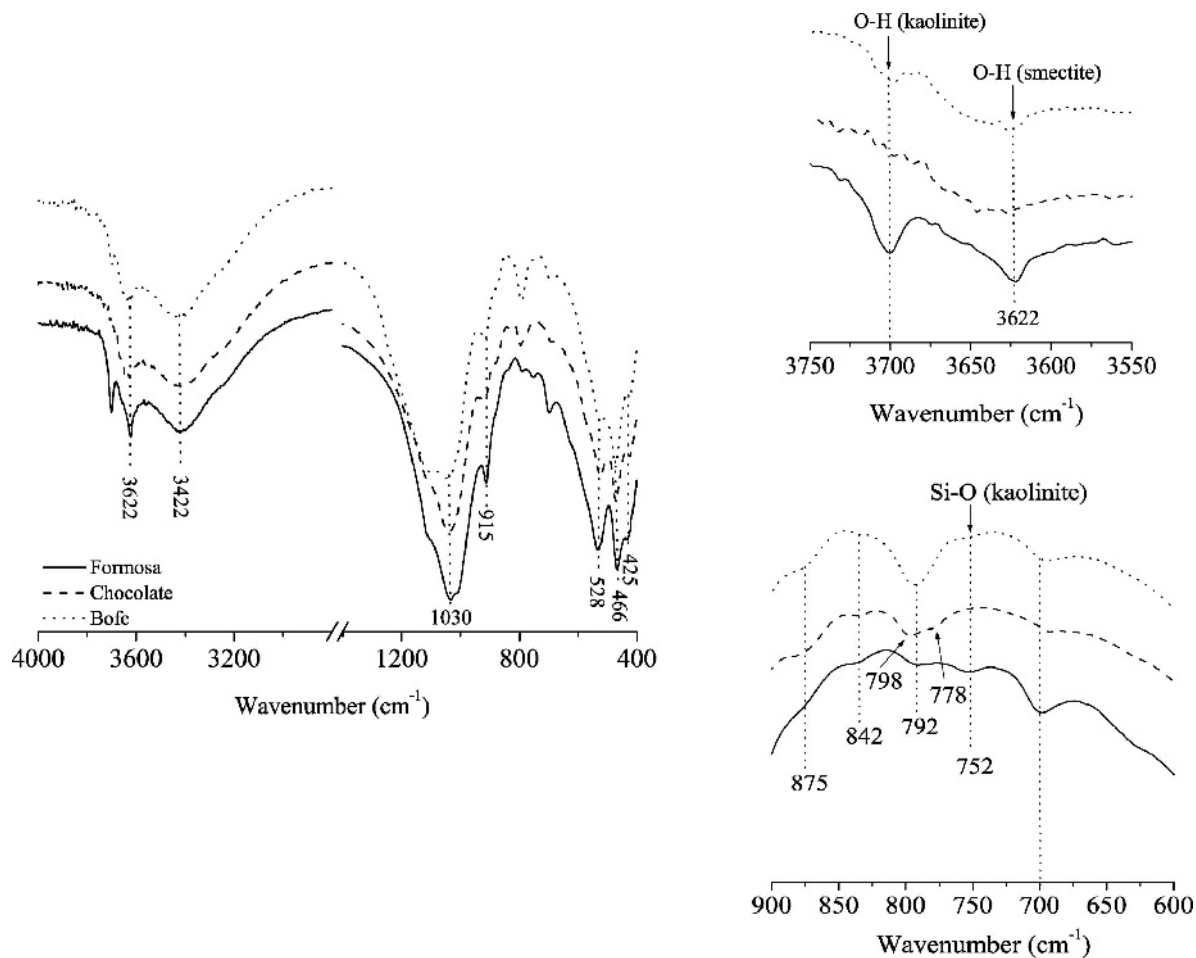* Methylene blue adsorption method; [a] Aranha (2007); [b] Borden and Giese (2001)

Figure 8. FTIR spectra of the Formosa, Chocolate, and Bofe bentonites (bulk samples).

the Brazilian samples (68.1 meq/100 g of dry clay). The CEC values for Bofe and Formosa were very similar (49.2 and 50.5 meq/100 g of dry clay, respectively). Although the absolute values obtained in the present work cannot be compared with those from the baseline studies of clays from the Source Clays Repository of The Clay Minerals Society (Borden and Giese, 2001) and from Aranha (2007) because different methods were employed in those studies, all the results are of the same order of magnitude and exhibit the same trends.

The ammonium acetate method was only used for the clay fraction of the Formosa bentonite (Table 4); the results revealed that Mg^{2+} is the major exchangeable cation at pH $\approx$ 7, even though Ca^{2+} has a greater selectivity than Mg^{2+}. This clearly implies that Formosa is a Mg-bentonite, as suggested above by the N_2 adsorption/desorption results. This result also showed that some of the Mg obtained by the total chemical analysis is unrelated to the octahedral cations, but rather is present as an interlayer cation. This point confirms the dioctahedral nature of the smectite studied, as already observed by XRD.

DISCUSSION

Some chemical characteristics usually found in Brazilian bentonites are that they contain more Fe_2O_3 and less Na_2O and CaO than the American bentonites (or smectites). The mean Fe_2O_3, Na_2O, and CaO contents found in the Brazilian bentonites studied here are as follows: 10.38, 0.41, and 0.49%, in comparison with 2.67, 2.09, and 0.83%, respectively, for the American bentonites. Such differences have been shown clearly here.

Table 4. Exchangeable cations and total* CEC of the clay fraction of the Formosa bentonite, as determined using the ammonium acetate method.

	– Dry clay (meq/100 g) –			
Mg^{2+}	Ca^{2+}	K^+	Na^+	CEC*
60.19	9.88	1.41	3.35	74.83

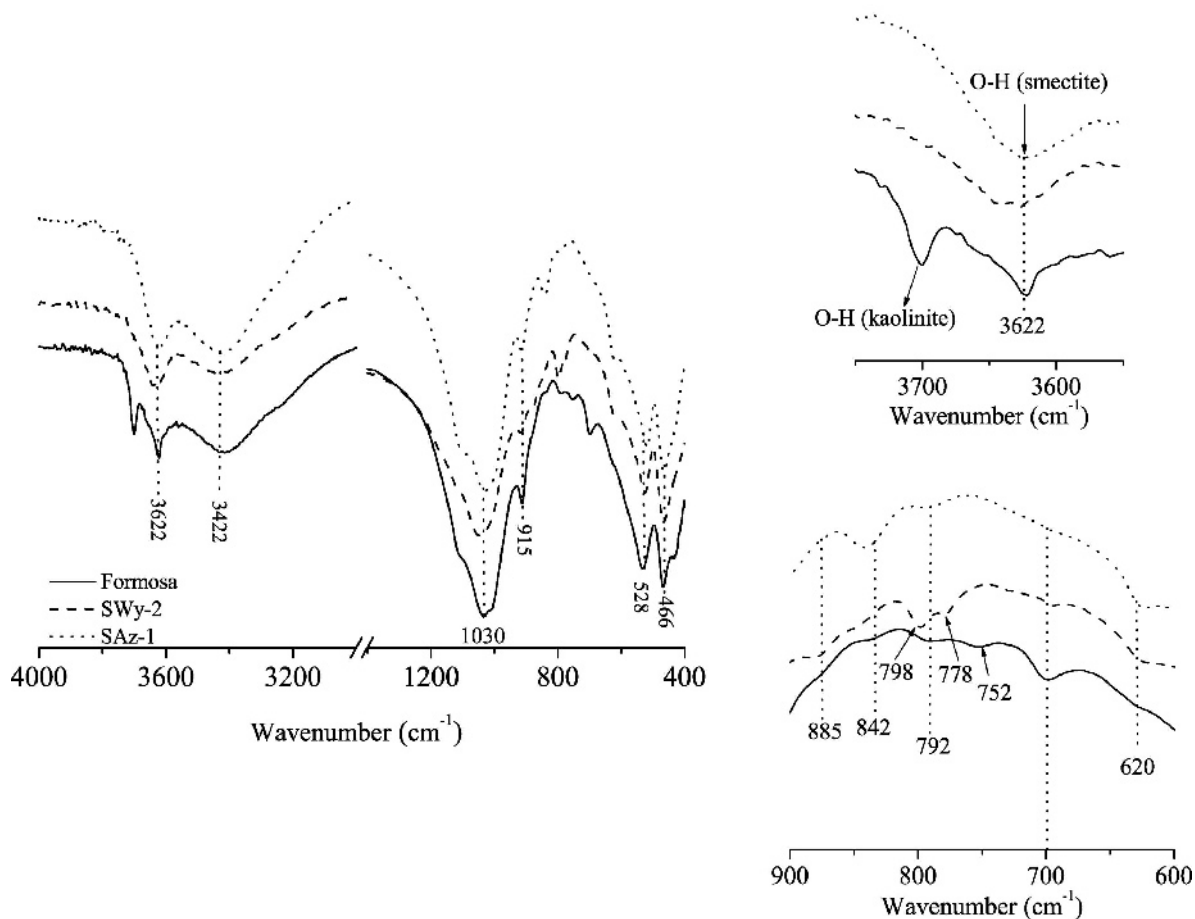* calculated as the sum of exchangeable Mg^{2+} + Ca^{2+} + K^+ + Na^+

Figure 9. FTIR spectra of the Formosa, SWy-2, and SAz-1 bulk samples.

In general, bentonites exhibit a wide crystallochemical range because of the different possibilities of cation replacement in the tetrahedral and octahedral sites. This will depend on the availability of the various elements in the environment of formation of the smectite and several other factors including types of physical-chemical processes (*e.g.* hydrothermal alteration, weathering) and time (Christidis and Huff, 2009; Wolters *et al.*,
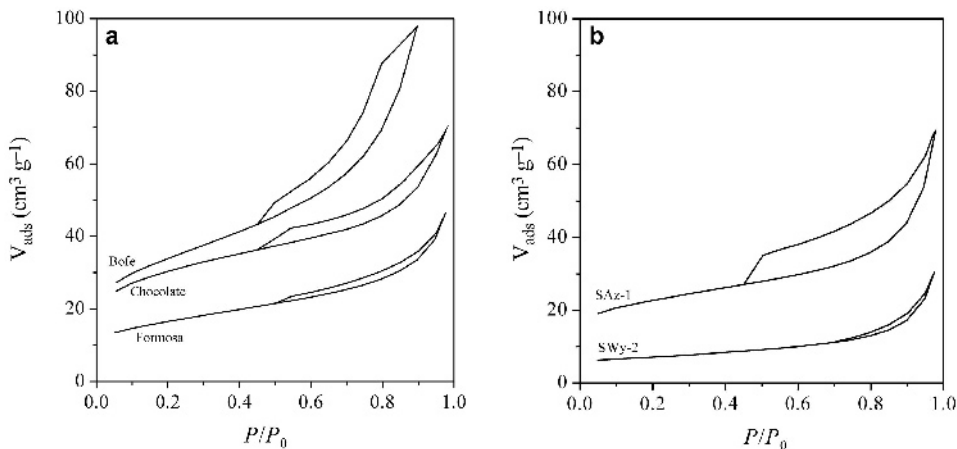

Figure 10. N$_2$ adsorption-desorption isotherms: (a) Formosa, Chocolate, and Bofe bentonites; (b) SWy-2 and SAz-1 smectites.

2009). Impurities (associated accessory minerals) also contribute to differences in the chemical-mineralogical compositions among the bentonites.

With regard to the mineralogical composition of the Formosa bentonite, the absence of quartz and the near absence of kaolinite are of interest. In bentonites to be used as binders for pelletizing iron ore, quartz is undesirable. According to recent economic data in Brazil (Coelho, 2009), the use of bentonite in the pelletizing of iron ore will surpass the current major use of bentonite (as pet litter) in 2012. The presence of hematite, although it may not be desirable for some applications, is not a problem for pelletizing of iron ore.

The detailed characterization of smectite has led to its determination as a montmorillonite with Mg as the main interlayer cation. This information will help to explore the structure-functionality (reactivity) relationship and to develop index tests for industrial applications and new-materials research.

The Wyoming montmorillonite (such as SWy-1 or SWy-2), a natural Na-smectite, has the best rheological and colloidal properties and the largest number of known applications that do not require chemical pretreatment. In countries without Na-bentonite deposits, such as Brazil, chemical processes for cation exchange are used to obtain Na-activated bentonites. Such treatment has helped to meet national demand in Brazil, with its main deposits being the Ca- and/or Mg-bentonites from Paraíba (Amorim *et al.*, 2004; Moraes *et al.*, 2010). Meanwhile, most of the high-quality varieties (*e.g.* Chocolate type) are nearly exhausted. The need for new areas of exploration in Brazil is urgent, and the Formosa Bentonite type is a possible candidate as an alternative for the Paraíba deposits.

CONCLUSIONS

Smectite associated with basalts of a common Mesozoic volcanism in northern Brazil was characterized in terms of its mineralogical and chemical compositions. Analysis showed that montmorillonite is the dominant phase, though small amounts of hematite, K-feldspar, and kaolinite are also present. The chemical composition, N_2 adsorption/desorption, and CEC results suggest that the Mg- or Ca/Mg-bentonite can function well as desiccants because of the greater first- and second-shell hydration energies of Ca^{2+} and Mg^{2+} cations relative to Na^+.

Further work on this bentonite occurrence is needed.

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