Clay Mineral Characterization in Kaolins and Ball Clays from Santa Catarina

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Short Running Title: Kaolins and Ball Clays from Santa Catarina.
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Abstract

Five kaolins and eight ball clays from the State of Santa Catarina, used industrially for whitewares production and other applications were characterized in relation to their clayminerals, specially those related to the kaolin group. The following methods were used: XRD, DTA, TEM, SEM and EDS / TEM (elemental microanalysis by EDS). The main objective was to prove that the electron optical methods are necessary to detect small amounts of 7Å-halloysite in presence of kaolinite because they are masked in the XRD curves. In conclusion, five kaolins and three ball clays were found being mixtures of kaolinites (either well crystallized or b-axis disordered) with different percentage of 7Å-halloysite (either long or short tubes), while the other five ball clays are constituted only by b-axis disordered kaolinite.

Keywords: kaolinite, halloysite, kaolin, ball clay.

Introduction

Publications on kaolins (or china clays) and plastic clays for whitewares (usually known as ball clays) from the State of Santa Catarina, describing the geology of the deposits and their ceramic properties have made only recently; the nature of the clay minerals present in these two clays has been pointed, usually, as being kaolinite; sometimes, halloysite is also mentioned. However, the precise characterization of both clay minerals and their structural varieties has not been described in any of these publications. As the precise characterization cannot be made in basis of only one X-ray powder diffraction curve (10), it is important that these publications should be complemented by more precise characterizations due to the necessity of a good knowledge of the dependence of the ceramic and non-ceramic properties of kaolins and ball clays on the varieties of kaolinite and halloysite -7Å, either isolate or in mixtures in several proportions (8; 26; 41; 42) that are the major component of these clays.

The purpose of this paper is to characterize, qualitatively, which are the varieties of kaolinite and/or halloysite present in some kaolin and ball clays of present industrial use in Santa Catarina; other clay minerals groups may exist in small quantities and their presence only will be registered.

Literature Review on Kaolins and Ball Clays from Santa Catarina

The oldest papers on kaolinitic clays from Santa Catarina are on the refractory underclay (fireclay from undercoal measures) of Formação Barro Branco; the name was given due to the light grey color of the clay. Besides the first papers (1; 30) some ceramic data and transmission electron microscospy are in references (14; 33; 35; 36).

Kaolins and ball clays, mostly from Formação Campo Alegre, were described from the points-of-view of geological and ceramic properties by Teixeira (12); Aumont *et al* (2; 3; 28); Poener *et al* (19-24); Morgado *et al* (17-22); Wilson *et al* (34; 39; 40); Melchiades *et al* (18) and more recently Biondi *et al* (5-7); Rocha (31) studied three kaolins from Santa Catarina as fillers for vulcanized rubber. Electron micrographs of some kaolins tested as fillers and coatings for paper were presented by Kiyohara (17). Toledo *et al* (38) presented the preliminary results of characterization of the clay minerals of kaolins and ball clays from that State.

Review on the Characterization of the Varieties of Kaolinite and -7Å Halloysite

The following facts are fundamental for the precise characterization of the varieties of kaolinite and -7Å halloysite that may exist in kaolins and ball clays, even as mixtures.

(1st) The kaolin group has a basal reflexion of 7Å and is constituted by the following clay minerals: kaolinite with order in the b axis or "well crystallized"; kaolinite with several degrees of disorder in the b-axis or "b-axis disordered kaolinite" or "poorly crystallized kaolinite" (wrongly named "fireclay mineral"); long tube 7Å-halloysite; short tube 7Å-halloysite; 10Å-halloysite; nacrite and dickite. Nacrite and dickite are rare clay minerals and not yet found in Brazil. 10Å-halloysite changes very easily into 7Å-halloysite by heating for some minutes at 105°C - 110°C; so, it can be easily characterized by XRD. The question exists for the four varieties, because they cannot be correctly characterized by only one XRD curve of a clay.

(2nd) According to Brindley *et al* (10), the b-axis ordered kaolinite presents a XRD curve which was called A; it is shown in Figure 1. The b-axis disordered kaolinite has a second type of XRD curve called B and it is shown in Figure 1; long tube 7Å-halloysite has the XRD curve C of Figure 1; short tube 7Å-halloysite has the XRD curve D of the same Figure.

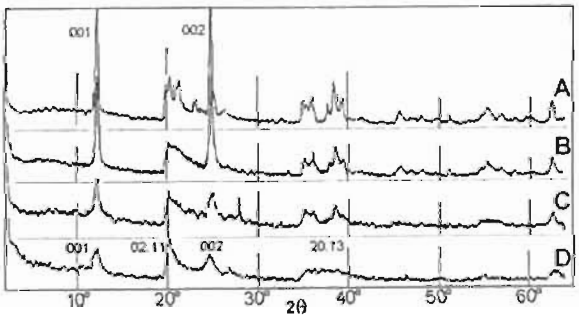

Figure 1. X-Ray diffraction curves of: (A) well-ordered or well-crystallized kaolinite; (B) b-axis disordered or poorly crystallized kaolinite; (C) 7Å-halloysite (long tubes); (D) 7Å-halloysite (short tubes). Adapted from Brindley *et al* (10).

If a clay, kaolin or ball clay, has only one of the four varieties as component, its XRD curve coincides with one of the four curves and a good and precise caracterization may be made. Churchman and Carr (12) agreed that the varieties of 7Å-halloysite may be differentiated from kaolinite on basis of the number, position and sharpness of the characteristic peaks of the respective XRD curves; however, they pointed that such differences are too much subtle to be useful when kaolinite and 7Å-halloysite occur together, as observed by Brindley *et al* (10) and listed in the 3rd item, as follows:

(3rd) (a) Mixture of 25% kaolinite A + 75% 7Å-halloysite C presents XRD curve of kaolinite B.

(b) Mixture of 40% kaolinite A + 60% 7Å-halloysite D presents XRD curve of kaolinite B.

(c) Small percentages (under 5%) of 7Å-halloysite C or D of kaolinite A or B are not detected in mixture with 95% of other kaolinitic clay mineral.

(d) There are kaolins constituted only by kaolinite, but they may be mixtures of varieties A plus B; an example is the kaolinite from Twiggs County, Georgia, USA, which is 30% A + 70% B (16).

(4th) 7Å-halloysite C and D exist as tubular shaped microcrystals easily detected in any proportion in mixture with platy kaolinite crystals by TEM. In very small percentages they can be missed by scanning electron microscopy, because the tubes may be occult between the kaolinite plates.

(5th) The use of TEM, combined with XRD, is a precise method for characterization of these two clay minerals, but it has been criticized because the TEM is a very expensive equipment and needs professional experience for its efficient operation. However, it has been adopted officially by the U.S. Dept. of Agriculture for Soil Taxonomy for kaolinite and 7Å-halloysite characterization.

(6th) If it is necessary a further confirmation of the presence of kaolinite and 7Å-halloysite, perhaps due to doubts cause by other particles shapes or mixtures, a differential intercalation of chemicals controlled by XRD may be used; examples of such chemicals are potassium acetate (4) and formamide (13).

(7th) The good crystallinity of a kaolinite is evaluated from its XRD curve; a well formed hexagonal platy crystal of kaolinite may or may not have a good crystallinity, because that is an internal property of the crystal, while morphology is external. The degree of crystallinity is usually evaluated by one of several indices, such as: Hinckley; Stoch; Liètard; Range and Weiss; Brown and Hughes; Plançon and Zacharie (27); however, their validity may be doubtfull for mixtures with minerals and / or with other clay minerals (15).

In conclusion: (a) the simultaneous use of XRD with another experimental method, like DTA or Elemental Chemical Analysis allows the characterization only of the kaolin group of clay minerals in a kaolin or ball clay. The XRD curve may be classified as one of the ABCD varieties, but no conclusion can be made if the clay is monomineralic or a mixture of kaolinitic clay minerals. (b) A TEM permits to caracterize the presence of plates (from kaolinite A ou B) and tubes (from 7Å-halloysitic C or D). (c) If mixtures are present, special procedures must be developed for evaluation of the percentages of the components.

Materials and Methods

Samples: In this study only industrially processed clays were used; all fraction larger that ABNT sieve n° 325 (44μm) were discarded (because they were clay mineral free). The processed samples were collected in the ceramic factories of Santa Catarina; their nomenclature is given by the users.

Kaolins: Serra São Miguel; Rio Molha; Kowalski; Floresta Padrão; Floresta Queijo.

Ball Clays: Linha Três Ribeirões; Rio das Pacas; Rio Turvo Arenosa; Rio Azul Branca; Rio Azul Marrom; Rio Azul Padrão; Rio Turvo Verde; Rio Azul Cinza.

Sample preparation: 50 grams of kaolin or ball clay were dispersed in 1 liter of distilled water, containing $10cm^3$ of 28% solution of NH_4OH, placed in a 2 liter beaker. The dispersion was boiled for 2 hours and cooled; it was floculated by drops of saturated solution of calcium chloride and left to sediment. The transparent supernatant was discarded and the sediment transferred to celophane bag for dialysis. The dialysis was made against destilled water until negative test for chloride. The bag was dried first at 70°C and later at 105°C-110°C. The clay was hand-homogeneized and placed in a polyethylene flask for characterization tests.

X-Ray Diffraction: The XRD curves were obtained in a Philips equipment X'Pert model operating at 40 kV and 40mA, between 2θ (1°) and 2θ (90°).

Differential Thermal Analysis: The DTA curves were obtained in an equipment from BP Engenharia, Campinas, SP, until 1050°C.

Transmission Electron Microscopy: The clay powder was prepared by the conventional methods for TEM as aqueous dispersions. The TEM observations as well as the elemental microanalysis were made in a CM200 Philips equipment operating at 200kV; it was also used as a diffraction camera for the identification of the phases (SAED); EDS / TEM (elemental microanalysis by EDS) was established by collecting either the halloysite or the kaolinite particles.

Scanning Electron Microscopy: The powder was glued to the conventional stub for SEM observation. The observation was conducted in a JEOL JSM 840A equipment.

Results

DTA: All samples presented the typical DTA curve of a clay mineral from the kaolin group, with a strong endothermic peak with maximum near 600°C and a sharp exothermic peak at 980°C. Figure 2 shows the DTA curves for a kaolin (Floresta Padrão) and a ball clay (Rio Azul Cinza); the endothermic peak at 150°C is due to decomposition of organic matter, which gives plasticity to the ball clay.

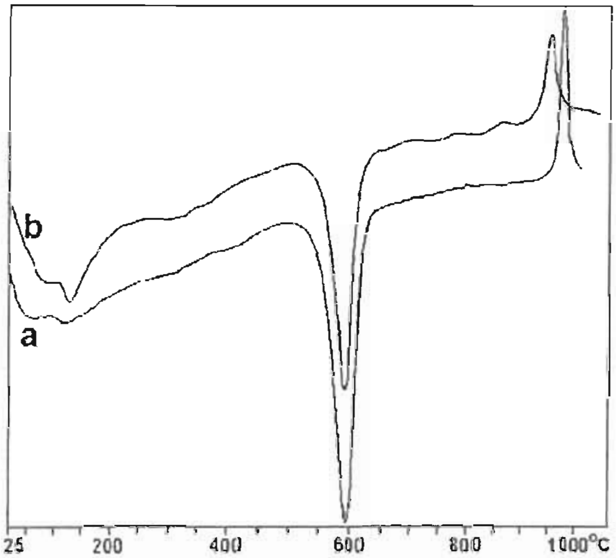

Figure 2. Differential thermal curves of: (a) Kaolin Floresta Padrão; (b) Ball Clay Rio Azul Cinza.

XRD Figure 3 shows the XRD curves for the kaolins and Figure 4 for the ball clays; all curves present a strong 7Å reflexion, which is the basal reflexion of the kaolin group of clay minerals. Both data, from XRD and DTA, indicate that members of the kaolin group are the major clay minerals present in all the 13 samples. Comparing with XRD curves of Figure 1, one may be induced to conclude that all curves are from kaolinites A or B, and no 7Å-halloysite is present in those clays. However, as pointed before, that conclusion must be checked by electron microscopy; so all 13 samples were examined by electron optical methods to detect if mixtures of kaolinite plates and 7Å-halloysite tubes may exist.

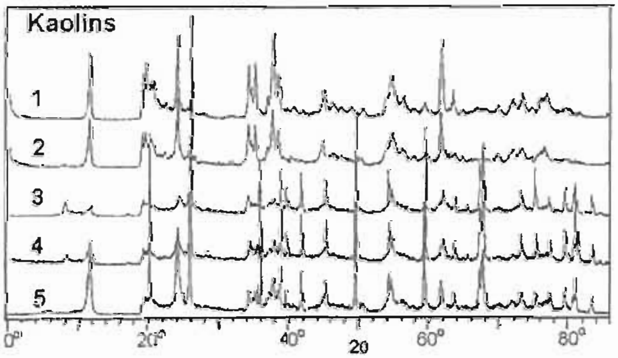

Figure 3. X-Ray diffraction curves of kaolins: (1) Serra São Miguel; (2) Rio Molha; (3) Kowalski; (4) Floresta Padrão; (5) Floresta Queijo. Radiação K-alfa do cobre entre 1°(2θ) e 90°(2θ).

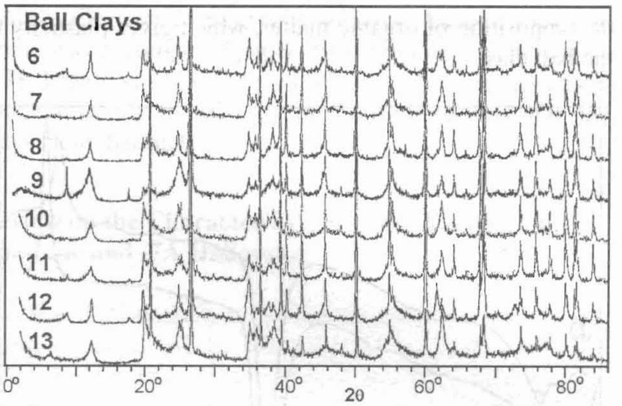

Figure 4 - X-Ray diffraction curves of ball-clays: (6) Linha 3: Ribeirões; (7) Rio das Pacas; (8) Rio Turvo Arenosa; (9) Rio Azul Branca; (10) Rio Azul Marrom; (11) Rio Azul Padrão; (12) Rio Turvo Verde; (13) Rio Azul Cinza. Radiação K-alfa do cobre entre 1º(2θ) e 90º(2θ).

The XRD curves also indicated the presence of minor amounts of "associated minerals", according to references (11; 15); these will be considered in first place.

The 3.34Å, the strongest peak of quartz, exists in all samples, indicating the presence of small amounts of very fine grained quartz; no 4.04 Å peak for cristobalite was observed. Two small intensity peaks were observed, curiously only one in each clay: 10Å and 14.5 Å. The 10Å was found in: Floresta Padrão; Kowalski; Rio Azul Branca; Turvo Arenosa; Rio Molha; Linha Três Ribeirões; Turvo Verde; e Turvo Pardo. The 14.5Å was found in: Floresta Queijo; Rio das Pacas; Rio Azul Cinza; Rio Azul Marrom. The kaolin Serra São Miguel did not presented neither of those two peaks; also in it, the 3.34Å quartz peak has the lowest intensity.

To check for the presence of 10Å-halloysite, the 10Å peak samples were heated at 105°C - 110°C for 3 hours, cooled and scanned at $\frac{1}{4}^{\circ}(2\theta)$ per minute by XRD: no contraction of the 10Å peak was observed in any sample; so it is due to the mica group found in the clays. Identification of the mineral species needs separation by fractionation, what is out of the scope of this paper.

The 14.5Å peak containing clays were treated with ethylene glycol for 24 hours to obtain information if the basal expansive groups (smectites; vermiculites; expansive chlorites) may be present. They were scanned at $\frac{1}{4}^{\circ}(2\theta)$ per minute by XRD for the expansion; it was not observed in any sample, which indicates non-expandable basal chlorite peak.

Concluding: the associated mineral in the 13 samples are very fine grained quartz and small quantities of clay minerals of the the mica and chlorite groups.

EDS: The elemental chemical analysis made by EDS on all samples showed the presence of the elements elements Aluminum and Silicon, thus confirming again XRD + DTA results pointing to the kaolin group. All ball clays presented the lines of iron and titanium. The kaolins and ball clays that had the small 10Å mica group peak presented the potassium line, what strongly suggests that muscovite mica is the clay mineral giving the 10Å peak.

Kaolinite and 7Å-halloysite: According to Brindley (9), in kaolinite with highest degree of crystallinity A, there is in the XRD curve resolution of the "doublet" peaks (d = 4.18Å and d = 4.13Å) and also of both "triplets" (2.56Å; 2.53Å; 2.49Å) and (2.38Å; 2.34Å; 2.29Å). In the lowest degree of crystallinity B there is no resolution and each group of peaks has coalesced in flat bands with values of 4.15Å; 2.55 Å and 2.50 Å; 2.38 Å and 2.33 Å, respectively. Using either the comparison with the shapes of the XRD curves of Figure 1, or the behavior of the groups of peaks, the XRD curves of the 13 samples could be classified as shown in Table I.

The classification of a XRD curve as B could be due either to the extreme of low crystalinity or to an "intermediate" curve between A and B, as observed before in several groups of clays (25; 32). On the other hand, both A's have very good resolution concerning the group peaks. So, all 13 samples were examined by TEM and SEM to confirm the presence of kaolinite and / or 7Å-halloysite.

Table I: Classification of the XRD Curve Varieties Based in Figure 1 from Brindley *et al* (10)

Sample nº	Name	XRD curve
1. Kaolin	Serra São Miguel	A
2. Kaolin	Rio Molha	A
3. Kaolin	Kowalski	B
4. Kaolin	Floresta Padrão	B
5. Kaolin	Floresta Queijo	B
6. Ball Clay	Linha Três Ribeirões	B
7. Ball Clay	Rio das Pacas	B
8. Ball Clay	Rio Turvo Arenosa	B
9. Ball Clay	Rio Azul Branca	B
10. Ball Clay	Rio Azul Marrom	B
11. Ball Clay	Rio Azul Padrão	B
12. Ball Clay	Rio Turvo Verde	B
13. Ball Clay	Rio Azul Cinza	B

Electron Microscopy: Each sample is represented by a Figure composed by TEM and SEM micrographs. The observations are directed to verify the presence of plates (kaolinite) and tubes (7Å-halloysite), that is, if the sample is mono or bimineralic in relation to these two clay minerals.

1. Kaolin Serra São Miguel - Figure 5A and 5B. Both show the presence of a mixture of hexagonal platy crystals of kaolinite and long tubes of 7Å-halloysite. Since the XRD curve is of the A variety, with vey good resolution of the triplets, the conclusion is that the kaolin is a mixture of well crystallized kaolinite A with 7Å-halloysite C, kaolinite being the major component.

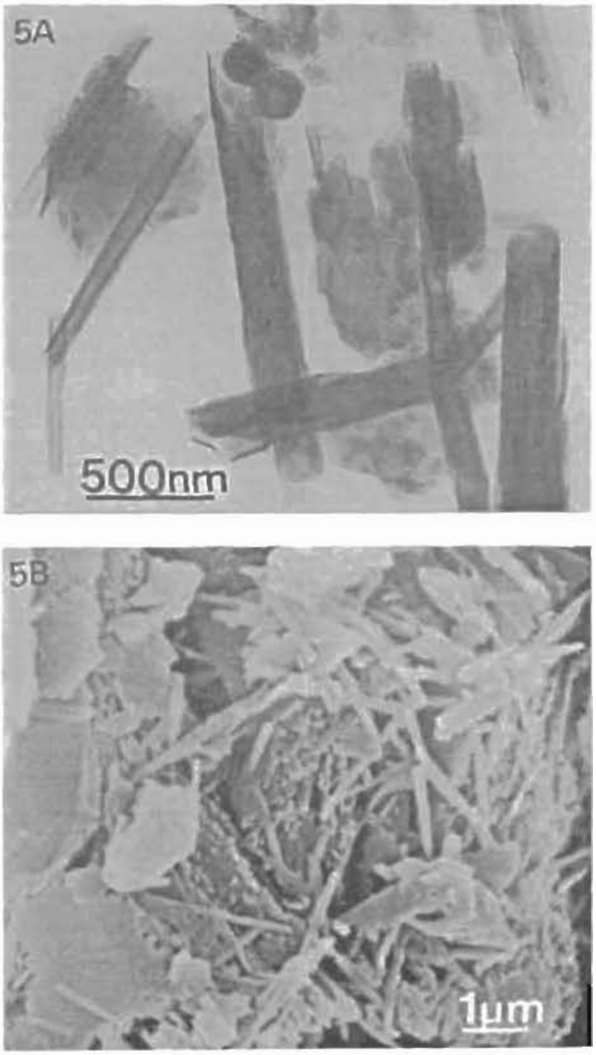

Figure 5. 5A (TEM) and 5B (SEM) of kaolin Serra de São Miguel. Componnets: plates of hexagonal profile and long tubes.

2. Kaolin Rio Molha - Figures 6A and 6B. Both, specially TEM, show a mixture of hexagonal platy crystals of kaolinite and long tubes of 7Å-halloysite. The same conclusion as São Miguel kaolin is valid.

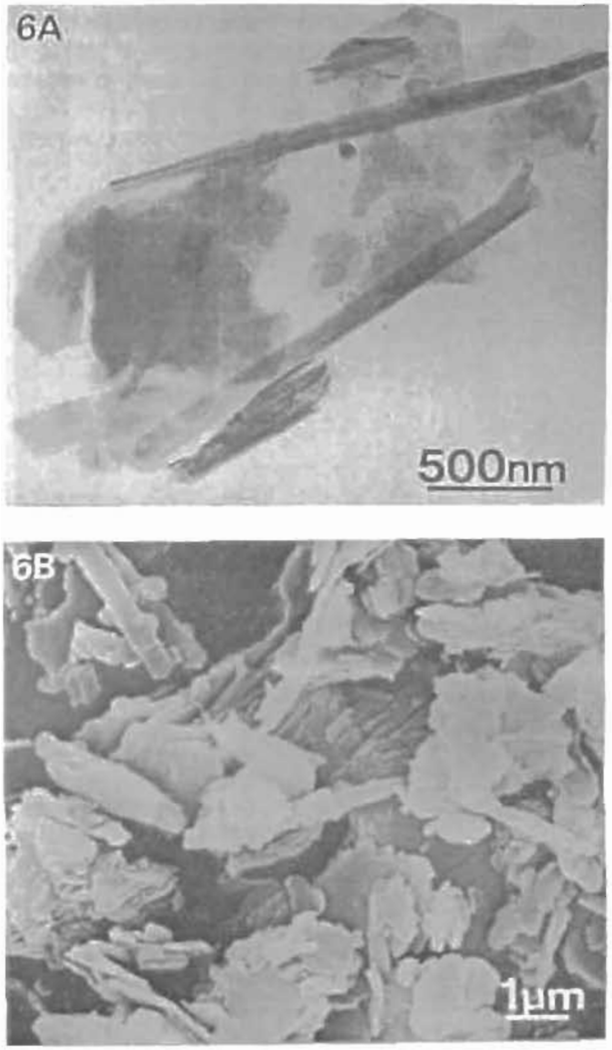

Figure 6. 6A (TEM) and 6B (SEM) of kaolin Rio Molha. Components: plates of hexagonal profile and long tubes.

3. Kaolin Kowalski - Figures 7A and B. Both show the presence of a mixture of irregularly shaped platy crystals of kaolinite and short tubes of 7Å-halloysite. The conclusion is that the kaolin is not monomineralic (only kaolinite), but a mixture of kaolinite and 7Å-halloysite D. Probably the kaolinite is b-disordered, that is, the kaolinite belongs to the B variety or poorly crystalized.

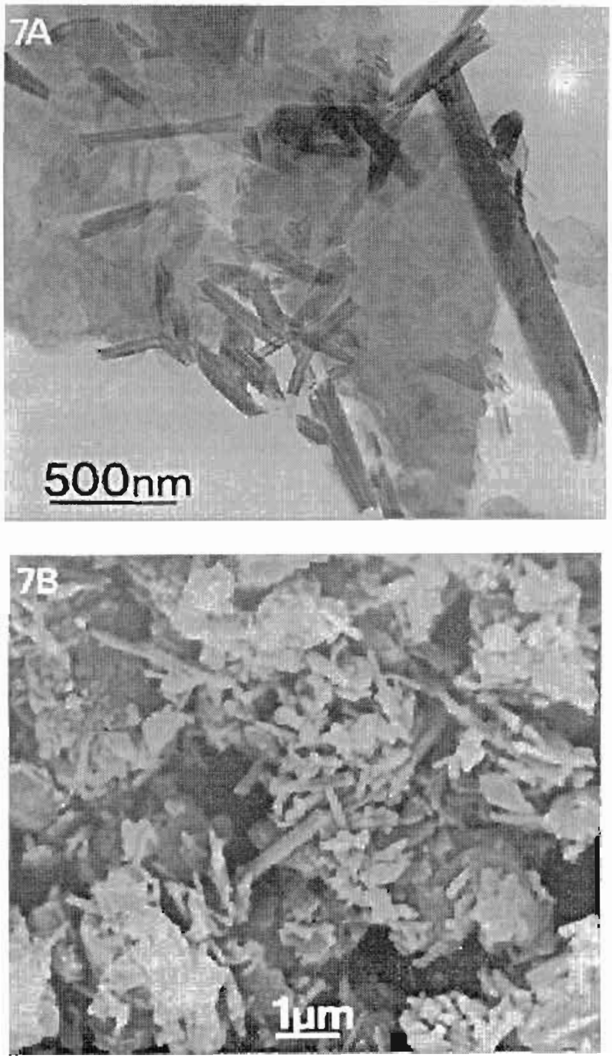

Figure 7. 7A (TEM) and 7B (SEM) of kaolin Kowalski Components: thick plates of irregular profile and short tubes.

4. Kaolin Floresta Padrão - Figures 8A and 8B. Both show, specially by TEM, the presence of a mixture of hexagonal platy crystals of kaolinite, a larger quantity of kaolinite booklets and long tubes of 7Å-halloysite. Since the XRD curve is of the B variety, the most problable conclusion is that the kaolin is not monomineralic (only kaolinite), but a mixture of kaolinite B with 7Å-halloysite C, kaolinite being the major component.

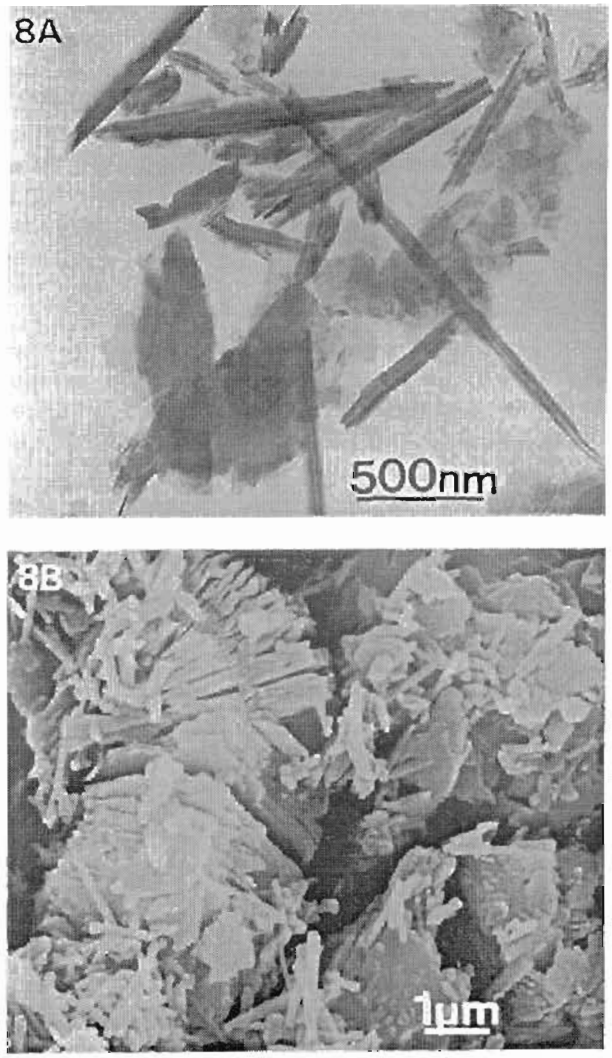

Figure 8. 8A (TEM) and 8B (SEM) of kaolin Fazenda Floresta Padrão. Components: plates of hexagonal profile; many "booklets" and long tubes.

5. Kaolin Floresta Queijo - Figures 9A and 9B. The same observations as for Floresta Padrão. Also, it is a mixture of kaolinite B with 7Å-halloysite C.

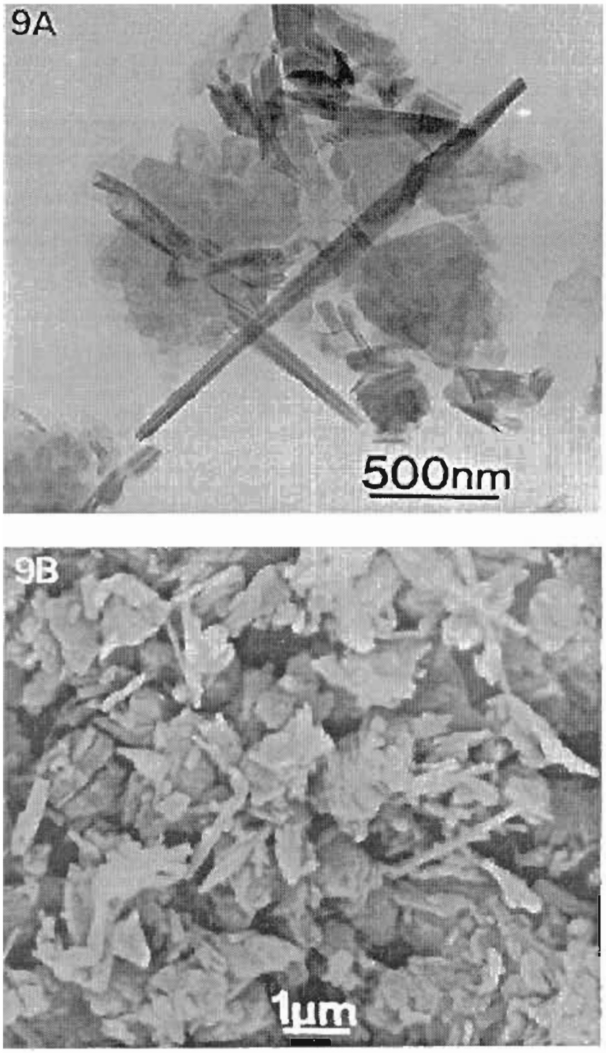

Figure 9. 9A (TEM) and 9B (SEM) of kaolin Fazenda da Floresta Queijo. Components: plates of hexagonal profile and long tubes.

6. Ball Clay Linha 3 Ribeirões - Figures 10A and 10B The TEM micrographs show a mixture of very thin, irregularly shaped plates of kaolinite mixed with short tubes of 7Å-halloysite. The SEM micrographs show clearly the disordered packing of the kaolinite plates, and the tubes are clearly visible. The XRD curve of the clay is the B variety: therefore, it is not monomineralic (only kaolinite), but is a mixture of the B variety of kaolinite with 7Å-halloysite D, kaolinite being the major component.

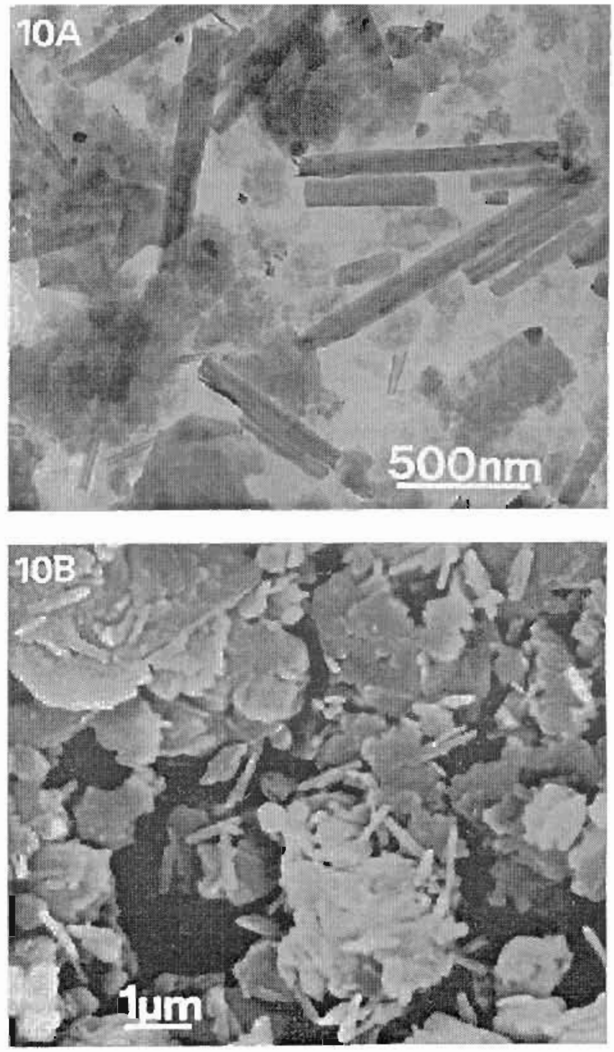

Figura 10. 10A (TEM) and 10B (SEM) of ball clay Linha 3 Ribeirões Components. plates of irregular profile and short tubes.

7. Ball Clay Rio das Pacas - Figures 11A and 11B. Both show only the presence of very thin irregularly shaped plates of kaolinite. As the XRD curve of the clay is of the B variety, then it is monomineralic, being constituted only by kaolinite of the B variety.

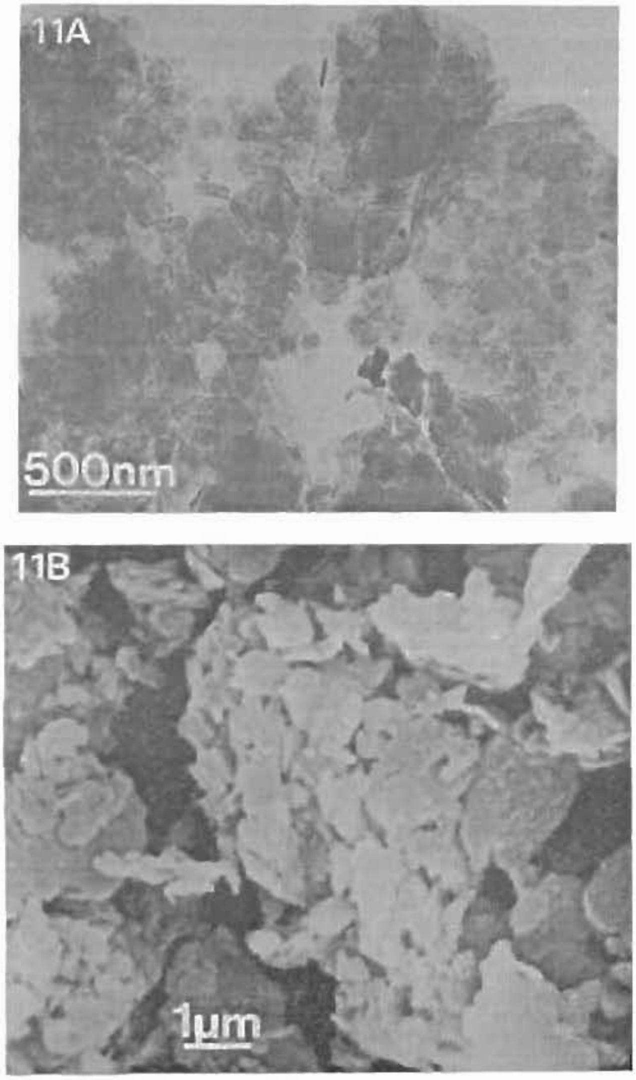

Figure 11. 11A (TEM) and 11B (SEM) of ball clay Rio das Pacas. Components: thin irregularly shaped plates.

8. Ball Clay Rio Turvo Arenosa - Figures 12A and 12B. In both micrographs, the kaolinite plates are euhedric (well formed) with hexagonal profile. 7Å-halloysite tubes are long, but only a few appear in TEM and SEM micrographs. So, the clay is not monomineralic (only kaolinite), but it is a mixture of the B variety of kaolinite with a small percentage of 7Å-halloysite C.

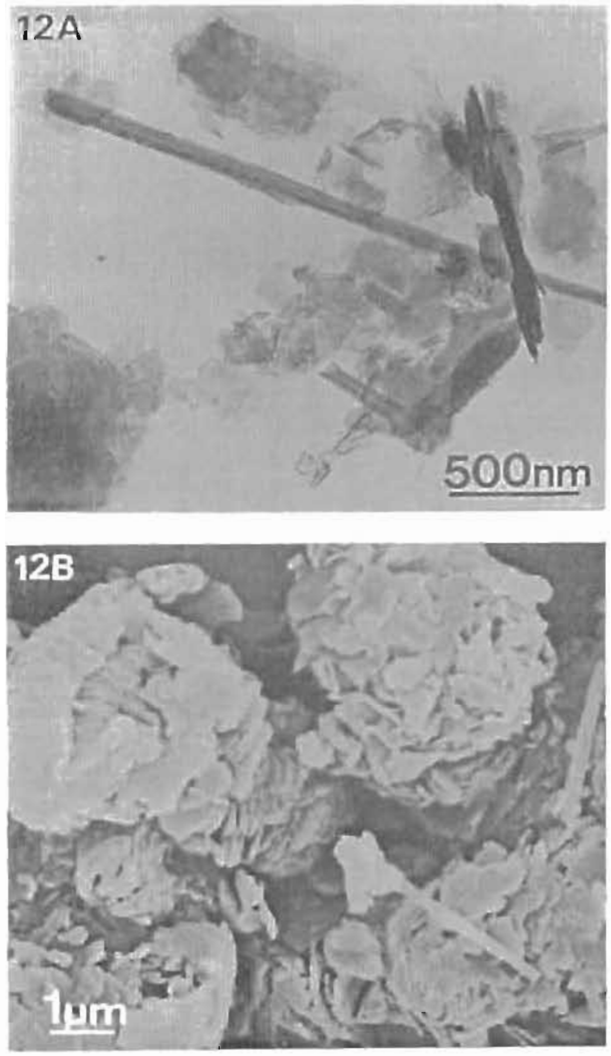

Figure 12. 12A (TEM) and 12B (SEM) of ball clay Rio Turvo Arenoso. Components: plates of irregular profile and short tubes.

9. Ball Clay Rio Azul Branca - Figures 13A and 13B. Both micrographs show the presence of very thin irregularly shaped plates of kaolinite; short tubes of 7Å-halloysite D are frequent in TEM, but are not seen in the SEM micrographs. Therefore, the clay is not monomineralic (only kaolinite), but it is a mixture of kaolinite B with 7Å-halloysite D.

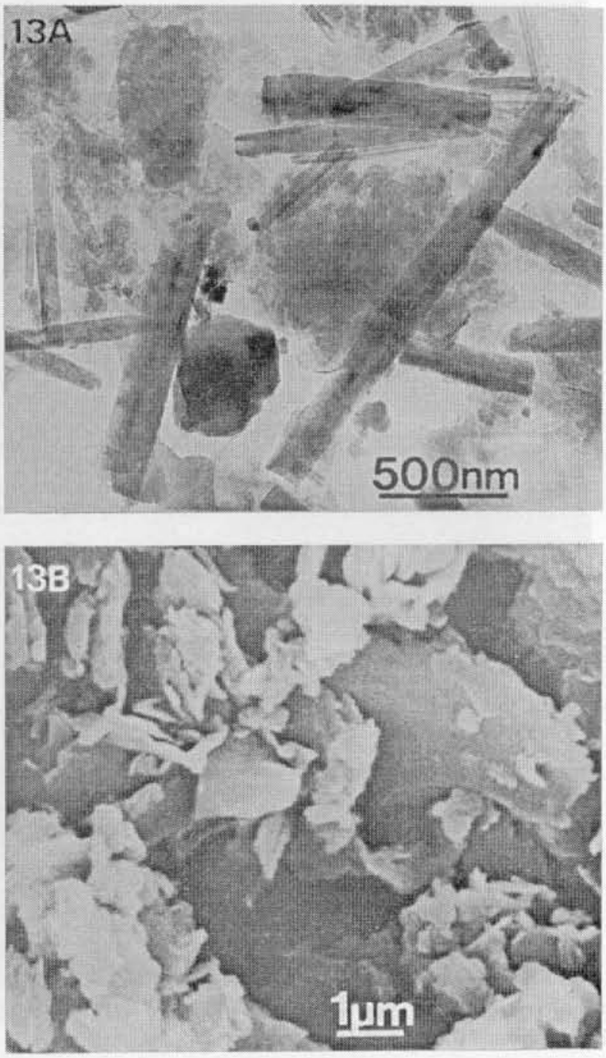

Figure 13. 13A (TEM) and 13B (SEM) of ball clay Rio Azul Branco. Components: plates of irregular profile and short tubes.

10. Ball Clay Rio Azul Marrom - Figures 14A and 14B. Both micrographs show only very thin plates of irregular shape of kaolinite. No 7Å-halloysite tube is observable. Some thin kaolinite plates have rolled borders, which may be confused with tubes (41); some have regular hexagonal profile. So, the clay is monomineralic and the kaolinite is of the B variety.

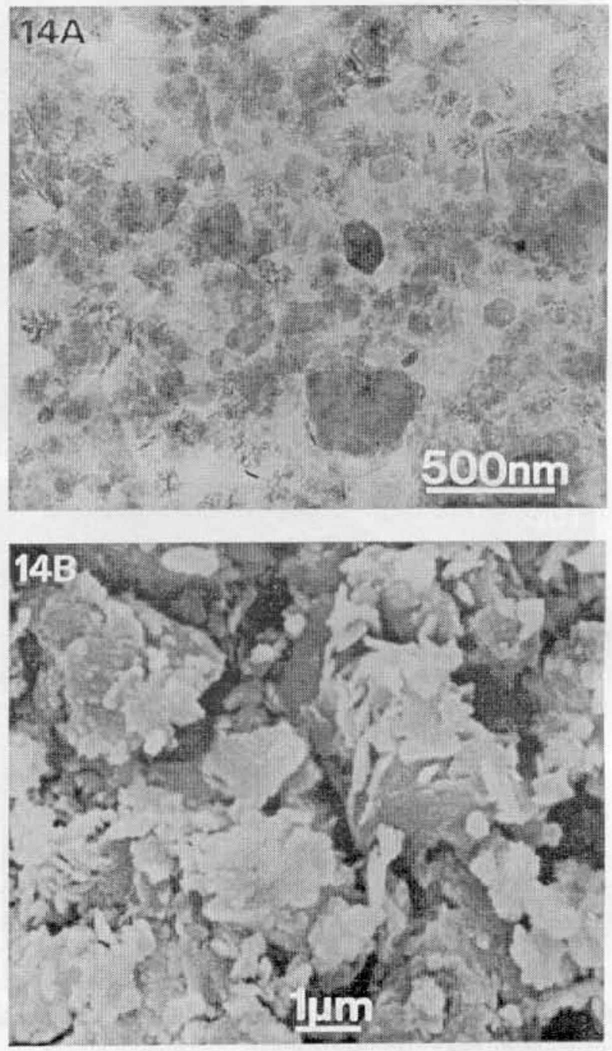

Figure 14. 14A (TEM) and 14B (SEM) of ball clay Rio Azul Marrom. Components: thin plates, some with hexagonal profile.

11. Ball Clay Rio Azul Padrão - Figures 15A and 15B. Both micrographs show only very thin hexagonal plates of kaolinite. No 7Å-halloysite tube is observable, but some rolled borders are. So, the clay is monomineralic and the kaolinite is of the B variety.

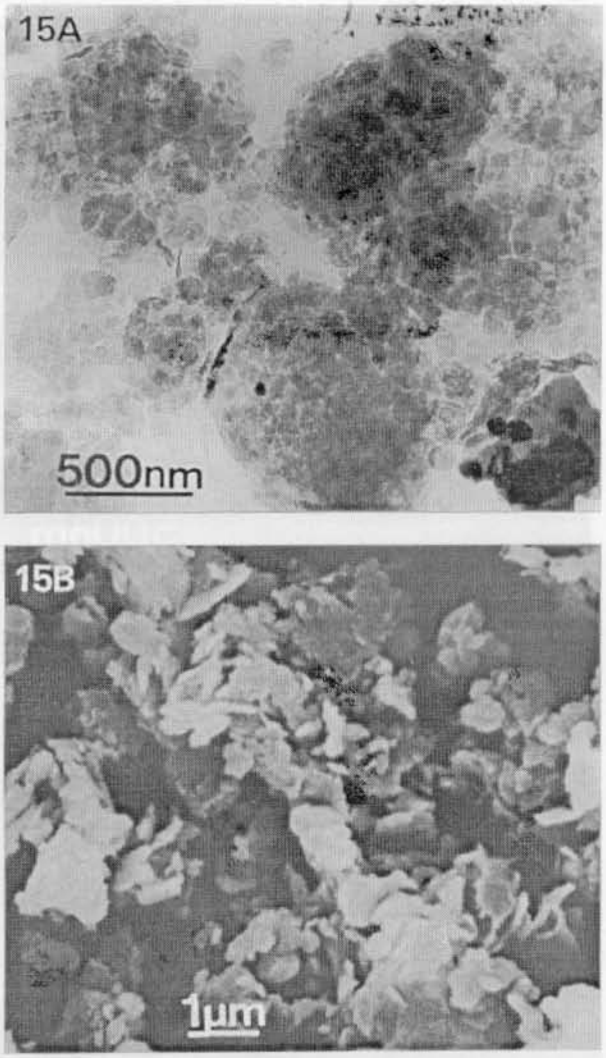

Figure 15. 15A (TEM) and 15B (SEM) of ball clay Rio Azul Padrão. Components: very thin hexagonal plates.

12. Ball Clay Rio Turvo Verde - Figures 16A and 16B. Both micrographs show only very thin hexagonal plates of kaolinite. No 7Å-halloysite tube is observable. So, the clay is monomineralic and the kaolinite is of the B variety.

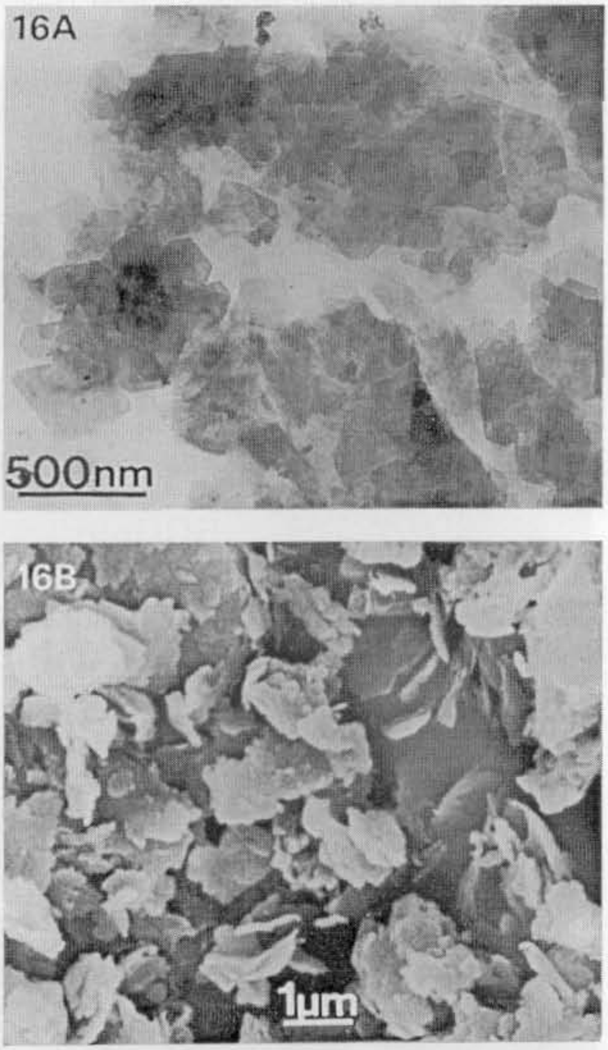

Figure 16. 16A (TEM) and 16B (SEM) of ball clay Rio Turvo Verde. Components: thin plates of hexagonal profile.

13. Ball Clay Rio Azul cinza - Figures 17A and 17B. Both micrographs show only very thin irregularly shaped plates of kaolinite. No 7Å-halloysite tube is observable. So the clay is monomineralic and the kaolinite is of the B variety.

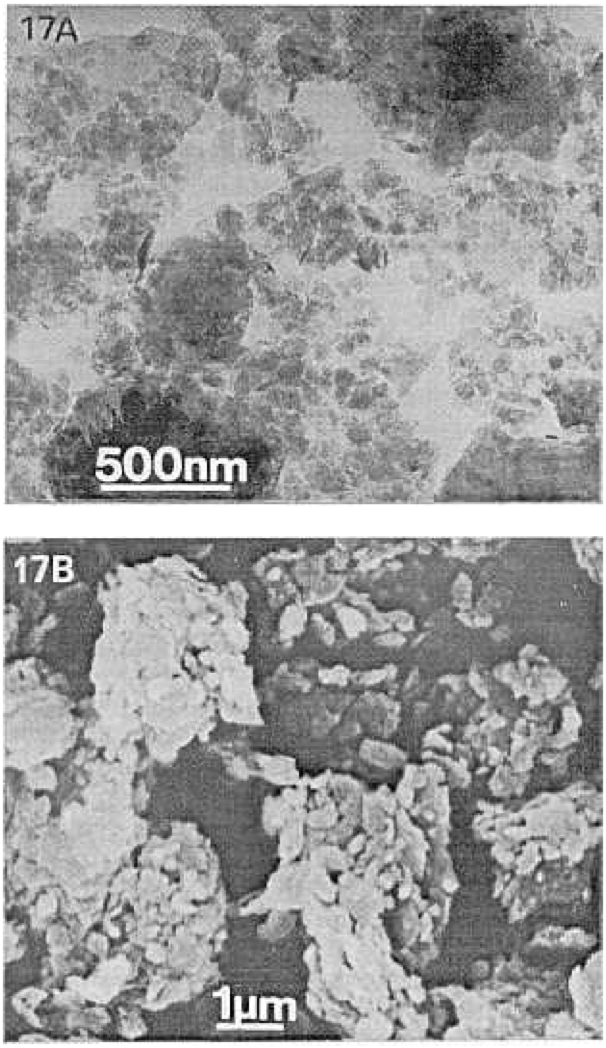

Figure 17 - 17A (TEM) and 17B (SEM) of ball clay Rio Azul Cinza. Components: very thin plates of irregular profile.

Discussion

1st) The conclusion that a clay contains only kaolinite by the examination of only one XRD curve plus a DTA curve or elemental chemical analysis may not be correct; 7Å-halloysite may be present in significant percentages and must be characterized by TEM. Scanning electron microscopy can also be used, but may not detect very small numbers of tubes of 7Å-halloysite.

2nd) By XRD, the kaolins Serra São Miguel and Rio Molha appear as being monomineralic, containing b-axis well ordered kaolinite as the only clay mineral component. However, TEM and SEM examination shows that both are mixtures of well ordered or well crystallized kaolinite with significant amount of 7Å-halloysite (long tubes variety).

3rd) By XRD, the kaolins Kowalski, Floresta Padrão and Floresta Queijo look as monomineralic, with b-axis disordered kaolinite as the clay mineral component. However, TEM and SEM examination show that they are mixtures of poorly crystalized b-axis disordered kaolinite with significant amounts of 7Å-halloysite (short and long tubes varieties, respectively).

4th) The ball clays Linha 3 Ribeirões, Rio Turvo Arenosa, Rio Azul Branca have the XRD curves of b-axis disordered kaolinite; by TEM and SEM examination, it is shown that they are mixtures of b-disordered kaolinite with 7Å-halloysite (either short or long tubes).

5th) The ball clays Rio das Pacas, Rio Azul Marrom, Rio Azul Padrão, Rio Turvo Verde and Rio Azul Cinza have the XRD curves of b-axis disordered kaolinite; by TEM and SEM it is shown that only kaolinite plates are present. Therefore, they are constitutted only by b-axis disordered kaolinite.

6th) Two interesting observations for comparing the composition of the ball clays: (a) Rio Turvo Arenosa contains 7Å-halloysite C tubes, while Rio Turvo Verde do not contain any halloysite; (b) Rio Azul Branca contains 7Å-halloysite C tubes, while Rio Turvo Marrom and Padrão Cinza do not contain any halloysite.

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