MINERALOGICAL STUDIES OF KAOLINITE-HALLOYSITE CLAYS: PART II. SOME BRAZILIAN KAOLINS


Abstract

A number of Brazilian kaolins are examined of the type which have been called "tubular kaolins"; they exhibit an x-ray pattern of the kind given by kaolinite, and in electron micrographs show an abundance of tubular and rolled particles, halloysite. When care is taken to avoid fractionation, electron micrographs reveal sufficient platy material to account for the type of x-ray pattern observed, but when a light fraction is separated by a sedimentation technique, then a halloysite-type x-ray pattern is observed. Such clays are considered to be intimate mixtures of kaolinite and halloysite, in which the halloysite has probably developed as a result of weathering conditions. In most cases, the halloysite component shows rather poorly formed tubes.

Introduction

The names "tubular kaolin" and "tubular kaolinite" were used by Visconti et al. (1956) to describe kaolin clays found in the states of Minas Gerais and São Paulo, Brazil, which gave x-ray diffraction patterns corresponding to well-ordered kaolinite, yet showed a large abundance of tubular particles in electron micrographs. Apparently no special precautions were taken in sample preparation to ensure that the electron micrographs were fully representative of the samples, and without such precautions, it can reasonably be thought that these materials are natural mixtures of kaolinite and halloysite, these terms being used in the sense of platy particles, and rolled, curled or tubular particles respectively, as discussed in an earlier paper (Part I) by Brindley, P. and H. de Souza Santos (1963). This opinion has been expressed previously by Urban (1958) concerning clays of this kind. In a general review of the problems of identifying kaolin minerals, Beutelspacher and van der Marel (1961) have emphasized the importance of applying a variety of techniques.

Materials and Experimental Methods

The present study presents data for a number of Brazilian kaolins of the kind described by Visconti et al. (1956). From amongst a large number of available materials, samples were selected which conformed to the description of the "tubular kaolins." Other materials which were clearly kaolinite or clearly halloysite require no description here. The samples came from the same general localities as those studied by Visconti et al.

1 On leave of absence from Instituto de Pesquisas Tecnológicas and Escola Politecnica, University of São Paulo, Brazil.
They are residual kaolins formed by weathering of the pegmatites of São Paulo and Minas Gerais. The samples studied were collected directly from the mines, were sun-dried, and sieved through a 400-mesh screen to eliminate coarse impurities. They were not subjected to grinding at any stage.

The following clays will be considered:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Name of mine, or locality</th>
<th>County and state</th>
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<tbody>
<tr>
<td>No. 11</td>
<td>Sitio das Lamas, Embu-guassu</td>
<td>Itapecerica da Serra, São Paulo</td>
</tr>
<tr>
<td>No. 12</td>
<td>Fazenda Belo Monte, Estevanó Pinto</td>
<td>Mar de Espanha, Minas Gerais</td>
</tr>
<tr>
<td>No. 14</td>
<td>Jazida Capoeirinha, Fazenda Linhares</td>
<td>Juiz de Fora, Minas Gerais</td>
</tr>
<tr>
<td>No. 19</td>
<td>Corte No. 1, Jazida de Pouso Alegre</td>
<td>Bicas, Minas Gerais</td>
</tr>
<tr>
<td>No. 25</td>
<td>Bairro Cateto, Rio Grande, via Anchieta</td>
<td>São Paulo, São Paulo</td>
</tr>
<tr>
<td>No. 61</td>
<td>Jazida Perereca, Sta. Helena</td>
<td>Pequeri, Minas Gerais</td>
</tr>
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</table>

Chemical analyses, x-ray diffraction data, and differential thermal curves confirmed that the materials were pure or nearly pure kaolin clays. The percentage of alumina was often somewhat above the ideal value, but detectable gibbsite was observed. Cation exchange capacities are in the range 4–5 me/100g.

Electron micrographs were taken using methods of sample preparation which avoid fractionation of the material, in particular, the aerosol method following dispersion in water with a few drops of ammonium hydroxide added (P. and H. de Souza Santos, 1957), and the pre-shadowed carbon replica technique (Comer and Turley, 1955).

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clearly that the supernatant fraction is largely halloysite, while the sedimented fraction shows kaolinite (probably with undetected halloysite).

**Results**

*X-ray data.* X-ray diffractometer patterns gave the following results. Sample no. 25 gave the pattern of a well-crystallized kaolinite. Samples nos. 11, 12, 19, and 14 gave patterns which suggest an increasing amount of lattice disorder, intermediate between types A and B described in Part I. Sample no. 61 gave a pattern similar to that of type B, which suggests considerable b-axis disorder. In view of the discussion given in Part I relating to the diffraction patterns of mixtures of kaolin minerals, where it is shown that serious confusion can arise in their interpretation, it is evident that only tentative statements can be made regarding the structural characteristics of most of these materials on the basis of their diffractometer data alone.

*Electron microscope data.* Results obtained by the carbon replica technique are shown in Fig. 1, where the order of the diagrams, (a) to (f), corresponds to that in which the x-ray data have been given. All the materials are intimate mixtures of platy particles (kaolinite) and elongated forms, rolled and curled in various ways (halloysite). Sample no. 25, Fig. 1a, contains the best platy material, and this is consistent with the type of x-ray pattern which is obtained. The tubular and rolled particles illustrated in Fig. 1 vary considerably in appearance. Some are relatively “clean” and well-formed (cf. Fig. 1c), but many are very irregular and have the appearance of being rolled sheets; see especially Fig. 1a. Brindley and Comer (1956) commented on similar appearances shown by a clay from Les Eyzies. Some of the rolled forms have a shattered appearance and some may have “blow holes” punctured by escaping vapor (see particularly Fig. 1b and f).

The point to be emphasized, however, is that all the micrographs show halloysitic forms. Samples prepared by taking a drop of a dilute suspension of such material could easily over-emphasize the halloysite and possibly lose altogether the platy material. When care is taken to avoid such a separation, then the platy material is quite evident.

*Clay fractionation results.* By means of the simple fractionation procedure, the presence of the halloysite can be demonstrated also by x-ray diffraction. Relevant parts of x-ray diffraction patterns are shown in Fig. 2, where on the right-hand side the patterns of supernatant material resemble those of halloysite (mainly the type C pattern discussed in Part I), and on the left-hand side the patterns of sedimented material
Fig. 1. Electron micrographs taken by carbon replica technique. Taken in order A to F are shown the following clays: Nos. 25, 11, 12, 19, 14, 61.
FIG. 2. X-ray diffractometer patterns comparing the light (right-hand side) and heavy (left-hand side) fractions obtained from the sedimentation procedure.

resemble those of kaolinites (types A and B discussed in Part I). However, only tentative statements can be made regarding the degree of crystalline order in the sedimented components because the fractionation procedure cannot have yielded a complete separation. There seems little doubt, however, that the light fraction is essentially halloysite.

**Discussion and Conclusions**

The present results are considered to show beyond any doubt that the so-called “tubular kaolins” from Brazil are mixtures of platy and rolled forms, respectively kaolinite and halloysite. They confirm the conclusions of Urban (1958) and are in line with those of Brindley and Comer (1956) for a similar clay from Les Eyzies. The electron micrographs, taken under conditions which eliminate fractionation, indicate a sufficient proportion of platy particles to account for the type of x-ray diffraction patterns given by the bulk samples. By simple fractionation, supernatant fractions are obtained which give x-ray patterns approximating to that described as type C in Part I. This pattern corresponds to im-
perfectly rolled forms rather than to well-formed tubes which give the type D pattern. The micrographs show many examples of very imperfect tubes.

The intimate association of platy and tubular particles in these clays may well be the result of a weathering process acting on the platy kaolinite crystals and causing them to curl and roll into poorly formed halloysite particles. Similar observations have been made by Oberlin and colleagues, and references to their work are given in Part I.

**ACKNOWLEDGMENTS**

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**References**


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