PROSPECTION AND MINERALOGICAL CHARACTERIZATION OF HALLOYSITIC KAOLIN OCCURRENCES FROM RIO BONITO CITY, SOUTHESTERN BRAZIL

PROSPECÇÃO E CARACTERIZAÇÃO MINERALÓGICA DE OCORRÊNCIAS DE CAULIM HALLOYSÍTICO NO MUNICÍPIO DE RIO BONITO, SUDESTE DO BRAZIL

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Abstract

The study aims the prospection and mineralogical characterization of halloysitic kaolin samples from Ro Bonito City, Rio de Janeiro State. There were collected 11 samples, which were dried, homogenized, quarted and granulometrically classified in 20 µm before x-ray diffractometry, scanning electron microscopy and chemical analysis by x-ray fluorescence studies. The samples are composed by less than 20 µm values between 3.55 and 31.38% and are constituted by quartz, muscovite and kaolinite, with feldspar and smectite occurrences in some of the samples. Tubular halloysite was identified in 2 samples with length between 3 and 9 µm and theoretical non-tubular halloysite occur in 5 samples. The chemical analyzes indicate that 4 samples showed SiO_2, Al_2O_3 and PPC contents close to those of theoretical kaolinite, indicating kaolinite/halloysite concentration. The occurrence of tubular halloysite would be associated to the high SiO2 contents and low Fe_2O_3 contents.

Keywords: Kaolin, Halloysite, Rio Bonito.

Resumo

O estudo teve como objetivo a prospecção e caracterização mineralógica de amostras de caulim halloysítico coletadas no município de Rio Bonito, no Estado do Rio de Janeiro. O trabalho se desenvolveu com 11 amostras, que foram secas, homogeneizadas, quarteadas e classificadas granulométricamente em 20 µm antes de serem analisadas por difratometria de raios X, microscopia eletrônica de varredura e análise química por fluorescência de raios X. As amostras apresentaram valores de partículas menores que 20 µm entre 3,55 e 31,38% e são compostas por quartzo, muscovita e caulinita, com ocorrência de feldspato e esmectita em algumas amostras. Halloysita tubular ocorre em 2 amostras com comprimento entre 3 e 9 µm e halloysita teórica não tubular em 5 amostras. As análises químicas mostraram que 4 amostras apresentaram teores de SiO_2, Al_2O_3 e PPC semelhantes ao da caulinita/halloysita teórica, indicando concentração dos minerais, sendo a ocorrência de halloysita tubular podendo estar associada a elevados teores de Al_2O_3 e baixos teores de Fe_2O_3.

Palavras chave: Caulim, Halloysita, Rio Bonito.

1. INTRODUCTION

Kaolin is a white color fine-grained rock composed mainly by kaolinite, being denominated halloysitic when rich in this mineral. Halloysite is a kaolinite polytype that aredifferentbecause of its tubular morphology and one more water molecule in its structure. The mineralhas been studied since 2005 to applications in nanoscience and nanotechnology, principally in the pharmaceutical and fertilizer industries as active principle carrier and potassium fixer in soils, respectively (Joussein et al. 2005; Churchman et al., 2016).

Just as in kaolin deposits, halloysite deposits are classified as primary, when derived from in situ feldspar alteration in rocks which are rich in this mineral, and as secondary, when from sedimentary origin. Recent studies indicate mineral occurrence of halloysite in the Niterói-Rio Bonito area, Rio de Janeiro Pegmatite Province (Santos, 2017). Because of it, prospection and mineralogical characterization studies of these occurrences should be made in order to understand the characteristics of these possible deposits.

2. OBJECTIVES

The study goals are the prospection and mineralogical characterization ofkaolin samples from Rio Bonito city (RJ) with focus on the identification of halloysite.

3. METHODOLOGY

The work was carried out with 11 samples named 1, 2A, 2B, 3A, 3B, 4, 5A, 5B, 6 e 7. These samples were dried, homogenized, quarted and granulometrically classified in wet conditions in vibratory sieve of 20 µm, being studied by X-ray diffractometry (XRD) (Bruker/Endeavor D4) with CoKα radiation (40 kV/ 40 mA), scanning electron microscopy (SEM) (TM3030 Plus/Hitachi) and chemical analysis by X-ray fluorescence (Axios MAX/PANalytical).

4. RESULTS AND DISCUSSIONS

In relation to the granulometric classification in 20 µm, the samples 2A, 2B, 4 and 7 werethe positive highlights with 27.23, 31.38, 21.56 and 61.25% of particles less than 20 µm, respectively, and the samples 1B, 1A, 3A e 3B were the negative highlights, with 3.55, 5.41, 11.52 and 13 of particles less than 20 µm, respectively.

Table 1: Mass balance after granulometric classification in 20 µm.

Samples	1A	1B	2A	2B	3A	3B	4	5A	5B	6	7
Less than 20 µm (%)	5.41	3.55	27.23	31.38	11.52	13.00	21.56	18.78	14.33	16.15	61.25

The XRD patterns of the fractionsless than 20 µm indicate kaolinite, by the 7.13 and 3.57 Å reflections, smectite, by the 15.42 Å reflection, muscovite/illite, by the 9.94 and 4.98 Å reflections, quartz, by the 4.25 and 3.34Åreflections and feldspar, by the 3.32 Å reflection (Figure 1).

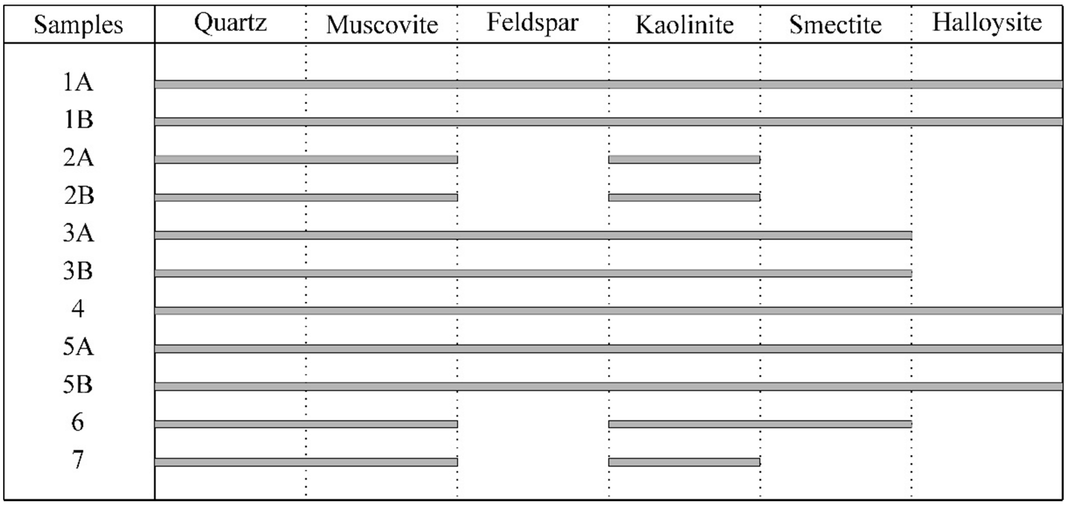

Figure 1: Less than 20 µm fractions mineralogical characterization made by XRD.

When the ratio between 9.98 Å and 4.98 reflections intensities are bigger than the theoretical value of 2.7, there is identification of halloysite(Papoulis et al., 2004). Because of that, theoreticalhalloysite was determinated in the fractions 1A, 1B, 4, 5A and 5B less than 20 µm (Figure 1 and Table 2).

Table 2: Ratio between 9.94 and 4.98 Å reflections of the XRD patterns of the less than 20 µm fractions.

Samples	1A	1B	2A	2B	3A	3B	4	5A	5B	6	7
9,94 Å	7.50	12.65	11.27	2.80	2.89	5.02	19.83	39.88	6.66	6.03	2.63
4,98 Å	1.88	2.48	4.83	1.64	2.55	6.80	5.78	12.51	2.41	2.72	1.89
Ratio	3.99	5.10	2.33	1.70	1.13	0.74	3.43	3.19	2.76	2.21	1.39

The images obtained by scanning electron microscopy indicate that kaolinite is subeudric and occur as booklets with thickness of 4 µm, approximately (Figures 2A, D and F). Halloysite is tubular with average length of 3 µm and occur as aggregates in the fraction 4 and is tubular with length between 5 and 9 µm and occur as isolated crystals in the fraction 5B (Figures 2A, B, C and D). Feldspar occur with granulometry between 7 and 18 µm in kaolinization process and quartz is euedric with granulometry of 7 µm, approximately (Figures 2E and F).

Because of the non-occurrence of tubular halloysite and its theoretical identification by x-ray diffraction in the samples 1A, 1B and 5A, halloysite was considered non-tubularin these cases (Table 2).

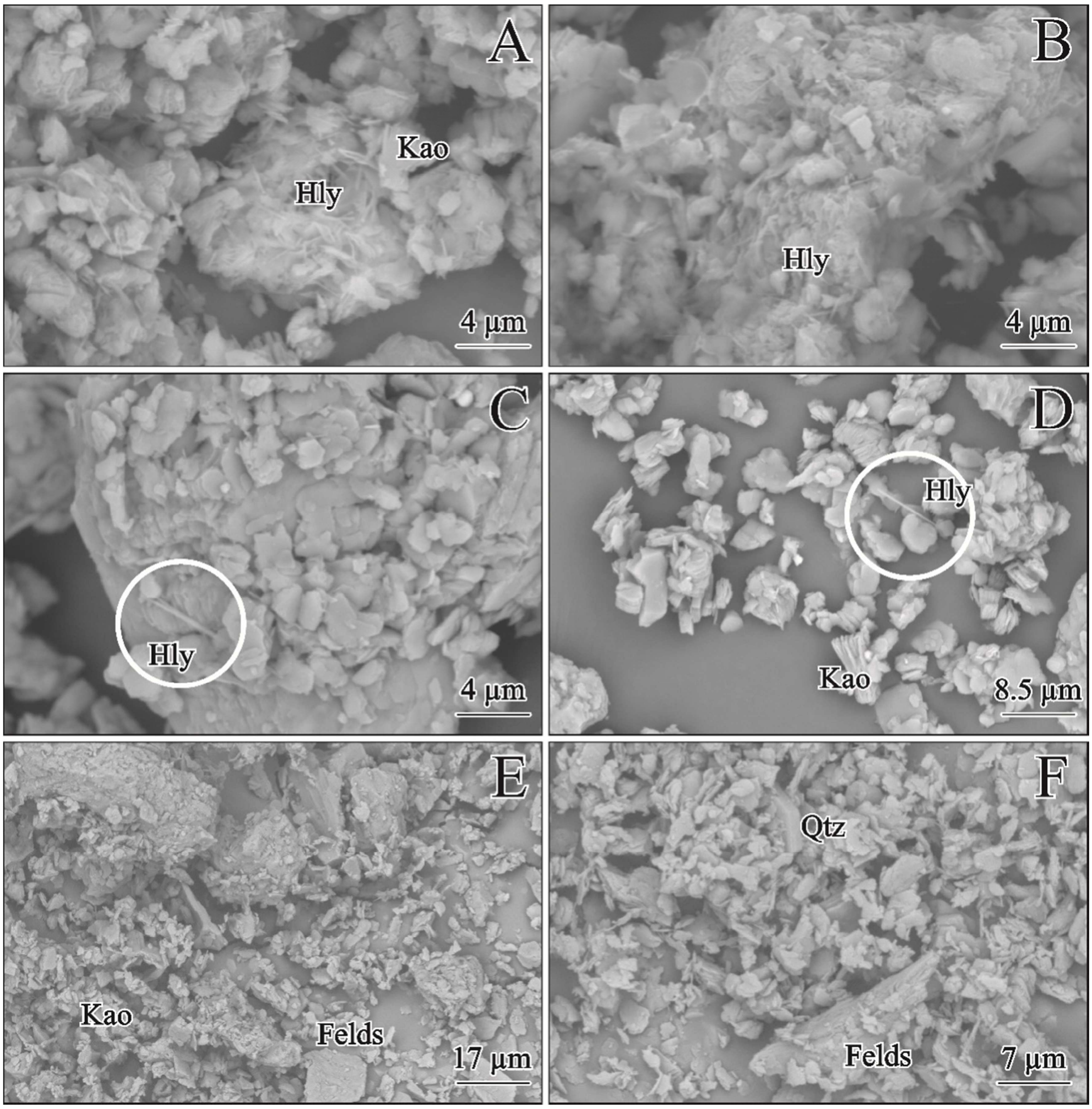

Figure 2: Imagens of the less than 20 µm fractions obtained by SEM. A, B) Agglomerated tubular halloysites with kaolinite in the fraction 4. C, D) Tubular and isolated halloysite crystals with kaolinite in the fraction 5A. E, F) Kaolinite, feldspar and quartz identified in the fractions 1A and 2A.

Chemical analyzesbyx-ray fluorescence

The chemical analyzes showed that the SiO_2 content is between 45.70 and 69.40%, Al_2O_3 is between 17.7 and 38%, loss on ignition is between 5.7 and 15.7% and Fe_2O_3 between 0.57 and 4.6%. The Na_2O content is between 0 and 3.4%, MgO content is between 0.37 and 1.2% and CaO is between 0 and 0.66% (Table 3).

The fractions 3, 5A and 5B showed SiO_2, Al_2O_3 and LOI contents close to those of theoretical kaolinite/halloysite, indicating mineral concentration. The fractions 1A and 1B showed elevated contaminations of Na_2O, CaO e MgO, indicating smectite presence. The fractions 4 and 5B showed the higher values of Al_2O_3 content and the lower values Fe2O3 content, which would be the main cause of tubular halloysite.

Table 3: Chemical analyzes (wt/%) of the less than 20 µm fractions. LOI – Loss on ignition.

Samples	**1A**	**1B**	**2A**	**2B**	**3A**	**3B**	**4**	**5A**	**5B**	**6**	**7**
SiO_2	57	57	53.3	69.4	62.2	51.1	45.7	48.3	47.6	46.4	56.2
Al_2O_3	27.2	23.6	30.1	17.7	23.5	27.1	38	36.2	37.1	35.4	30.6
Fe_2O_3	1.7	3.2	3.8	2.9	1.2	4.6	0.57	0.95	1.3	1.3	1.1
Na_2O	3.2	2.9	0	0	3.4	0.16	0	0	0	0	0
MgO	0.61	1.2	0.58	0.95	0.96	1.3	0.37	0.53	0.25	0.63	0.53
CaO	0.24	0.66	0	0	0.32	0.16	0	0	0	0	0.0
LOI	8	8.4	8.9	5.7	6.8	11.6	14.2	12.7	11.7	15.7	9.2

5. CONCLUSION

The samples showed values of particles less than 20 µm between 3.55 and 31.38%, with positive highlights to the samples 2A, 2B, 4 and 7, with 27.23, 31.38, 21.56 and 61.25%, respectively, the negative highlights were the samples 1B, 1A, 3A e 3B, with values of 3.55, 5.41, 11.52 and 13% of particles less than 20 µm, respectively.

The mineralogical characterization was responsible for the identification of quartz, muscovite and kaolinite, with occurrences of feldspar restrict to the samples 1A, 1B, 3A, 3B, 4, 5A and 5B and smectite restrict to the samples 1A, 1B, 3A, 3B, 4, 5A e 5B and 6.

Tubular halloysite occur in the samples 4 and 5A with length between 3 and 9 µm. Theoretical non-tubular halloysite occur in the samples 1A, 1B and 5A. The occurrence of tubular halloysite would be related to the higher Al_2O_3 contents and lower Fe_2O_3 contents.

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