A DISORDERED KAOLINITE FROM CONCEPCION DE BUENOS AIRES, JALISCO, MEXICO

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ABSTRACT

A random-layer disordered kaolinite from Concepcion de Buenos Aires, Jalisco, Mexico, gives an X-ray diffraction pattern resembling that of halloysite but has a kaolinite morphology. The mineral was located in a lignite deposit and, apparently was formed by alteration of volcanic rocks from the Cenozoic, with rapid cooling and sedimentation in lacustrine deposits. It is associated with plagioclase, quartz, cristobalite, montmorillonite, goethite and organic material. The analysis of purified material (44.84 per cent SiO_2, 40.36 per cent Al_2O_3, 0.30 per cent Fe_2O_3, 0.31 per cent CaO, and 13.99 per cent ignition loss) corresponds to the formula $(Si_{3\cdot88} \ Al_{0\cdot11} \ Fe_{0\cdot01}) \ (Al_{3\cdot99} \ Fe_{0\cdot01})O_{10} \ (OH)_8$. X-ray diffraction indicated a d_{001} of 7.56 Å, an intense 020, and displaced and nonsymmetrical reflections corresponding to a bi- and tridimensional diffracting system closer to halloysite than to kaolinite. Computed cell edges were $a = 5.18$ Å, $b = 8.97$ Å, and $c = 7.45$ Å. Electron micrographs showed anhedral rounded particles averaging $0.22 \ \mu$ in size, while infrared absorption indicated some displacement in the absorption bands. The relationships of the mineral to kaolinite, halloysite and disordered kaolinites are discussed in terms of the 7°38' twist of the tetrahedra, the intensities of the reflections, and the calculated Al^{IV} substitution.

INTRODUCTION

In the course of studies on a low-grade coal deposit located at Concepcion de Buenos Aires, Jalisco, Mexico, a clay mineral was found whose plasticity and moldability suggested a possible use as a ball clay. The mineral occurs in a sedimentary deposit apparently formed by alteration of volcanic rocks from the Cenozoic (Fig. 1, after de Cserna, 1961); with rapid cooling and sedimentation in lacustrine deposits. Initial analysis of bulk samples revealed plagioclase, quartz, cristobalite, goethite, organic material, montmorillonite and, as the main component, a clay mineral similar to kaolinite but with differences that did not readily allow its classification as such.
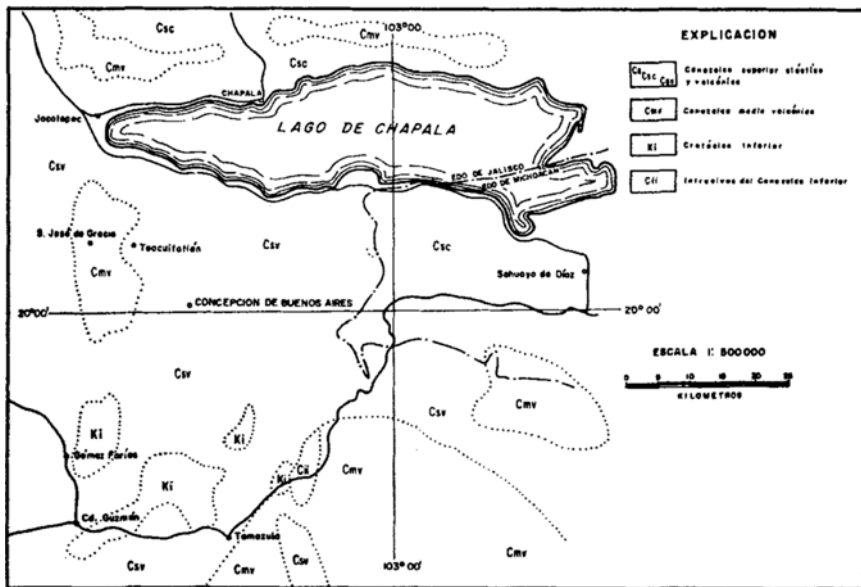
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FIG. 1. Location and geology of Concepcion de Buenos Aires, Jalisco, Mexico.

EXPERIMENTAL DATA

Samples for detailed study were prepared by suspending the bulk material in water, sedimentation and separation of the clay fraction prior to iron oxide removal by dilute hot sodium hydrosulfite solution. The washed clay was dried at 80°C and gently disaggregated before it was chemically analyzed and studied by X-ray diffraction, infrared absorption and electron microscopy.

X-ray Diffraction

X-ray diffraction analysis, using a Philips unit with iron-filtered Co $K\alpha$ radiation, Soller slits of 1, 0.2, and 1°, and a scanning speed of 2° per min., indicated, for the bulk samples, plagioclase, quartz, cristobalite, goethite, montmorillonite, and a kaolinitelike mineral (Fig. 2). Similar analysis on the clay fraction (Fig. 2) revealed a kaolinitic material of low crystallinity, with displaced and nonsymmetrical reflections of relative intensities differing from those normally accepted for kaolinite. This was particularly evident when the material was compared with a well-developed kaolinite (Fig. 2) or with Brindley and Robinson's (1946) data; the present data suggested a disordered structure similar to those reported by Robertson, Brindley, and MacKenzie (1954) for samples from Pugu, Tanganyika, and von Engelhardt and Goldschmidt (1954) for material from Provins, France.
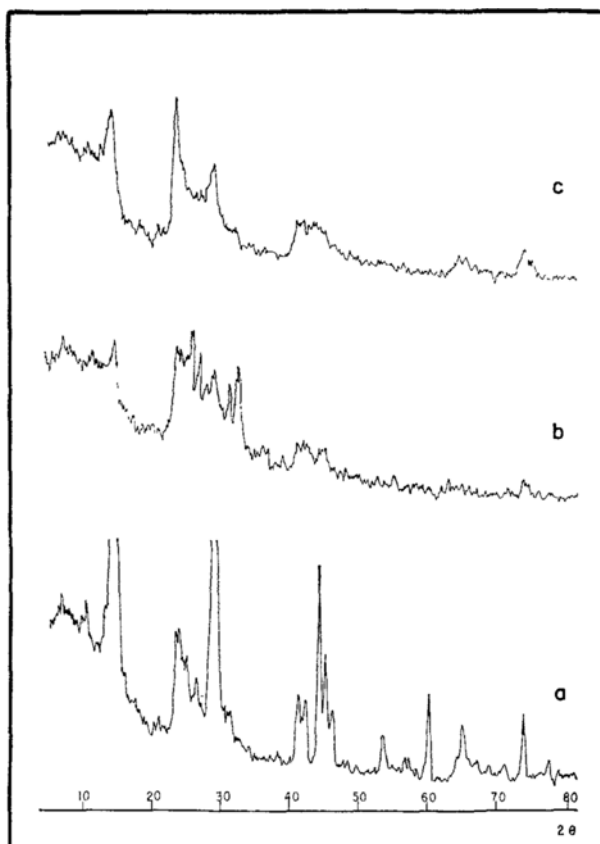
FIG. 2. X-ray diffraction traces for (a) kaolinite from Chihuahua, Mexico,
(b) bulk material from Concepcion de Buenos Aires, Jalisco, Mexico,
(c) disordered kaolinite from Concepcion de Buenos Aires.

Interplanar distances and relative intensities (see Table 1), when compared to those reported for well-crystallized kaolinite (Brindley and Robinson, 1946) and disordered kaolinite (Robertson, Brindley, and MacKenzie, 1954; von Engelhardt and Goldschmidt, 1954), indicate that (1) basal reflections 001, 002, 003 and 004 are displaced (001 particularly toward lower Bragg angles) and are slightly asymmetrical; (2) 020 is displaced, asymmetrical and more intense than 001; (3) $1\bar{1}0$, $02\bar{1}$, 111, (060, $3\bar{3}\bar{1}$, $33\bar{1}$) are also displaced toward lower angles; (4) observed intensities differ from those of well-crystallized kaolinite and some reflections ($24\bar{2}$, 310, $1\bar{5}1$, 133, $2\bar{4}\bar{2}$), ($15\bar{2}$, $13\bar{4}$), (241, $2\bar{2}\bar{4}$, $1\bar{1}4$, $1\bar{3}\bar{4}$, $31\bar{3}$, 203) are absent, and (4) there are sharp, tridimensional reflections as well as bidimensional scattering diffused toward higher and lower Bragg angles.

Table 1.—Interplanar Distances Computed for the Disordered Kaolinite from Concepcion de Buenos Aires, Jalisco, Mexico

| hkl	d(cal.)	d(obs)	I(obs.)	Shape
001	7.23	7.56	5.0	Acute, asymmetrical, diffuse toward higher angles
021	4.48	4.49	10.0	Broad, toward higher angles
$1\bar{1}0$	4.38	4.40	6.5	Broad, toward higher angles
$11\bar{1}$ $1\bar{1}\bar{1}$	4.17	4.14	5.0	Acute
$02\bar{1}$	3.82	3.90	5.0	Acute
002	3.62	3.65	6.5	Broad, toward higher and lower angles
$1\bar{1}1$	3.42	3.49	3.5	Acute
$11\bar{2}$	3.15	3.15	1.5	Acute
$1\bar{3}0$ $20\bar{1}$ 130	2.57 2.56 2.57	2.59	2.5	Broad, toward higher angles
$13\bar{1}$ $1\bar{1}2$ $1\bar{3}\bar{1}$ 200 112	2.52 2.52 2.52 2.51 2.52	2.53	3.0	Broad, toward higher angles
003	2.41	2.39	2.5	Acute
$20\bar{2}$ $1\bar{3}1$ $11\bar{3}$ $1\bar{1}3$ 131	2.36 2.33 2.34 2.33 2.33	2.33	2.0	Broad, toward higher angles
$13\bar{2}$	2.23	2.26	1.5	Acute
040 $2\bar{2}0$ $02\bar{3}$	2.25 2.19 2.13	2.22	1.0	Acute
041	2.14	2.14	1.0	Acute
$2\bar{2}\bar{2}$	2.09	2.05	0.5	Broad
$1\bar{3}2$ 132	1.98 1.98	1.97	0.5	Broad
$2\bar{2}2$	1.71	1.71	1.0	Broad, toward higher angles
$24\bar{1}$	1.69	1.69	1.0	Broad, toward higher angles
$20\bar{4}$	1.68	1.67	1.0	Broad, toward higher angles
133	1.65	1.65	1.0	Broad, toward higher angles
060 $3\bar{3}\bar{1}$ $33\bar{1}$	1.49 1.49 1.49	1.49	2.5	Broad, toward higher angles
$06\bar{1}$ $33\bar{2}$	1.46 1.47	1.46	0.5	Acute
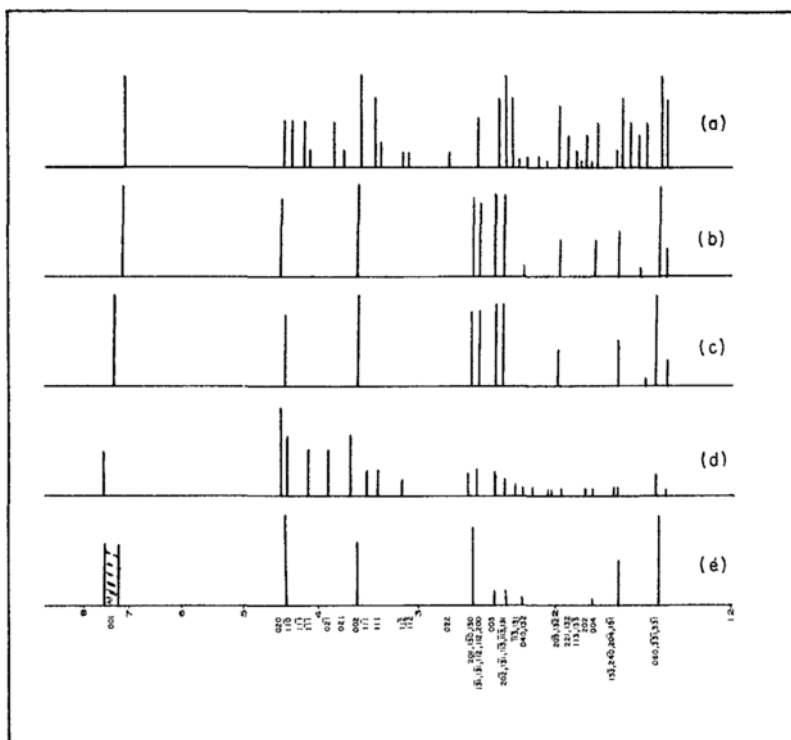
FIG. 3. Interplanar distances for (a) kaolinite (Brindley and Robinson, 1946), (b) disordered kaolinite from Pugu, Tanganyika (Robertson, Brindley, and Mackenzie, 1954), (c) disordered kaolinite from Provins, France (Engelhardt and Goldschmidt, 1954) (d) disordered kaolinite from Concepcion de Buenos Aires, Jalisco, Mexico, and (e) halloysite (Brindley and Robinson, 1946).

Cell dimensions computed from the diffraction data using d values from the 060 and basal reflections and assuming a monoclinic cell, are $a = 5.18$ Å, $b = 8.97$ Å, and $c = 7.45$ Å. From these parameters, the interplanar distances indicated in Table 1 and graphically recorded in Fig. 3 were calculated. The clay mineral from Concepcion de Buenos Aires differs markedly from kaolinite, disordered kaolinites and halloysite in the interplanar distances and the intensities of the reflections.

Infrared absorption

Infrared absorption spectroscopy was used in the study of the mineral by suspending it in Nujol and analyzing through a Perkin-Elmer 21 spectrometer from wavelengths of 2.00–15.25 μ. The absorption spectra (Fig. 4)
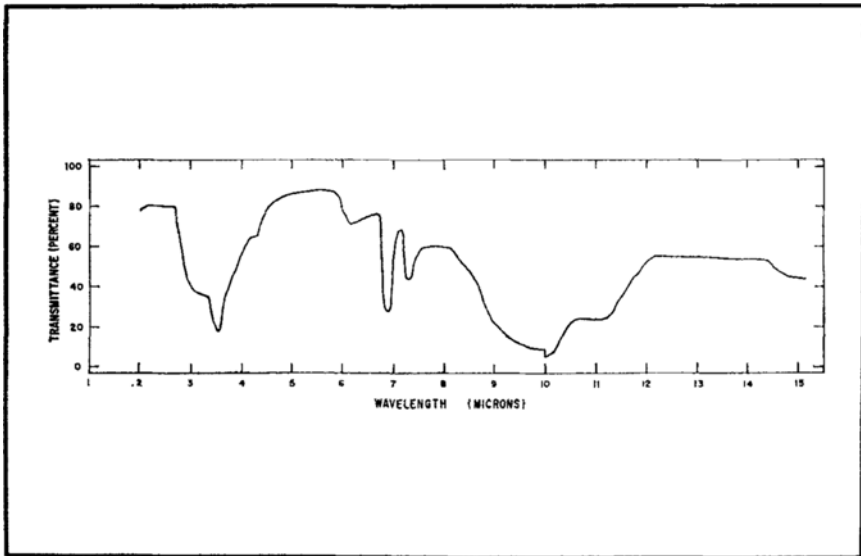
Fig. 4. Infrared absorption spectra of the disordered kaolinite from Concepcion de Buenos Aires, Jalisco, Mexico.

indicated (1) a band starting at 2.70 μ with maxima at 3.10, 3.53, and 4.30 μ due to O—H bands; (2) a low intensity band at 6.17 μ characteristic of the layer silicates (Stubičan and Roy, 1961); (3) a diffuse and intense band starting at 8.10 μ with maxima at 9.00 and 10.00 μ caused by Si—O—Si and displaced possibly by lengthening or distortion of the bond; (4) a low intensity slightly displaced absorption at 11.00 μ due to H—O—Al, and (5) a final absorption band starting at 14.30 μ with a weak maximum at 14.50 μ and possibly others at higher wavelengths caused by the Si—O bond. Comparing the recorded spectra with the published data (Stubičan and Roy, 1961) the mineral could be considered as a kaolinite with, possibly, some structural distortions that cause displacement of the bands. There could be some montmorillonite or absorbed water, as the 3.10 μ band suggests.

Chemical analysis

The chemical analysis of the mineral using common wet techniques indicated 44.84% SiO_2, 40.36% Al_2O_3, 0.30% Fe_2O_3, 0.31% CaO and 13.99% ignition loss at 900°C. Assuming that (1) the only component is a kaolinitelike mineral, (2) lime is an impurity, (3) the Al_2O_3 plus Fe_2O_3 in excess of the equivalent SiO_2 is divided equally between the tetra- and octahedral layers, and (4) the theoretical layer compositions are $Si_4O_6O_2$ and $O_2(OH)_2 Al_4(OH)_6$, the following formula is computed:

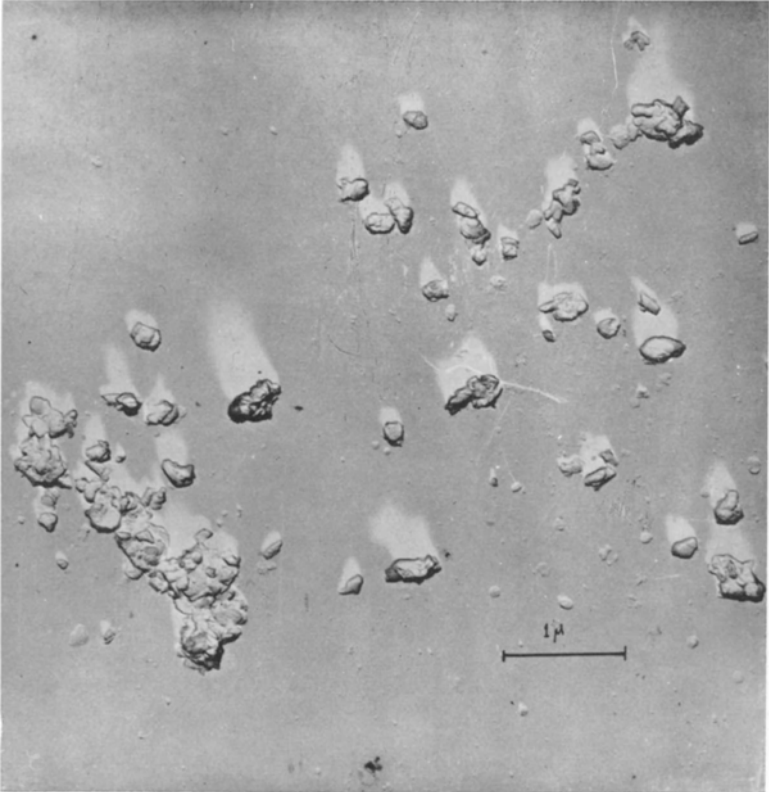$$O_6(Si_{3.88}Al_{0.11}Fe_{0.01}) \, O_4(OH)_2 \, (Al_{3.99}Fe_{0.01}) \, (OH)_6.$$
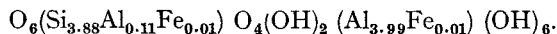
PLATE 1. Electron microscopy of the clay mineral from Concepcion de Buenos Aires, Jalisco, Mexico.

Electron microscopy

The electron microscopy of the mineral is illustrated in Plate 1. The sample was prepared by smearing on a glass slide and taking a platinum-shadowed carbon replica. The particles are anhedral, rounded, with an average size of 0.22 μ and show no hexagonal kaolinite or tubular halloysite forms; at the most, one or two hexagonal edges are observed. In this respect, the mineral differs markedly from the small well-formed hexagonal crystals found by Robertson, Brindley and MacKenzie (1954) in Pugu, Tanganyika, material and by von Engelhardt and Goldschmidt (1954) in material from Provins, France.

DISCUSSION

The preceding results reveal that the clay mineral from Concepcion de Buenos Aires, Jalisco, Mexico, is a disordered kaolinite with random-layer displacement parallel to the b-axis, with substitution of aluminum in the tetrahedral layer and crystallizing as anhedral rounded particles averaging 0.22 μ in size. The interest of the mineral lies in its morphology and its unusual X-ray diffraction data.

The X-ray data indicate displaced and nonsymmetrical reflections corresponding to a bi- and tridimensional diffracting system suggesting halloysite. A b cell edge of 8.97 Å was computed assuming a monoclinic cell. From the chemical analysis and the regression equations given by Radoslovich (1962), b was calculated as 8.92 Å—and as 9.05 Å for the tetrahedral layer assuming no appreciable effect of the aluminum substitution. This allowed one to compute an O—Si—O angle of twist (Radoslovich and Norrish, 1962) of 7° 38′, which is less than the range normally considered for kaolinites.

Electron microscopy revealed quite small, anhedral, rounded particles without the morphology characteristic of halloysite or of kaolinite, while the chemical analysis suggested aluminum substitution in the tetrahedral layer; the infrared absorption spectra suggested slight displacement of the absorption bands difficult to correlate to the layer displacement. Any relations between the experimental data and existing theories of the structures of kaolinite and halloysite are difficult to establish. Some authors have reported a relationship between morphology and structure for clay minerals, but the material from Concepcion de Buenos Aires diffracts as a disordered kaolinite and not as a poorly crystallized solid—in fact, different from the well-formed hexagonal plates from Pugu, Tanganyika, and Provins, France. Other authors have suggested that halloysite forms by structural disorder or substitution in kaolinite, and recently, Brindley and P. and H. de Sousa Santos (1963) suggested a transition between kaolinite, disordered kaolinite, and halloysite. Although the mineral studied shows a diffraction pattern of a disordered kaolinite closer to that of halloysite than of kaolinite, and has aluminum substitution in the tetrahedral layer, the data are insufficient from which to discuss in detail the relationships of the mineral to kaolinite or to halloysite.

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