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ANTIGORITE—ITS OCCURRENCE AS A CLAY MINERAL

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Abstract—A white clay from the Jatoba talc mine, Castro, Paraná, Brazil, is shown by chemical analysis, X-ray and electron diffraction, and by thermal analysis to be essentially pure antigorite in the strict sense of the term. Single crystal electron diffraction patterns give various values for the long a parameter, with 43·5 Å perhaps the most commonly occurring, $b = 9{\cdot}25$ Å, $d(001) = 7{\cdot}25$ Å. X-ray powder diffraction gives $d(001) = 7{\cdot}26$ Å and $b = 9{\cdot}23$ Å. Electron micrographs show irregular platy and lath-like crystals of about 0·5–2 μ size with large development of (001) planes and with b in the direction of elongation. Other crystals are observed with very unusual forms, some having holes through them. They show mainly $0kl$ diffraction patterns and lie with the basal (001) planes normal to the stage of the instrument. The chemical analysis agrees closely with the ideal serpentine composition and the differential thermal analysis curve is consistent with antigorite.

INTRODUCTION

THE TERM "antigorite" is used here in its strict sense for a platy serpentine mineral with the a parameter of the unit cell commonly about 43·5 Å or about eight times that of the a parameters of other serpentine-group minerals, about 5·30–5·35 Å. This long a parameter, first recognized by Aruja (1945), is the result of a wave-like modulation of the normal serpentine layer structure (Zussman, 1954; Kunze, 1956, 1957, 1958, 1961). The clearest and probably the most easily obtained evidence for the long a parameter is contained in single-crystal electron diffraction patterns. These data show that within a single sample of antigorite, different crystals may have different values for the a parameter, so that the structural modulation is variable from crystal to crystal (Zussman *et al.*, 1957; Brindley *et al.*, 1958).

It appears that antigorite in this strict sense is found mainly in massive or coarsely crystalline platy forms of serpentine. Its occurrence as a clay mineral on a considerable scale and in a pure or nearly pure state has not (within the knowledge of the writers) previously been reported. Its discovery in this form merits a description.

OCCURRENCE AND APPEARANCE

The antigorite clay occurs associated with talc in the Jatoba talc mine, Castro, near Ponta Grossa in the state of Paraná, Brazil. The geology of the region has been described by Elimar Trein (1967). The present open-mine workings show talc on both sides of, and above, a 1–2 meters wide and several meters high development of a white clay material which by chemical analysis, X-ray and electron diffraction examination, and thermal analysis is found to be essentially a pure antigorite. The associated talc is somewhat reddish in tint and is easily distinguished from the white antigorite.

The clay-like antigorite is soft and crumbles easily, and is readily dispersed in water. It is smooth and largely without gritty particles when rubbed on the palm of the hand, and has a drier and less greasy feel than talc. It has been extracted and used for 2 yr as a diluent for insecticides and as "talc" for pharmaceutical uses.

CHEMICAL ANALYSIS

Table 1 gives a chemical analysis of the Castro antigorite together with data for the theoretical serpentine composition and for two other analysed antigorites. The Castro material conforms very closely to the theoretical composition and contains less Al_2O_3 and Fe_2O_3 than the other analyzed materials. The only crystalline impurity detected by X-rays was a possible trace of quartz, so that the percentage of SiO_2 may be slightly high.

Table 1. Chemical analysis of antigorite clay, from the Jatoba Mine, Castro, Paraná, Brazil. Percentage composition

	Jatoba mine	Theoretical	Other antigorites *	†
SiO_2	43·6	43·36	43·60	43·45
TiO_2	absent		0·01	0·02
Al_2O_3	0·33		1·03	0·81
Fe_2O_3	0·41		0·90	0·88
Cr_2O_3	nd		0·02	nd
FeO	nd		0·81	0·69
NiO	nd		0·16	nd
MnO	nd		0·04	0·00
MgO	43·5	43·64	41·00	41·90
CaO	trace		0·05	0·04
Na_2O	0·01		0·01	0·05
K_2O	0·02		0·03	0·02
H_2O^+	12·2	13·00	12·18	12·29
H_2O^-			0·08	0·04
Totals	100·07	100·00	99·92	100·19

*Antigorite, vicinity of Caracas, Venezuela (Hess, *et al.* 1952).

†Antigorite, Cropp River, Mikonnui, New Zealand (Zussman, 1954).

Theoretical: $3MgO{\cdot}2SiO_2{\cdot}2H_2O$.

X-RAY DIFFRACTION ANALYSIS

X-ray powder diffraction patterns have been recorded with a Norelco diffractometer and filtered CuK_α radiation using a side-packed sample holder to eliminate (or greatly to reduce) the preferential orientation encountered with front- or back-packed holders; slurried samples oriented on glass slides have been used to record the basal, 00*l* reflections. Slow recording, 0·5° 2θ/min, and a chart speed of 1 in./deg. 2θ (or 2·54 cm/deg. 2θ) have been used to facilitate resolution of many groups of closely spaced peaks. The only crystalline impurity detected was a possible trace of quartz, shown only by a very weak reflection in the position of the strongest reflection of the quartz pattern. The X-ray data are summarized in Table 2, where they are compared with powder data compiled by Whittaker and Zussman (1956). The agreement for the most part is very close. The basal spacing, *d*(001), of the present material is $7{\cdot}26_5 \pm 0{\cdot}00_7$ Å, which is a weighted average from six basal reflections, and *b* from the 060 reflection is 9·23 Å. Indexing of the powder diagram is impracticable in the absence of single crystal X-ray data because of the large *a* parameter and the very large number of calculated spacings to compare with observed

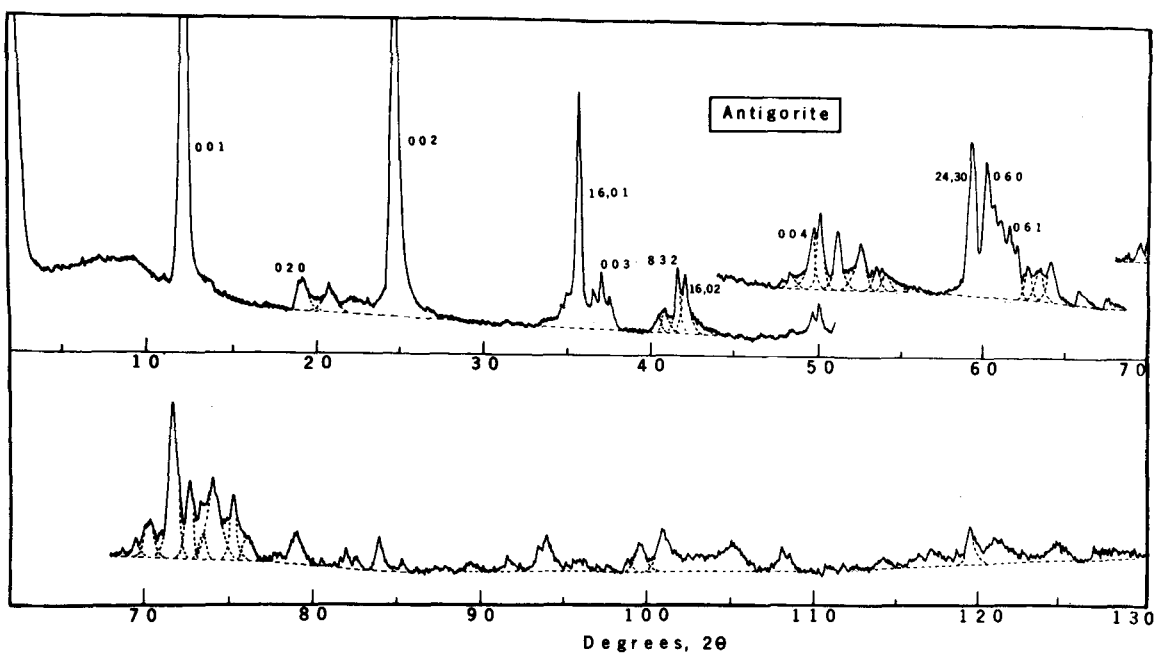

Fig. 1. Diffractometer recording of X-ray powder pattern of antigorite from Jatoba Mine, Castro, Paraná, Brazil, with CuK_α radiation, and recorded at 1° (2θ)/min. 2–52° taken with 1° slits, scale factor 16, multiplier 1, time constant 4 sec; 44–68° taken with 4° slits, scale factor 16, multiplier 1, time constant 4 sec; 70–130° taken with 4° slits, scale factor 8, multiplier 1, time constant 4 sec.

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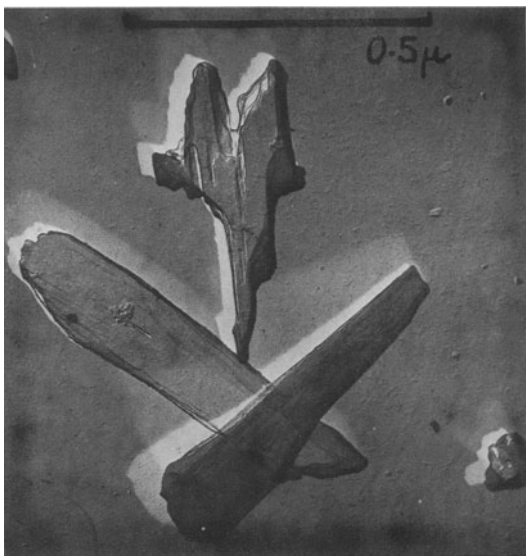

Fig. 2. Electron micrograph of elongated platy particles of antigorite.

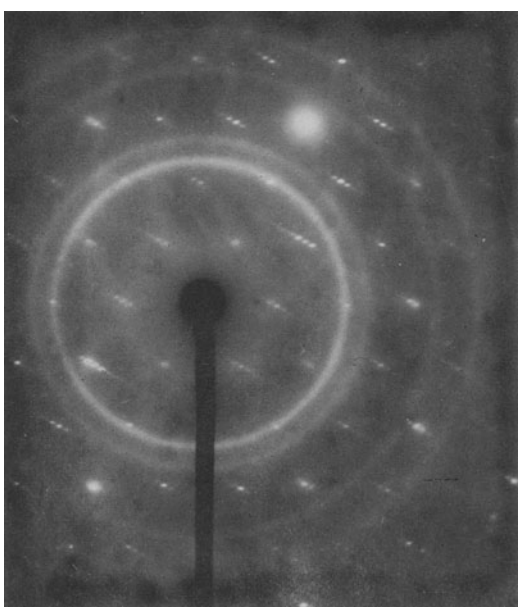

Fig. 3. Electron diffraction pattern from a platy particle of antigorite. Rings produced by light platinum shadowing on the particles.

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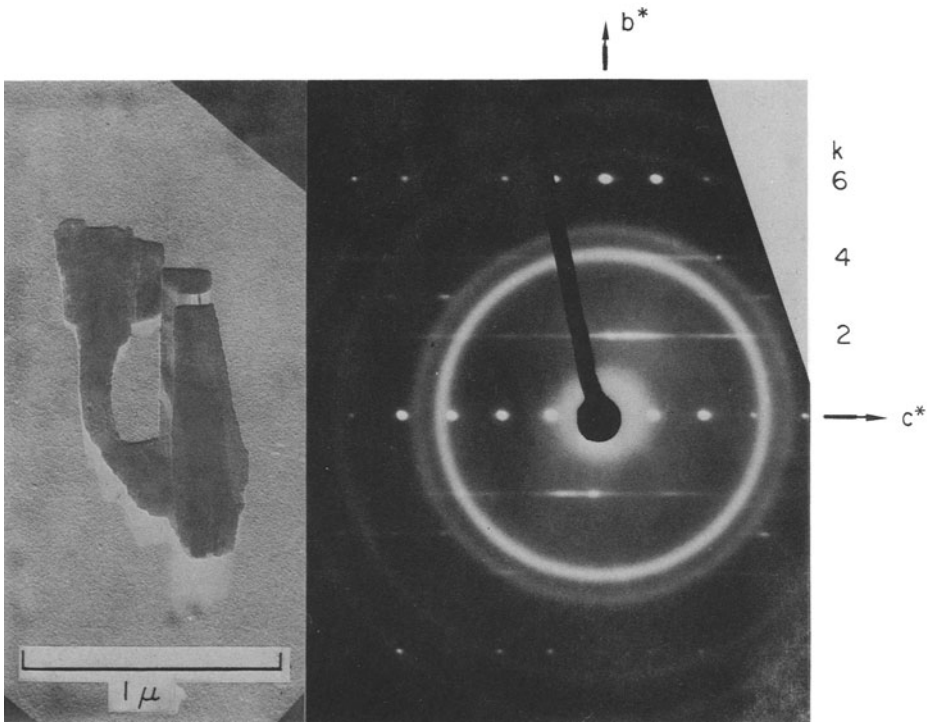

Fig. 4. Antigorite particle of unusual shape, and the corresponding electron diffraction pattern. Rings are produced by Pt-shadowing of the particle.

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spacings. Whittaker and Zussman (1956, p. 120) state that their "indexing of the antigorite patterns was carried out with the aid of single-crystal Weissenberg and oscillation photographs". Fig. 1 shows a diffractometer recording taken at 1° 2θ/min and recorded with 0·5 in./deg. 2θ. Most of the reflections listed in Table 2 are seen in Fig. 1.

ELECTRON-OPTICAL DATA

Electron micrographs show the individual crystals to be about 0·5–2 μ in size. They exhibit very variable morphology. Many are of platy form, and some are lath- and rod-shaped (Fig. 2), but others exhibit a very extraordinary appearance, sometimes with holes through them.

The platy crystals are oriented with the basal (001) planes on the stage of the instrument, and single crystal diffraction patterns (Fig. 3) show the *hk*0 diffractions typical of antigorite, i.e. with closely-spaced clusters of spots parallel to a^* corresponding to various values of a such as 36·2, 39·7 and 43·5 Å for different crystals. Zussman, Brindley and Comer (1957) found similar variations of a within given samples of antigorite. In the present material, the 43·5 Å value is perhaps the most commonly occurring. The b parameter

Table 2. X-ray powder data for antigorite; d, in Å; I, relative values

(1)		(2)			(1)		(2)		
d	I	d	I	hkl	d	I	d	I	hkl
7·24	500	7·30	400	001	1·559	43	1·563	12	24.3.0
		6·95	24	$20\bar{1}$	1·539	42	1·541	9	060
		6·52	16	$30\bar{1}$	1·532	10	1·534	9	$24.3.\bar{1}$
		5·80	8	401	1·520	20	1·523	13	15.0.4, 16.0.$\bar{4}$, 22.3.$\bar{2}$
		5·11	3	710	1·507	20	1·508	8	061
		5·67	6	810	1·498	10	1·497	10	17.0.$\bar{4}$, $93\bar{4}$
4·61	10	4·64	7	020	1·481	8	1·480	7	934
4·25	4	4·27	4	910	1·469	8	1·468	6	18.0.$\bar{4}$
4·02	3	3·95	6	$81\bar{1}$			1·462	6	10.3.4
3·619	210	3·63	300	102, $10\bar{2}$	1·454	9	1·452	10	$20\bar{5}$
		3·52	24	302, 202			1·448	9	205
		2·88	2	$14.0.\bar{1}$	1·417	4			
		2·66	3	$15.0.\bar{1}$	1·387	2			
2·600	4	2·60	4	930	1·349	2			
2·569	7	2·57	8	17.0.0, $16.0\bar{1}$	1·339	5			
2·521	70	2·53	70	16.0.1	1·315	24			
2·454	10	2·46	9	$93\bar{1}$	1·300	10			
2·424	15	2·42	38	003, 18.0.0	1·287	3			
2·395	7	2·39	9	17.0.1, $30\bar{3}$, $10.3.\bar{1}$	1·279	10			
		2·35	5	403?	1·263	8			
2·232	4	2·24	6	$15.0.\bar{2}$	1·252	4			
2·212	6	2·21	7	$16.0.\bar{2}$	1·211	4			
2·168	17	2·169	22	$83\bar{2}$	1·176	2			
2·148	14	2·153	20	16.0.2	1·152	4			
2·121	4‡	2·127	4	$93\bar{2}$	1·096	1			
		2·113	4	$17.0.\bar{2}$	1·074	2			
		2·035	4	$11.3.\bar{2}$	1·054	5			
1·877	4	1·879	3	$15.0.\bar{3}$	1·0145	1			
1·834	13	1·832	12	15.0.3	1·0093	4			
1·819	18	1·813	23	004, $10\bar{4}$, 833	0·9998	6			
1·782	14	1·782	14	$93\bar{3}$	0·9710	4			
1·754	5	1·755	4	$10.3.\bar{3}$	0·9523	3			
1·739	10	1·738	10	17.0.3	0·9032	2			
1·695	4	1·680	2	21.3.1	0·8924	4			
		1·638	2	22.3.1	0·8853	3			
		1·587	3	$14.0.\bar{4}$	0·8699	2			

(1) d,I values for antigorite clay from Castro, Paraná, Brazil. The I values are relative to 70 for d = 2·521.

(2) Combined values of d given by Whittaker and Zussman (1956) for five antigorites, including one set of data by Hess *et al.* (1952). I values are by Hess *et al.* (1952). Indices *hkl* given by Whittaker and Zussman (1956).

‡Below this line, pattern recorded with 4° slits; above this line, with 1° slits.

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averages 9·25 ± 0·02 Å in good agreement with the X-ray value of 9·23 Å. The diffraction patterns are calibrated by the rings originating from a light platinum shadowing of the crystals. When the crystals are elongated, the elongation appears to be generally parallel to b.

Figure 4 shows a particle of extraordinary form together with its diffraction pattern. Crystals of this kind appear to have the (001) basal planes normal to the stage of the instrument; the diffraction pattern shows c^* normal to the striations seen in the micrograph which probably indicate the edges of basal planes. Usually b^* is seen normal to c^*. From the Pt-calibrated patterns, values of b, 9·25 Å, and $d(001)$, 7·25 Å, are obtained, which agree with the X-ray data.

In diffraction patterns of the kind shown in Fig. 4, sharp spots are found on lines corresponding to $k = 0$ and 6, and more or less continuous streaks on lines corresponding to $k = 2$ and 4. These and other results (see below) can be explained as follows: If the total diffraction pattern of antigorite is regarded as derived from a small pseudo-cell* with $a \simeq 5{\cdot}3$, $b = 9{\cdot}25$, $c \simeq 7{\cdot}3$ Å and $\beta = 91{\cdot}6°$, and centered on the C-face, then $0kl$ diffractions will be of the types $00l$, $02l$, $04l$, $06l$, ... If the structural layers are randomly displaced by $nb/3$ (as frequently happens in these minerals) then $00l$ and $06l$ diffractions will remain as spots and $02l$ and $04l$ diffractions will be continuous streaks. This is the appearance of the diffraction pattern in Fig. 4. Additionally, patterns have been obtained showing continuous streaks with $k = 1, 2, 4, 5, 7, 8$, i.e. $l \neq 3n$ and with spots on $k = 3$ and $k = 9$ rows. None of the diffractions with k an odd number is in accordance with the C-centering of the small pseudo-cell. Their occurrence almost certainly arises from the true a parameter being large and giving rise to clusters of spots along a^*. Thus some of these additional diffractions must be coming sufficiently near to the recording position so that they show up as spots for $k = 3$ and 9, and as streaks for other odd values of the k index.

*The value of β is taken from Whittaker and Zussman (1956); the precise value is unimportant for the argument given in the text.

THERMAL ANALYSIS

Figure 5 shows a differential thermal analysis curve of the Castro antigorite with one main endothermic reaction commencing at about 600°C, with a peak at about 760°C, and a sharp exothermic effect at about 830°C. The curves were obtained with 0·6 g samples packed into nickel holders with a temperature increase of 12°C/min. These curves are entirely consistent with the clay being a pure antigorite (Caillère and Hénin, 1957).

CONCLUSIONS

The white clay mineral associated with talc in the Jatoba talc mine, Castro, Paraná, Brazil, is a pure or nearly pure antigorite, with particle size about 0·5–2 μ, a chemical composition very close to the theoretical serpentine composition, and an X-ray powder diagram in good agreement with data of Whittaker and Zussman (1956). Electron micrographs show a variety of particle morphologies, and electron diffraction shows that platy crystals tend to lie on (001) basal planes and to give $hk0$ diffractions, and that other crystals tend

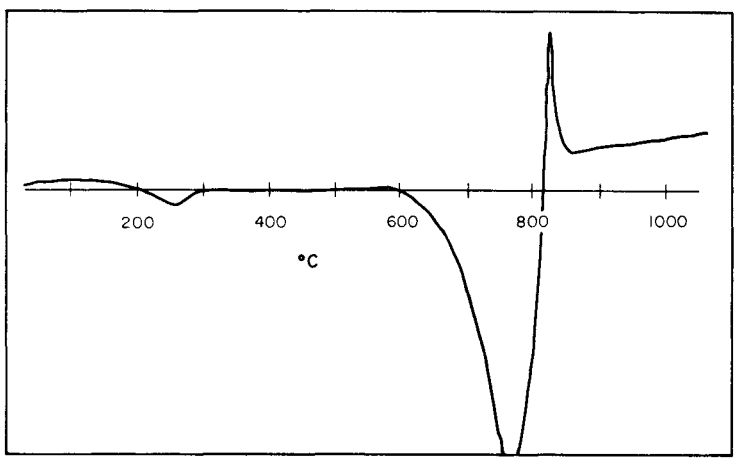

Fig. 5. Differential thermal analysis diagram of the antigorite from Jatoba Mine, Castro, Paraná, Brazil.

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to have the (001) planes normal to the stage of the instrument and to give 0*kl* diffractions. The long *a* parameter is variable, with the value 43·5 Å probably the most commonly occurring, $b = 9{\cdot}23$ Å, and $d(001) = 7{\cdot}26_5 \pm 0{\cdot}00_7$ Å.

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Résumé—On démontre au moyen de l'analyse chimique, des diffractions de rayons X et d'électrons, et de l'analyse thermique, qu'une argile blanche provenant de la mine de talc Jatoba, Castro, Paraná, Brésil, est une antigorite essentiellement pure, au sens strict du terme. Des diagrammes de diffraction électronique de cristaux uniques fournissent pour le paramètre de plus grand allongement *a*, des valeurs variables parmi lesquelles 43,5 Å est peut être la plus couramment rencontrée; $b = 9{,}25$ Å et $d(001) = 7{,}25$ Å. La diffraction des rayons X sur poudre donne $d(001) = 7{,}26$ Å et $b = 9{,}23$ Å. Les micrographies électroniques montrent des cristaux irréguliers plats en forme de lattes d'environ 0,5 à 2 microns, avec un grand développement des plans (001), et *b* dans la direction de l'allongement. On observe d'autres cristaux d'une forme très inhabituelle, certains d'entre eux présentent des perforations. Ils donnent principalement des diagrammes de diffraction 0*kl* et ont les plans basaux (001) dirigés normalement au plan de référence de l'instrument. L'analyse chimique est en très bon accord avec la composition idéale de la serpentine, et la courbe d'analyse thermique différentielle est compatible avec l'antigorite.

Kurzreferat—Ein weisser Ton aus der Jatoba Talkgrube, Castro, Paraná, Brasil wird mittels chemischer Analyse, Röntgen—und Elektronen—beugung, sowie mittels thermischer Analyse als im wesentlichen reiner Antigorit, im wahren Sinne des Wortes, erkannt. Einzelne Kristallbeugungsbilder geben verschiedene Werte für den langen *a* Parameter, wobei 43,5 Å der am häufigsten vorkommende Wert ist, $b = 9{,}25$ Å, $d(001) = 7{,}25$ Å. Röntgenpulverbeugung gibt $d(001) = 7{,}26$ Å und $b = 9{,}23$ Å. Elektronenmikrographien zeigen unregelmässige plättchen—und stabförmige Kristalle von etwa 0,5–2 Mikron Grösse mit weiter Entwicklung der (001) Flächen und mit *b* in der Längsstreckung. Andere Kristalle mit sehr ungewöhnlichen Formen werden beobachtet, manche mit Durchlochungen. Sie zeigen meist 0*kl* Beugungsbilder und liegen mit den Basisflächen (001) senkrecht zu dem Gerätetisch. Die chemische Analyse stimmt eng mit der idealen Serpentinzusammensetzung überein und die thermische Analysenkurve steht im Einklang mit Antigorit.

Резюме — Методами химического анализа, рентгенографии, дифракции электронов и термического анализа установлено, что белая глина из талькового месторождения Джатоба (Параná, Бразилия), представляет собой почти чистый антигорит в строгом смысле слова. По данным дифракции электронов от монокристаллов определены различные значения для большого параметра **a**; его наиболее часто встречающееся значение равно 43,5 Å, $b = 9{,}25$ Å, $d(001) = 7{,}25$ Å. Данные рентгеновских порошкограмм приводят к значениям $d(001) = 7{,}26$ Å и $b = 9{,}23$ Å. На электронномикроскопических снимках видны кристаллы-пластинки неправильной формы и ленты (0,5–2 мк) с сильно развитыми гранями (001), вытянутые по *b*. Наблюдались также кристаллы весьма необычной формы, частью со сквозными отверстиями. Подобные кристаллы давали, главным образом, дифракционные картины с набором рефлексов (0*kl*) и ориентировались базальной плоскостью (001) перпендикулярно препаратодержателю прибора. Данные химического анализа хорошо согласуются с формулой серпентина идеального состава, а кривая ДТА характерна для антигорита.