SKETCH MAP OF VENEZUELA
showing locations mentioned in text
general areas of white clays

LOCATION

THE WHITE CLAYS OF LARA STATE
(LAS ARCILLAS BLANCAS DEL ESTADO LARA)

by Manuel Rivero Palacio[1]

SUMMARY

The main objective of this paper is to discuss the results of the tests carried on by INVESTI on the white clays of Lara State, bearing on the identification of its minerals. Emphasis is laid on the identification of pyrophyllite because of the rareness of the occurrence of this mineral in sedimentary beds. The conclusion reached is that the main components of these clays are pyrophyllite and illite accompanied by many other minerals in small proportions. This conclusion contradicts the previously held idea that these clays were kaolinitic. The similarity of the white clays with the pyrophyllitic schists of North Carolina is discussed. A discussion of the occurrence both in time and space of pyrophyllitic clays elsewhere in Venezuela is given.

RESUMEN

Este artículo tiene por objetivo principal la discusión de los resultados de las pruebas hechas por INVESTI sobre las arcillas blancas del Estado Lara, relacionadas a la identificación de sus minerales. Se hace hincapié sobre la identificación de pirofilita, en razón a la rareza de dicho mineral en capas sedimentarias. Se llega a la conclusión de que los componentes principales en las arcillas son pirofilita e ilita, acompañadas por cantidades menores de muchos otros minerales. Esta conclusión contradice la idea previa de que las arcillas son caoliníticas. Se discute la similaridad entre las arcillas blancas y los esquistos pirofilíticos de Carolina del Norte, y también las ocurrencias y las edades de arcillas pirofilíticas encontradas en otras partes de Venezuela.

INTRODUCTION

Our intention in this paper is to bring out all the information INVESTI has collected bearing on the identification of the minerals of the white clays of Lara, in particular pyrophyllite. Some of the information given has already been published, either in INVESTI's or in this author's other publications (see "References"), but we will repeat it here and thus have in one single paper all the data we can give on the subject. In our estimation it is important enough, because in the world literature, so far as we have been able to find out, there has been no mention of pyrophyllite in sedimentary beds, certainly not as one of the main components. Furthermore, it is the intention of this paper to focus attention on the white clays of Lara with the object of arousing discussion. It seems impossible to us that such an unusual occurrence does not have any stratigraphic significance. For one thing, the absence of organic matter (judging by the color and by extractions with carbon tetrachloride) in an area where the sediments to either side, both vertically and horizontally, contain it abundantly, should be a topic of extensive discussion.

For the purposes of the present paper the age of the sediments involved is irrelevant. We have dealt with the stratigraphy of these sediments in previous publications (Rivero Palacio, 1962a, 1964b). However, for the purpose of easy reference we shall refer to one group of white clays as Bobare-type (those that outcrop around Bobare, Carorita and Carora) and to another as Pegón-type (those that outcrop around Sanare and the villages of Yay and El Yeso) (Jefferson, 1964). We are quite aware that there is a large difference of opinion as regards the age of these white clays and in this particular paper we do not want to complicate the subject by bringing in problems of stratigraphy. Moreover, the geographic names leave no doubt as to what group of outcrops one has in mind in any particular instance. On the enclosed map we have sketched the general area where these clays outcrop, to the knowledge of this writer, for purposes of reference. The areas outlined are not the result of field mapping but generalizations derived from the examination of roadside outcrops in hasty weekend trips. No claim to accuracy is made.

We have studied the white clays of Lara in two series of samples. In one series, amounting to 37, a large number of chemical and physical tests were run including X-ray diffraction and differential thermal analysis. In the other series of samples, amounting to several hundred, only X-ray patterns were obtained. This paper will deal mostly with the samples of the first series and we will describe the tests that have a bearing on the identification of the minerals composing the white clays and in particular pyrophyllite.

In the author's opinion, the pyrophyllite present in the white clays is entirely detrital. In the samples that have come to the laboratory or in the outcrops examined in the field, we have not seen any sign of metamorphism. For the most part, judging by the material examined, the term "clay" applied to this rock is more appropriate than "shale".

The X-ray diffraction work for this paper was obtained by the author in the X-ray diffraction laboratory of IVIC with instrument setting described in our other publications (see "References"). Information of chemical or physical nature as well as information on differential thermal analysis was obtained in INVESTI's laboratories by its own staff, to whom we are indebted for a large volume of work. We also wish to acknowledge the help received from INVESTI's management in the preparation of this paper and in the permission for its publication.

PREVIOUS WORK

As far as this author is aware, the only previous work of a mineralogic nature on the white clays of Lara is that of Evanoff et al. (1957). These authors conclude that these clays are kaolinitic in nature and assign to them various ages. We will limit ourselves to comment on the first point without referring to the age assignments.

For the characterization of the white clays of Lara as kaolinitic, Evanoff et al. adduce some organoleptic properties and chemical analysis.

Organoleptic properties.- On page 85 the following properties are given for the white clays:

a) Se desintegran rápidamente en el agua y se vuelven plásticas.
(They disintegrate rapidly in water and become plastic).

b) Producen un olor a tierra mojada al humedecerlas con el aliento.
(They produce a smell of damp earth when one breathes on them).

c) Poseen marcada tendencia a adherirse a la lengua.
(When touched with the tongue, they have a strong tendency to adhere to it).

d) Son untuosas al tacto. (They have a soapy feel).

On page 86 the same paper reads: "Las propiedades físicas y la composición química de las arcillas descritas sugieren que son muy caoliníticas". (The physical properties and the chemical composition of the clays described suggest that they are very kaolinitic).

Comments on a): It strikes us as a very singular idea to consider the rate of disintegration in water as a criterion for the mineralogic composition of a clay. It will suffice to say that at least three quarters of the 1300 odd clay samples studied by INVESTI, with a great variety of mineralogic composition, disintegrate rapidly in water.

Concerning plasticity what we can say is that all of the Bobare-type clays on which plasticity tests have been run turned out to be not plastic. However, the white clays of the Pegón-type are very plastic. On Table 1 we give the results of the plasticity tests we have carried out: (ASTM D 423-61T and D 424-65). We have added in this table a column with the quartz content, as estimated from X-ray diffraction, to show that the presence or absence of this mineral does not seem to affect the plasticity of these clays.

We will add as general information that typical kaolinite is not plastic. This property, or rather lack of it, gives a great deal of trouble in the ceramic industry, forcing the ceramist to add materials to give the paste the adequate plasticity, such as "ball clay" which is a naturally occurring plastic kaolinite of very dark color. Its plasticity is probably due to the presence of finely divided organic matter.

Comments on b) and c): These properties may be true of kaolinite but they are also true of many other earthy minerals and rocks.

Comments on d): In our opinion, the fact that the white clays have a soapy feel should mean that probably they are not kaolinitic. The soapy feel makes us think of the talc family. Typical kaolinite is rather harsh to the touch.

Comments on chemical analyses: Ten chemical analyses are given which we summarize on Table 2. Only three analyses are complete (Nos. I, II and III from El Yeso). These three have an average silica-alumina ratio of 3.2*. This value is far too high for kaolinite which has a silica-alumina ratio of 2.0. If we take all the analyses into consideration, the average silica-alumina ratio is 6.8, further still from the value of kaolinite.

In the analyses given, only four have water determination, which averages 5.6%. The value for kaolinite is 13.9 or nearly two-and-a-half times higher. Again the chemical analyses do not suggest kaolinite.

Summing up the evidence, we must say that neither the organoleptic characters nor the chemical analyses suggest kaolinite. That is to say, taken by themselves they do not point towards kaolinite any more than towards any other clay mineral. The only legitimate conclusion that can be derived from the evidence adduced is that the white clays are hydrous aluminum silicates.

In a recent meeting in Barquisimeto of the Asociación Venezolana de Geología, Minería y Petróleo, after this author pointed out the virtual absence of kaolinite in the white clays, somebody on the floor suggested that the term "kaolinitic clay" was a field term, and as such was properly used to refer to the white clays. Keeping this suggestion in mind (which implies that any light colored clay is a "kaolin"), we notice that in the work we are commenting on the authors nowhere use the mineral name kaolinite in the text. They always refer to the white clays as "kaolinitic" clays. This leaves one in doubt as to what the authors mean, whether they are referring to presence of the mineral kaolinite (Ross and Kerr, 1931, 1934) or of the rock kaolin. This latter term is widely used in commerce and as such has perhaps a looser meaning than the strict mineralogic term. Even so, if we give credence to Ross and Kerr (with whom this writer concurs wholeheartedly), the main component of kaolin deposits is the mineral kaolinite. Therefore to qualify a clay as "kaolinitic" without adducing valid evidence of the presence in large proportion of the mineral kaolinite is to violate the rules of nomenclature.

In view of the foregoing, it seems to us that using the word "kaolinitic" as a field term to refer to the white clays of Lara, which contain very little kaolinite, is entirely unjustified. Of course a field man has no way of telling the minerals composing a particular clay, but some other term of a descriptive nature should be used and not the highly specific one of "kaolinitic". After all, in field work one does not call a rock "dolomite" that is entirely made up of calcite, or "gypsum" if it is composed of anhydrite. Taking a very specific term and giving it a loose meaning seems a vicious practice that should be discouraged, particularly in this case where there is a term, widely used and

* Editor's Note: In clay mineralogy the term "silica-alumina ratio" refers to the molecular proportions of the two compounds. Their molecular weights (approximately 60 and 102 respectively) have been applied in deriving the ratios mentioned from the sample analyses tabulated in this paper.

TABLE 1

PLASTICITY TEST. (ASTM D-423-61T and D-424-65)

Pegón-type Clays					Bobare-type Clays				
Sample	LL %	PL %	PI %	QC %	Sample	LL %	PL %	PI %	QC %
INV 59	49	22	27	--	INV 33	33	--	--	10
60	46	31	15	35	34	29	--	--	0
61	43	29	14	--	35	33	--	--	?
62	48	23	25	45	36	31	--	--	5
63	41	22	19	--	37	30	--	--	0
64	34	16	18	60	38	35	--	--	10
65	48	27	21	20	39	33	--	--	5
66	46	26	20	30	40	30	--	--	5
67	40	22	18	40	41	33	--	--	5
68	55	24	31	20	44	41	--	--	10
69	32	20	12	50	45	37	--	--	5
70	40	25	15	40	46	37	--	--	5
140	44	29	15	20	52	31	--	--	0
141	29	19	10	50	78	32	--	--	0
142	42	25	17	40	79	32	--	--	5
143	33	22	11	50	80	32	--	--	0
144	36	24	12	40	81	31	--	--	0
145	26	19	7	30	114	34	--	--	10
					115	28	--	--	10
					134	40	--	--	0
					135	34	--	--	0
					136	30	--	--	10

LL : Liquid Limit

PL : Plastic Limit

PI : Plastic Index

QC : Quartz Content

TABLE 2

CHEMICAL ANALYSES GIVEN BY EVANOFF ET AL. (1957)

	EL YESO				EL PAPAYO		EL TANQUE		LA LAGUNA	CARORITA
	I	II	III	IV	1	2	1	2		
SiO_2	59.92	61.10	56.28	62.75	81.10	72.50	78.45	78.57	62.50	73.00
Al_2O_3	33.54	33.34	27.82	29.47	12.85	20.62	14.97	15.78	28.33	7.09
Fe_2O_3	0.37	0.40	0.37	0.18	0.32	0.73	0.38	0.27	0.67	0.41
CaO	1.00	1.03	1.10	--	--	--	--	--	--	--
MgO	0.66	0.48	0.58	--	--	--	--	--	--	--
P.R.	5.02	5.00	6.44	6.04	--	--	--	--	--	--
	100.51	101.35	92.59	98.44	94.27	93.85	93.80	94.62	91.50	80.50
Silica-alumina ratios	3.0	3.1	3.4	3.6	10.7	6.0	8.9	8.4	3.7	17.4

sufficiently specific, of "white clays". By "specific" I mean that if one asks any laborer in Sanare, for instance, where is there "tierra blanca" (white earth) he will lead one without hesitation to the nearest white clay outcrop.

BOBARE-TYPE CLAYS

Chemical Composition.- As can be seen in Table 3 these white clays are almost pure hydrous aluminum silicates. The alkaline earths are totally absent or nearly so. Iron, for the most part, is also absent or in very low proportion. The water content, in general, is on the low side, precluding the presence in any significant amounts of hydroxides with a high water content (like gibbsite, etc.).

There is a slight difference in chemical composition between the clays towards the western side of Lara, around Carora, and those around Bobare. The alkaline earths, although in low proportion, are higher in the former. It is possible that this difference in chemical composition might be due to contamination by surface waters under the prevailing arid climate, since the samples near Carora were collected from very weathered road cuts and those from the vicinity of Bobare come from commercial pits where all the weathered material had been removed. Another possibility is that at least the magnesium and the iron are due to the presence of chlorite, which is often found towards the west in small amounts. However, no chlorite can be detected in the samples for which we have chemical analyses and no chemical analyses are available from Los Gavilanes, the only commercial pit near Carora where chlorite was found in a few samples.

At the bottom of Table 3 we give the silica-alumina ratio (see preceding footnote) of the analyses available. The first two lines are self explanatory. The last line, silica-alumina ratio from X-ray diffraction, is in fairly good agreement with the figures of the second line. However, this agreement is not very meaningful because the silica-alumina ratio of illite used to obtain the third line of the table was that derived from the mineralogic interpretation of the chemical analysis. Since the other minerals present have their silica-alumina ratio fixed by their formula the only difference between the two lines is just how much modification the quantitative estimates of X-ray diffraction received to make them agree with the chemical analysis. In other words, the two variants that were manipulated to make the mineralogic analysis fit into the chemical one were the quantity of any one mineral and the silica-alumina ratio of illite. Therefore, the difference between the two lines is a rough measure of the accuracy of the original X-ray quantitative estimates. Since the agreement, on the average, is fairly good and there is a comparatively large number of analyses, the conclusion is justified that the X-ray quantitative estimates, in this particular case, are accurate.

Titanium Determination.- No titanium determinations were made. Therefore, if this element is present at all, it is included in the figures for aluminum.

Potassium Determination.- We have a total of eight potassium determinations of these clays. These determinations were made in a flame spectrophotometer manufactured by Optica Milano. The technique for preparing the samples for spectrophotometric work consisted mainly in treating the clay with hydrofluoric acid, dissolving the residue in H_2O and diluting to the proper concentration for the instrument. Hydrofluoric acid treatment in general is supposed to dissolve the clays completely but in our case this did not happen. A large insoluble residue was left in every case, which in one sample amounted to 21%. Mme. de Brass de Guedon of the Societé Francaise de Ceramique, in a written communication to

INVESTI, is of the opinion that probably all the potassium compounds have been dissolved and therefore the potassium determinations are accurate. However, she advises a great deal of caution and further study of the problem. She also mentions that a large insoluble residue may point towards the presence of corundum. This last observation has been completely discarded by the writer on X-ray evidence. Unfortunately, no further chemical work has been done and this writer offers the results to date at their face value.

Only two chemical analyses that include potassium are available:

	MR 59H	MR 60
$Si O_2$	64.44%	62.68%
Al_2O_3	19.36	23.28
Fe_2O_3	4.70	2.35
$Ca O$	2.75	3.30
$M_g O$	2.70	2.26
Ignition Loss	5.50	5.99
	99.45	99.86
K_2O	3.20	3.70
	102.65%	103.56%

As can be seen above, the sum of the oxides, other than potassium, add up to a figure very close to one hundred giving one the impression that the analyses are accurate. However, when we add to the sum of the other oxides the value obtained for potassium we get very high figures (102.65 and 103.56% respectively), turning the analyses which at first sight seemed to be of very good quality into very poor ones.

Exactly the same difficulty is experienced in the mineralogical interpretation we give of the chemical analyses elsewhere in this paper. For the most part, the analyses are of fairly good quality, that is, they add up to nearly one hundred percent. However, when we add the hypothetical value for potassium derived from the formulas of feldspar and illite we find that the sum in most cases is too high, thus rendering the analysis suspect. This situation makes us believe that either the potassium determinations are inaccurate or that the standard wet technique of silicate analysis is not applicable to the white clays of Lara. This writer is not qualified to discuss the finer points of silicate analysis and merely limits himself to presenting the evidence available. Further chemical research is indeed desirable.

One possible way to get around the difficulty of the consistently high figures we obtain for the sums of the chemical analyses when we add potassium, would be to assume that the reflection at 3.17 Å is not feldspar, or that if it is feldspar, it has been leached of most of its potassium while still retaining most of its structure. Lower potassium content of the illite would help in this connection. None of these assumptions fits well with the evidence available.

TABLE # 3

BOBARE TYPE CLAYS

CHEMICAL ANALYSIS

	INV 33	INV 34	INV 35	INV 36	INV 37	INV 38	INV 39 NEAR BOBARE	INV 40	INV 41	INV 78	INV 79	INV 80	INV 81	INV 44 NEAR CARORITA	INV 45	INV 46	INV 52	INV 114 PANAM. ROAD W. of Pte.Torres	INV 115	INV 134 LARA-ZULIA ROAD	INV 135	INV 136	$\bar{x}$
Si O2	62.31	54.86	62.33	65.19	62.32	67.47	65.99	62.19	60.83	59.31	59.82	57.82	62.07	57.56	62.52	65.38	58.03	59.60	64.58	49.36	58.06	69.02	61.22
Al2 O3	33.97	40.69	32.42	29.59	32.20	27.50	27.29	32.03	27.81	32.72	33.00	34.13	30.64	34.13	32.07	28.32	33.25	32.11	27.46	31.03	30.39	21.61	31.10
Fe2 O3	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	1.60	Tr.	2.71	1.04	Tr.	Tr.	Tr.	1.96	Tr.	Tr.	0.80	Tr.	Tr.	1.64	1.48	1.36	0.57
Ca O	0.79	1.14	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	0.67	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	0.75	0.18	Tr.	4.90	2.49	1.32	0.56
MgO	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	0.72	0.73	0.57	0.30	Tr.	Tr.	0.25	0.58	0.45	0.16
H2O (110°C)	0.40	0.27	0.40	0.22	0.42	0.34	0.34	0.26	0.54	0.41	0.50	0.56	0.55	0.45	0.51	0.21	0.84	0.61	0.53	1.86	1.51	0.73	0.58
H2O (1000°C)	5.0	5.63	5.07	4.44	5.58	4.22	4.73	5.73	6.83	5.41	5.08	5.55	4.82	6.27	4.75	5.14	6.22	4.62	4.56	11.25	6.15	3.86	5.30
TOTAL	102.47	102.59	100.22	99.44	100.52	99.53	99.95	100.21	98.72	99.56	98.40	98.06	98.08	100.09	100.58	99.62	100.19	97.12	97.13	100.29	100.66	98.35	98.50

SILICA - ALUMINA RATIO OF CLAY MINERALS

	INV 33	INV 34	INV 35	INV 36	INV 37	INV 38	INV 39	INV 40	INV 41	INV 78	INV 79	INV 80	INV 81	INV 44	INV 45	INV 46	INV 52	INV 114	INV 115	INV 134	INV 135	INV 136	AVERAGE
AS COMPUTED FROM ANALYSIS	3.1	2.3	3.2	3.7	3.3	4.2	4.1	3.3	3.7	3.1	3.1	2.9	3.4	2.9	3.3	3.9	3.0	3.1	4.0	2.7	3.2	3.4	3.4
CORRECTED FOR FREE ALUMINA OR SILICA	2.6	2.3	–	3.5	3.3	3.5	3.8	3.0	3.4	3.1	2.8	3.0	3.4	2.3	3.0	3.6	3.7	3.1	4.1	2.7	3.9	5.4	3.3
FROM X-RAY DIFFRACTION	3.7	3.4	–	3.5	3.9	3.6	3.7	3.4	3.8	3.5	3.4	2.9	3.7	3.2	3.7	3.1	3.2	2.7	3.7	3.4	3.8	4.2	3.5

For the mineralogical interpretation of the chemical analyses, the potassium content of the illite is of great importance, since this mineral is one of the main components of the clays. However, we encounter a difficulty here. In two of the samples with potassium determination small amounts of feldspar are present, presumably orthoclase. The presence of feldspar in the Bobare-type white clays is so widespread that, even when no feldspar appears in the X-ray pattern, we still suspect that it may be present in small amounts. Since the potassium content of pure orthoclase is very high, amounting to 16.2% the potassium ascribed to illite will be greatly influenced by the amount of feldspar present. If we disregard the feldspar completely and ascribe all the potassium to illite, we obtain an illite with an average potassium content of 8.6% and a range of 6.2 to 12.1%, which seems to us a very large spread (Table 4). On the other hand, if we assume the presence of small amounts of feldspar (despite having positive evidence in only two cases), we obtain an average potassium content for the illite of 5.1% and a range of 2.2 to 6.7%. These latter figures, with a much narrower spread, seem a little more reasonable than the ones obtained with no allowance for feldspar.

In the mineralogical interpretation of the chemical analyses, we had to assume an illite with still lower potassium content, namely 4.0%. With this lower value, the average sum of 20 analyses is 102.0% and the sum never exceeds 104%.

From the preceding it is obvious that the assumed potassium content of the illite is not much better than an educated guess but until more data are available it is all we have to offer.

Probable Composition of Illite.- The chemical composition of illite, derived from the mineralogic interpretation of the chemical analyses, is as follows:

Silica-alumina ratio	2.6
Water	5.1%
Potassium	4.0%

The variation of the silica-alumina ratio in the various analyses goes from 2.0 to 3.5. The variation of the water content goes from 4.5 to 9.0% (only one sample goes this high).

Comparing this probable composition with that of muscovite, we get:

	Illite	Muscovite
Silica-alumina ratio	2.6	2.0
Water	5.1%	4.5%
Potassium	4.0%	11.8%

As can be seen here, the silica-alumina ratio and the water content are very close. Slight leaching of Al_2O_3 and very slight hydration have taken place. However, a marked difference exists in the potassium content, which in the illite is only one-third that of the muscovite. Were this comparison correct, we would conclude that the only alteration suffered by the muscovite as it went into illite was a large leaching of potassium, which probably would not imply a great change in the structure. If this is so, the illite present in the white clays is almost a mica. The sharpness of the peaks in the patterns of the Bobare-type white clays would tend to confirm this idea. Such is not the case

TABLE 4

Samples ⟶	Los Gavilanes No. 1	Los Gavilanes No. 2	Los Gavilanes No. 3	Los Gavilanes No. 5	Los Gavilanes No. 7	MR 59 B	MR 59 H	MR 60
(1) Illite content (X-ray)	30%	15%	15%	10%	?	20%	50%	60%
(2) K_2O content (chemical)	2.81%	1.81%	1.14%	0.98%	1.92%	1.7%	3.2%	3.7%
(3) K_2O content of illite if no feldspar present (2) ÷ (1)	9.4%	12.1%	7.6%	9.8%	-	8.5%	6.4%	6.2%
(4) Feldspar content: queries mark assumed values	5.0% (?)	5.0% (?)	5.0% (?)	2.5%	-	5.0%	5.0% (?)	5.0% (?)
(5) K_2O content attributed to feldspar (4) x 16.2*	0.8%	0.8%	0.8%	0.4%	-	0.8%	0.8%	0.8%
(6) K_2O content attributed to illite (2) − (5)	2.0%	1.0%	0.3%	0.6%	-	0.9%	2.4%	2.9%
(7) K_2O content expressed as percentage of illite (6) ÷ (1)	6.7%	6.7%	2.2%	5.8%	-	4.5%	4.8%	4.8%

Average values : (3) K_2O content of illite if no feldspar present : 8.6%

(7) K_2O content of illite adjusted for feldspar : 5.1%

* - K_2O content of feldspar (orthoclase) = 16.2%

in the Pegón-type white clays which, for the most part, give X-ray patterns showing both the illite and the kaolinite with broad-based peaks of low intensity, even though chemically the two types of clay are very similar.

Mineralogic Composition.- (X-Ray diffraction). By averaging twenty samples, we obtain the following average composition of the Bobare-type white clays:

Pyrophyllite	33%
Illite	33%
Kaolinite	9%
Feldspar	9%
Quartz	4%
	83%

Other minerals occasionally present in very small amounts are: gibbsite, corundum, montmorillonite, dolomite, chlorite and calcite. In a few patterns, small unidentified reflections are present. Summing up, this can be read as one third pyrophyllite, one third illite and one third the other minerals.

Kaolinite is occasionally a major component, but this situation was observed in two samples only. The composition then is:

Pyrophyllite	25%
Illite	25%
Kaolinite	25%
Others	25%

The average value for the basal spacing of pyrophyllite obtained in this study is 9.16°A. This value compares very well with Card No. 2-0613 of Powder Data File (ASTM, 1960) of 9.14°A and with Molloy and Kerr, 1961 of 9.2°A. In this letter work if one multiples the various orders of the basal reflection by the corresponding integer and takes off the average, the result is 9.16°A.

The Powder Data File gives another pattern for pyrophyllite (Card No.3-0576) with a basal spacing of 9.5°A. Benjamin Post, Associate Editor of the Powder Data File and professor at the Polytechnic Institute of Brooklyn, in a written communication to us, is of the opinion that this pattern was very carelessly prepared and should be discarded as invalid.

The range of variation of both the pyrophyllite and the illite content is large. From time to time, samples are found in which one or the other of these two minerals completely disappears and the other one takes its place. So we have samples in which the illite reaches about 70% of the total and pyrophyllite is completely absent and others in which the opposite is true. In two localities near Carora, we have had a chance to observe this change. It takes place over a stratigraphic interval of a few meters. This rapid change could be interpreted as meaning that the illite and the pyrophyllite came from different sources with varying predominance of one source-area or the other in the course of time, though generally the sediments coming from these two sources were in about the same proportions. The areal distribution of the pyrophyllitic sediments tends to confirm this idea. Judging by the material we have studied, which is condensed in a schematic section in Rivero Palacio, 1964b, the pyrophyllitic sediments seem to be confined to a zone that does not go much further west than Carora. Still further west the sediments become very illitic with pyrophyllite absent until one gets to a zone in which the predominantly kaolinitic sediments

of the Uribante trough are encountered. However, in this connection it must be kept in mind that if the sediments change often from mostly illitic to mostly pyrophyllitic throughout the column and if the column is not sampled closely enough, it is possible that all samples might show only one or the other of these two minerals. The samples studied in Rivero Palacio, 1964b were very far apart stratigraphically, therefore our idea of the distribution of the illitic and the pyrophyllitic sediments may be at fault.

In Table 5 we give the patterns of a Bobare-type clay in which both the illite and pyrophyllite are in about equal proportions (bottom); one in which pyrophyllite predominates (center) and one in which illite is the main component (top).

Mineralogic Interpretation of the Chemical Analyses.- To make this interpretation we started, as a first approximation, with the quantitative estimate of the mineralogic content as worked out from X-ray diffraction. For the composition of most of the minerals we took that of the formula generally assigned to them. In the case of illite, for a first approximation, we assumed the silica-alumina ratio of 3.6 which is the average silica-alumina ratio obtained from the analyses of illite given by Grim, 1953. Derived from the same source we assumed 7% at first for the water content. In the subsequent juggling of figures to make the chemical and the mineralogic analyses agree, we arrived at the composition of illite given on page 150.

The nature of the feldspar present is not known. In our analyses we have assumed it to be orthoclase but it could be albite or even, sometimes, anorthite. However, since many of the samples do not contain any calcium, we have assumed that the anorthite molecule is not present and since we do not even know if sodium is at all present we have assumed the absence of albite.

In Tables 6 to 13 we give the mineralogic analysis as well as the chemical analysis and a table in which we show in detail the modifications made in the mineralogic analysis to fit the chemical one. Study of these tables will show that the modifications of the quantitative estimates derived from X-ray work are for the most part below ten units percent, very seldom going to 15 units percent. (By units percent we mean a simple subtraction of two values expressed in percentage and not a ratio.) This higher figure seems reasonable to us since we feel that the quantitative X-ray estimates are accurate only within that range. (Rivero Palacio, 1964b). At the bottom of each table we have added a section entitled "minerals that might be present", in order to complete the arithmetic of the table. There is no evidence in the X-ray patterns of the minerals assumed here. On the average the amount represented is only 2.5% of the sample. However, in one case this amount goes up to 14% (INV 134, Table 11). The interpretation of this particular analysis is no better than an educated guess and not too well educated at that. We have included this sample purposely to show that at times the mineralogic interpretation is not an easy matter. In this particular instance we think that the difficulty lies in the presence of many other minerals in such small proportion that no trace of them can be found in the X-ray pattern, and yet their sum constitutes a considerable fraction of the sample.

DIFFRACTION PATTERNS OF WHITE CLAYS

Diffraction patterns of white clays (three stacked patterns with 2θ axis from 52 to 4).
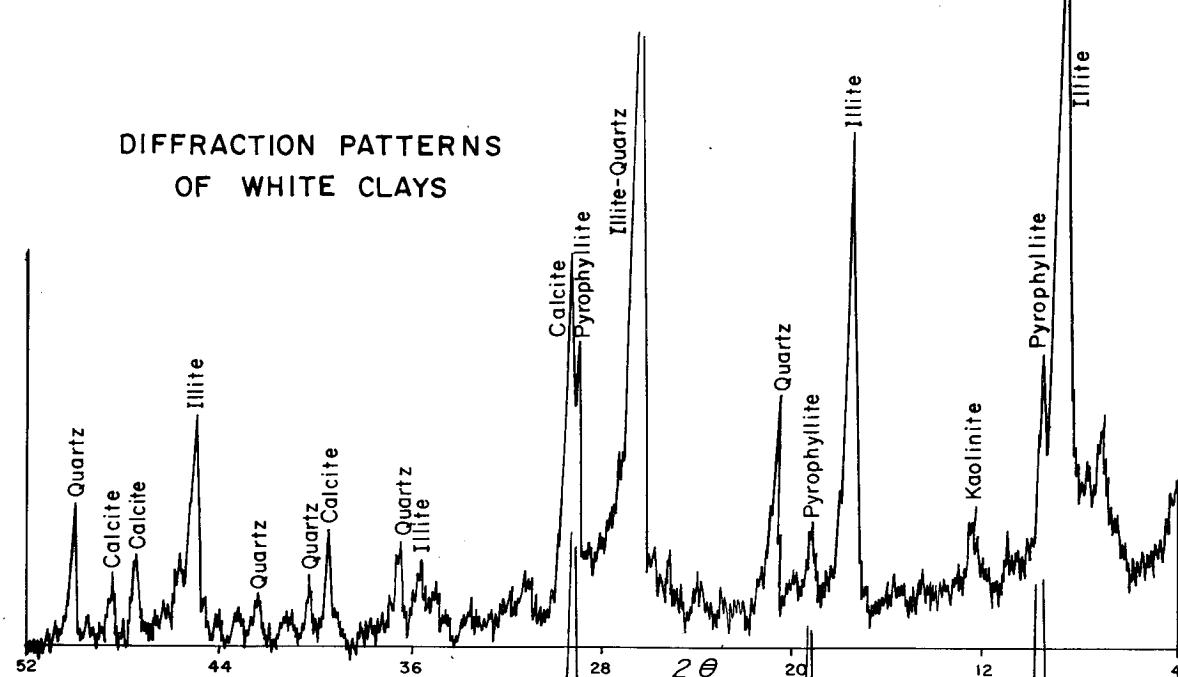
SAMPLE # INV 36

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	H_2O	TOTAL
Pyrophyllite	27.4	11.6					2.0	41.0
Illite	21.9	14.8				1.6(?)	2.2	40.5
Kaolinite	1.2	0.9					0.3	2.4
Quartz	8.1							8.1
Feldspar	6.6	1.8				1.6(?)		10.0
Moisture							0.2	0.2
Sub-total	65.2	29.1				3.2(?)	4.7	102.2

Minerals that might be present

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	H_2O	TOTAL
Corundum and/or Rutile		0.5						0.5
TOTAL	65.2	29.6				3.2(?)	4.7	102.7

MINERALOGIC COMP. (X-ray)

Pyrophyllite	35
Illite	35
Kaolinite	5
Quartz	5
Feldspar	10
	90

CHEM. COMP. (Wet analysis)

SiO2	65.19
Al2O3	29.59
Fe2O3	Tr.
CaO	Tr.
MgO	Tr.
H2O (110)	0.22
I.L.	4.44
	99.44
K2O	3.2 (?)
	102.6

SAMPLE # INV 37

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	H_2O	TOTAL
Pyrophyllite	48.1	20.4					3.6	72.1
Illite	8.6	4.9				0.6(?)	0.9	15.0
Kaolinite	2.3	2.0					0.7	5.0
Quartz	—							
Feldspar	3.3	0.9				0.8(?)		5.0
Moisture							0.4	0.4
Sub-total	62.3	28.2				1.4(?)	5.6	97.5

Minerals that might be present

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	H_2O	TOTAL
Corundum and/or Rutile		1.7						1.7
Bohemite		2.3					0.4	2.7
TOTAL	62.3	32.2				1.4(?)	6.0	101.9

MINERALOGIC COMP. (X-ray)

Pyrophyllite	70
Illite	15
Kaolinite	5
Feldspar	5
	95

CHEM. COMP. (Wet analysis)

SiO2	62.32
Al2O3	32.20
Fe2O3	Tr.
CaO	Tr.
MgO	Tr.
H2O (110°)	0.42
I.L.	5.58
	100.52
K2O	1.4 (?)
	101.9

SAMPLE # INV 38

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	H_2O	TOTAL
Pyrophyllite	29.7	12.5					2.2	44.4
Illite	18.0	12.2				1.3(?)	1.8	33.3
Kaolinite	1.0	0.9					0.3	2.2
Quartz	12.2							12.2
Feldspar	6.6	1.8				1.6(?)		10.0
Moisture							0.3	0.3
Sub-total	67.5	27.4				2.9(?)	4.6	102.4

Minerals that might be present

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	H_2O	TOTAL
Corundum and/or Rutile		0.1						0.1
TOTAL	67.5	27.5				2.9(?)	4.6	102.5

MINERALOGIC COMP. (X-ray)

Pyrophyllite	35
Illite	35
Kaolinite	5
Quartz	10
Feldspar	10
	95

CHEM. COMP. (Wet analysis)

SiO2	67.47
Al2O3	27.50
Fe2O3	Tr.
CaO	Tr.
MgO	Tr.
H2O (110°)	0.34
I.L.	4.22
	99.53
K2O	2.9 (?)
	102.4

TABLE 6

SAMPLE # INV 39

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	H₂O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
Pyrophyllite	28.6	12.1					2.1	42.8	Pyrophyllite 35	SiO2 65.99
Illite	20.3	11.5				1.4(?)	1.8	35.0	Illite 35	Al2O3 27.29
Kaolinite	2.3	2.0					0.7	5.0	Kaolinite 5	Fe2O3 1.60
Quartz	8.2							8.2	Quartz 5	CaO Tr.
Feldspar	6.6	1.7				1.6(?)		9.9	Feldspar 10	MgO Tr.
Moisture							0.3	0.3	90	H2O(110°) 0.34
Sub-total	66.0	27.3				3.0(?)	4.9	101.2		I.L. 4.73
Minerals that might be present										99.95
Goethite			1.6				0.2	1.8		K2O 3.0(?)
										103.0
TOTAL	66.0	27.3	1.6			3.0(?)	5.1	103.0		

SAMPLE # INV 40

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	H₂O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
Pyrophyllite	21.3	9.1					1.6	32.0	Pyrophyllite 30	SiO2 62.19
Illite	21.7	15.2				1.6(?)	2.0	40.5	Illite 15	Al2O3 32.03
Kaolinite	7.0	5.9					2.1	15.0	Kaolinite 5	Fe2O3 Tr.
Quartz	5.6							5.6	Quartz 5	CaO Tr.
Feldspar	6.6	1.8				1.6(?)		10.0	Feldspar 10	MgO Tr.
Moisture							0.3	0.3	90	H2O(110°) 0.26
Sub-total	62.2	32.0				3.2(?)	6.0	103.4		I.L. 5.73
										100.21
										K2O 3.2(?)
										103.4
TOTAL	62.2	32.0				3.2(?)	6.0	103.4		

SAMPLE # INV 41

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	H₂O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
Pyrophyllite	28.0	11.9					2.1	42.0	Pyrophyllite 35	SiO2 60.83
Illite	17.9	12.2				1.4(?)	3.1	34.6	Illite 35	Al2O3 27.81
Kaolinite	2.3	2.0					0.7	5.0	Kaolinite 5	Fe2O3 2.71
Quartz	9.3							9.3	Feldspar 10	CaO Tr.
Feldspar	3.3	0.9				0.8(?)		5.0	Quartz 5	MgO Tr.
Moisture							0.5	0.5	90	H2O(110°) 0.54
Sub-total	60.8	27.0				2.2(?)	6.4	96.4		I.L. 6.83
Minerals that might be present										98.72
Limonite			2.7				0.6	3.3		K2O 2.2(?)
Gibbsite			0.8				0.4	1.2		100.9
TOTAL	60.8	27.8	2.7			2.2(?)	7.4	100.9		TABLE 7

SAMPLE # INV 44

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	H₂O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
Pyrophyllite	16.7	7.1					1.2	25.0	Pyrophyllite 25	SiO2 57.56
Illite	18.9	12.9			0.7	1.4(?)	1.8	35.7	Illite 25	Al2O3 34.13
Kaolinite	9.3	7.9					2.8	20.0	Kaolinite 25	Fe2O3 1.96
Quartz	9.4							9.4	Quartz 10	CaO Tr.
Feldspar	3.3	0.9				0.8(?)		5.0	Feldspar 10	MgO 0.72
Moisture							0.5	0.5	95	H2O(110°) 0.45
Sub-total	52.6	28.8			0.7	2.2(?)	6.3	95.6		I.L. 6.27
Minerals that might be present										101.09
Hematite			2.0					2.0		K2O 2.2(?)
Cliachite		4.6					0.4	5.0		103.3
Corundum and/or Rutile		0.7						0.7		
TOTAL	52.6	34.1	2.0		0.7	2.2(?)	6.7	103.3		

SAMPLE # INV 45

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	H₂O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
Pyrophyllite	23.4	9.9					1.7	35.0	Pyrophyllite 30	SiO2 62.52
Illite	24.0	16.2			0.7	1.8(?)	2.2	44.9	Illite 30	Al2O3 32.07
Kaolinite	2.3	2.0					0.7	5.0	Kaolinite 10	Fe₂O₃ Tr.
Quartz	5.6							5.6	Quartz 5	CaO Tr.
Feldspar	7.2	1.9				1.7(?)		10.8	Feldspar 15	MgO 0.73
Moisture							0.5	0.5	90	H2O(110°) 0.51
Sub-total	62.5	30.0			0.7	3.5(?)	5.1	101.8		I.L. 4.75
Minerals that might be present										100.58
Cliachite		1.8					0.2	2.0		K2O 3.5(?)
Corundum and/or Rutile		0.3						0.3		104.1
TOTAL	62.5	32.1			0.7	3.5(?)	5.3	104.1		

SAMPLE # INV 46

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	H₂O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
Pyrophyllite	32.8	13.9					2.5	49.2	Pyrophyllite 40	SiO2 65.38
Illite	15.9	10.8			0.6	1.2(?)	1.5	30.0	Illite 40	Al2O3 28.32
Kaolinite	4.0	3.4					1.2	8.6	Kaolinite 10	Fe2O3 Tr.
Quartz	12.7							12.7	Quartz 5	CaO Tr.
Moisture							0.2	0.2	95	MgO 0.57
Sub-total	65.4	28.1			0.6	1.2(?)	5.4	100.7		H2O(110°) 0.21
Minerals that might be present										I.L. 5.14
Corundum and/or Rutile		0.2						0.2		99.62
										K2O 1.2
										100.8
TOTAL	65.4	28.3			0.6	1.2(?)	5.4	100.9		TABLE 8

SAMPLE # INV 52

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	H₂O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
							1.5	30.0	Pyrophyllite 30	SiO2 58.03
Pyrophyllite	20.0	8.5							Illite 30	Al2O3 33.25
Illite	25.7	15.9		0.7	0.3	1.5(?)	2.0	46.1	Kaolinite 15	Fe2O3 00.80
Kaolinite	5.7	4.8					1.7	12.2	Feldspar 10	CaO 0.75
Feldspar	6.6	1.8			1.6(?)			10.0	Gibbsite 10	MgO 0.30
Gibbsite		1.9					1.0	2.9	95	H2O(110°) 0.84
Moisture							0.9	0.9		I.L. 6.72
	58.0	32.9		0.7	0.3	3.1(?)	7.1	102.1		100.19
Sub-total										K2O 3.1(?)
Minerals that might be present								0.4		103.3
Corundum and/or	0.4									
Rutile								0.8		
Hematite			0.8							
TOTAL	58.0	33.3	0.8	0.7	0.3	3.1(?)	7.1	103.3		

SAMPLE # INV 78

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	H₂O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
							2.0	40.0	Pyrophyllite 35	SiO2 59.31
Pyrophyllite	26.7	11.3							Illite 35	Al2O3 32.72
Illite	18.6	12.6		0.7		1.4(?)	1.5	34.8	Kaolinite 10	Fe2O3 1.04
Kaolinite	6.4	5.4					1.9	13.7	Feldspar 10	CaO 0.67
Feldspar	7.6	2.0			1.9(?)			11.5	90	MgO Tr.
Moisture							0.4	0.4		H2O(110°) 5.41
Sub-total	59.3	31.3		0.7		3.3(?)	5.8	100.4		99.56
Minerals that might be present										K2O 3.3(?)
Hematite			1.0					1.0		102.9
Corundum and/or										
Rutile		1.4						1.4		
TOTAL	59.3	32.7	1.0	0.7		3.3(?)	5.8	102.8		

SAMPLE # INV 79

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	H₂O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
							1.7	35.0	Pyrophyllite 35	SiO2 59.82
Pyrophyllite	23.4	9.9							Illite 35	Al2O3 33.00
Illite-	21.7	18.3				1.7(?)	2.0	43.7	Kaolinite 5	Fe2O3 Tr.
Kaolinite	4.7	3.9					1.4	10.0	Feldspar 10	CaO Tr.
Feldspar	3.3	0.9			0.8(?)			5.0	Quartz 5	MgO Tr.
Quartz	6.7							6.7	90	H2O(110°) 0.50
Moisture							0.5	0.5		I.L. 5.08
								100.9		98.40
										K2O 2.5(?)
										100.9
TOTAL	59.8	33.0				2.5(?)	5.6			

SAMPLE # INV 80

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	H₂O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
Pyrophyllite	26.7	11.3					2.0	40.0	Pyrophyllite 35	SiO2 57.82
Illite	17.4	14.7				1.4(?)	1.6	35.1	Illite 35	Al2O3 34.13
Kaolinite	6.3	5.3					1.9	13.5	Kaolinite 5	Fe2O3 Tr.
Feldspar	7.4	2.0			1.8(?)			11.2	Feldspar 10	CaO Tr.
Corundum		0.8						0.8	Corundum 5	MgO Tr.
Moisture							0.6	0.6	90	H2O(110°) 0.56
										I.L. 5.55
										98.06
										K2O 3.2(?)
										101.3
TOTAL	57.8	34.1				3.2(?)	6.1	101.2		

SAMPLE # INV 81

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	H₂O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
Pyrophyllite	29.8	12.6					2.2	44.6	Pyrophyllite 40	SiO2 62.07
Illite	23.4	13.2				1.6(?)	1.9	40.1	Illite 40	Al2O3 30.64
Kaolinite	2.3	2.0					0.7	5.0	Kaolinite 5	Fe2O3 Tr.
Feldspar	6.6	1.8			1.6(?)			10.0	Feldspar 10	CaO Tr.
Moisture							0.6	0.6	95	MgO Tr.
Sub-total	62.1	29.6				3.2(?)	5.4	100.3		H2O 0.55
Mineral that might be present										I.L.(110) 4.82
Corundum and/or										98.08
Rutile		1.0						1.0		K2O 3.2
										101.3
TOTAL	62.1	30.6				3.2(?)	5.4	101.3		

SAMPLE # INV 114

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	H₂O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
Pyrophyllite	16.7	7.1					1.2	25.0	Pyrophyllite 25	SiO2 59.60
Illite	22.4	19.0	0.2			1.8(?)	2.0	45.4	Illite 45	Al2O3 32.11
Kaolinite	4.6	4.0					1.4	10.0	Kaolinite 5	Fe2O3 Tr.
Quartz	15.9							15.9	Quartz 10	CaO 0.18
Corundum		2.0						2.0	Corundum 5	MgO Tr.
Moisture							0.6	0.6	90	H2O(110°) 0.61
										I.L. 4.62
										97.12
										K2O 1.8(?)
										98.9
TOTAL	59.6	32.1	0.2			1.8(?)	5.2	98.9		

TABLE 9

TABLE 10

SAMPLE # INV 115

	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	H2O	TOTAL
Pyrophyllite	20.0	8.5					1.5	30.0
Illite	17.6	9.9			1.2(?)	1.3		30.0
Kaolinite	5.9	5.1					1.8	12.8
Quartz	14.5							14.5
Feldspar	6.6	1.8				1.6(?)		10.0
Corundum		2.2						2.2
Moisture							0.5	0.5
TOTAL	64.6	27.5			2.8(?)	5.1		100.0

MINERALOGIC COMP. (X-ray)

Pyrophyllite	30
Illite	30
Kaolinite	10
Quartz	10
Feldspar	10
Corundum	5
	95

CHEM. COMP. (Wet analysis)

SiO2	64.58
Al2O3	27.46
Fe2O3	TR.
CaO	Tr
MgO	Tr.
H2O(110°)	0.53
I.L.	4.56
	97.13
K2O	2.8(?)
	99.9

SAMPLE # INV 134

	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	H2O	CO2	TOTAL
Pyrophyllite	14.6	6.2					1.1		21.9
Illite	14.4	8.1			1.0(?)	1.5			25.0
Kaolinite	11.6	9.9					3.5		25.0
Feldspar	3.3	0.9				0.8(?)			5.0
Montmorillon.	5.4	1.9		1.1			2.6		11.0
Moisture							0.2		0.2
Minerals that might be present									
Quartz	0.1								0.1
Limonite			1.6				0.4		2.0
Dolomite				0.4	0.3		0.6		1.3
Clichite		4.0					0.5		4.5
Calcite				3.4				2.7	6.1
TOTAL	49.4	31.0	1.6	4.9	0.3	1.8(?)	9.8	1.3	102.1

MINERALOGIC COMP. (X-ray)

Pyrophyllite	25
Illite	25
Kaolinite	25
Feldspar	10
Montmorillon.	5
	90

CHEM. COMP. (Wet analysis)

SiO2	49.36
Al2O3	31.03
Fe2O3	1.64
CaO	4.90
MgO	0.25
H2O(110°)	1.86
I.L.	11.25
	100.29
K2O	1.8(?)
	102.1

SAMPLE # INV 135

	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	H2O	CO2	TOTAL
Pyrophyllite	18.8	7.9					1.4		28.1
Illite	34.5	19.5	1.7		2.4(?)	3.6			61.7
Feldspar	4.8	1.3				1.1(?)			7.2
Corundum		1.7							1.7
Moisture							1.5		1.5
Dolomite				0.8	0.6		1.2		2.6
Sub-total	58.1	30.4		2.5	0.6	3.5(?)	6.5	1.2	102.8
Mineral that might be present									
Hematite			1.5						1.5
TOTAL	58.1	30.4	1.5	2.5	0.6	3.5(?)	6.5	1.2	104.3

MINERALOGIC COMP. (X-ray)

Pyrophyllite	20
Illite	50
Feldspar	15
Corundum	5
Dolomite	5
	95

CHEM. COMP. (Wet analysis)

SiO2	58.06
Al2O3	30.39
Fe2O3	1.48
CaO	2.49
MgO	0.58
H2O(110°)	1.51
I.L.	6.15
	100.66
K2O	3.5(?)
	104.2

TABLE 11

SAMPLE # INV 136

	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	H2O	CO2	TOTAL
Pyrophyllite	16.7	7.1					1.2		25.0
Illite	20.4	9.9	1.0		0.2	1.4(?)	1.5		34.4
Kaolinite	2.3	2.0					0.7		5.0
Feldspar	10.0	2.6				2.4(?)			15.0
Dolomite				0.3	0.2			0.5	1.0
Quartz	19.6								19.6
Moisture							0.7		0.7
Sub-total	69.0	21.6		1.3	0.4	3.8(?)	4.1	0.5	100.7
Minerals that might be present:									
Hematite			1.4						1.4
TOTAL	69.0	21.6	1.4	1.3	0.4	3.8(?)	4.1	0.5	102.1

MINERALOGIC COMP. (X-ray)

Pyrophyllite	25
Illite	25
Kaolinite	5
Feldspar	15
Dolomite	5
Quartz	10
	85

CHEM. COMP. (Wet analysis)

SiO2	69.02
Al2O3	21.61
Fe2O3	1.36
CaO	1.32
MgO	0.45
H2O(110°)	0.73
I.L.	3.86
	98.35
K2O	3.8(?)
	102.2

SAMPLE # INV 68

	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	H2O	TOTAL
Pyrophyllite	23.4	9.9					1.8	35.1
Illite	12.2	9.5		0.8	0.7	1.0(?)	1.3	25.5
Kaolinite	7.0	5.9					2.1	15.0
Quartz	20.0							20.0
Goethite			3.2				0.4	3.6
Moisture							1.8	1.8
TOTAL	62.6	25.3	3.2	0.8	0.7	1.0(?)	7.4	101.0

MINERALOGIC COMP. (X-ray)

Pyrophyllite	25
Illite	5
Kaolinite	5
Quartz	20
Goethite	5
	60

CHEM. COMP. (Wet analysis)

SiO2	62.60
Al2O3	25.30
Fe2O3	3.19
CaO	0.84
MgO	0.68
H2O(110°)	1.76
I.L.	5.61
	99.98
K2O	1.0(?)
	101.0

SAMPLE # API 47

	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	H2O	TOTAL
Pyrophyllite	19.2	8.1					1.4	28.7
Muscovite	6.1	5.2				1.3	0.5	13.1
Kaolinite	3.8	3.2					1.0	8.0
Quartz	48.3							48.3
Moisture						0.1		0.1
Other oxides							1.3	1.3
TOTAL	77.4	16.5				1.3	3.0	99.5

CHEM. COMP. (Wet analysis)

SiO2	77.43
Al2O3	16.51
Fe2O3	0.47
FeO	----
MgO	0.05
CaO	0.41
Na2O	0.22
K2O	1.26
H2O+	2.87
H2O-	0.11
TiO2	0.18
MnO	----
	99.51

TABLE 12

SAMPLE #INV 1103	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	H_2O	SO_3	TOTAL	MINERALOGIC COMP. (X-ray)		CHEM. COMP. (Wet analysis)	
Pyrophyllite	16.7	7.1						1.2	25.0	Pyrophyllite	25%	SiO_2	51.31
Illite	17.6	11.4		0.8	1.40	2.6			33.8	Illite	35	Al_2O_3	32.96
Kaolinite	7.0	5.9					2.1		15.0	Kaolinite	10	Fe_2O_3	1.57
Quartz	10.0								10.0	Quartz	10	CaO	0.88
Gypsum			0.9				0.7	1.7	3.3	Gypsum	10	MgO	0.79
Bohemite		8.5					1.5		10.0	Bohemite	10	SO_3	1.73
Moisture							2.2		2.2		100	H_2O(110)	8.42
Minerals that might be present												I.L.	99.84
Limonite		1.6					0.3		1.9			K_2O(?)	1.4
													101.2
TOTAL	51.3	32.9	1.6	0.9	0.8	1.40	10.6	1.7	101.2				

SAMPLE #	Si_2O_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	H_2O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
TOTAL										

SAMPLE #	Si_2O_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	H_2O	TOTAL	MINERALOGIC COMP. (X-ray)	CHEM. COMP. (Wet analysis)
TOTAL										

TABLE 13

Differential Thermal Analysis.- The curves we give on Tables 14, 15 and 16 were obtained in INVESTI's instrument. This instrument, manufactured by Harrop, is equipped with a recorder for rate of temperatures rise and an X-Y recorder for the difference of temperature against temperature ("dt" versus "t"). It has three kilns, one of which has platinum windings for high temperature work and the others nickel-chrome windings.

This instrument has certain idiosyncracies. As can be seen on the graphs, it records temperatures against a non-linear scale. It has the vagary of producing a sharp exothermic peak at about 50°C, and also sometimes plots graphs with a certain amount of electronic "noise" (wavy instead of smooth plots). In the latter case the graphs were smoothed out in tracing, but except for this they are presented here as recorded by the instrument.

The heating rate used in all the graphs was 12°C per minute. The instrument keeps this rate constant within less than 10%.

The graphs given on Table 14 are all of Bobare-type clays. On Table 15 the first four on the top of the page are also of Bobare-type clays (INV 114, 134, 135 and 136) but the other four on this table (INV 68, 66, 64 and 61) are of Pegón-type clays. Of the graphs given on Table 16, INV 59 is of Pegón-type, INV 1103 belongs to a clay from Eastern Venezuela that in our opinion is also pyrophyllitic and which we discuss in the text elsewhere.

Since talc is a very close relative of pyrophyllite, we have included for the purposes of comparison a graph of "welders' chalk" which we started studying under the impression that it was pyrophyllite. We also have included a differential thermal curve of API No. 49, supplied by Ward, supposedly exactly the same material as the original API No. 49. Finally, so that the reader may appreciate the qualities of the instrument we have included the familiar curve of kaolinite taken at half the scale of the other graphs because of lack of space. The sample for this curve is commercial "china clay".

According to Mackenzie, 1957, pyrophyllite gives a shallow endothermic effect from 650°C to 850°C with the peak at about 775°C. As can be seen in Table 16 the pyrophyllite of sample API No. 49 gives a very shallow endothermic effect with the peak at about 820°C. On the other hand, the Bobare-type of white clay gives a shallow endothermic peak around 700°C (excepting INV 44, which does not give this effect at all). Therefore it appears that the pyrophyllite of the white clays has a lower dehydroxylation temperature than that assigned to regular pyrophyllite. We are at a loss to explain this lower temperature and all we can say is that apparently in the process of erosion and sedimentation the structure of this mineral was altered so that the hydroxyl is held more loosely.

The intensity of the peak around 580°C varies with the kaolinite content of the sample. So it is practically non-existent in INV 37, which has a kaolinite content of only 5%, and reaches maximum size in samples INV 44 and INV 134 which contain 25%.

As can be seen in Table 16 kaolinite gives a large, sharp peak around 980°C, generally ascribed to the formation of gamma alumina. In this region some of the white clays give a broad, shallow exothermic effect, particularly noticeable in INV 44 and INV 134, which might be due to the formation of gamma alumina. If such were the case, the broadness of the peak and its small size would indicate that the kaolinite present here is poorly crystallized. The main endothermic

DIFFERENTIAL THERMAL ANALYSIS

INV 34 INV 37 INV 40 INV 41 INV 44 INV 46 INV 52 INV 78

TABLE 14

DIFFERENTIAL THERMAL ANALYSIS

INV 114 INV 134 INV 135 INV 136 INV 68 INV 66 INV 64 INV 61

TABLE 15

40°C 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000° 1100°

INV 59 INV 1103 WELDER'S CHALK API 49 KAOLINITE TABLE 16

DIFFERENTIAL THERMAL ANALYSIS
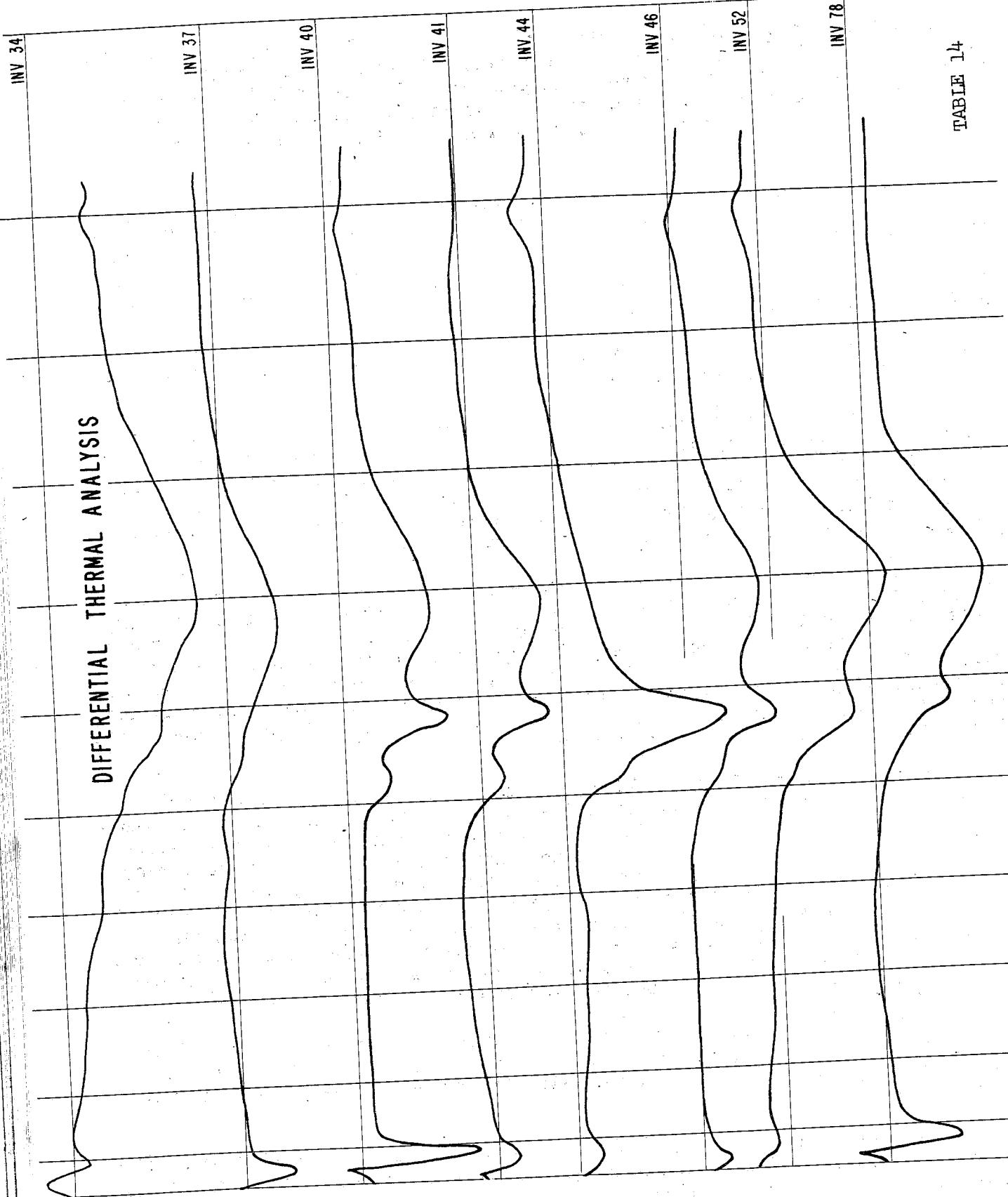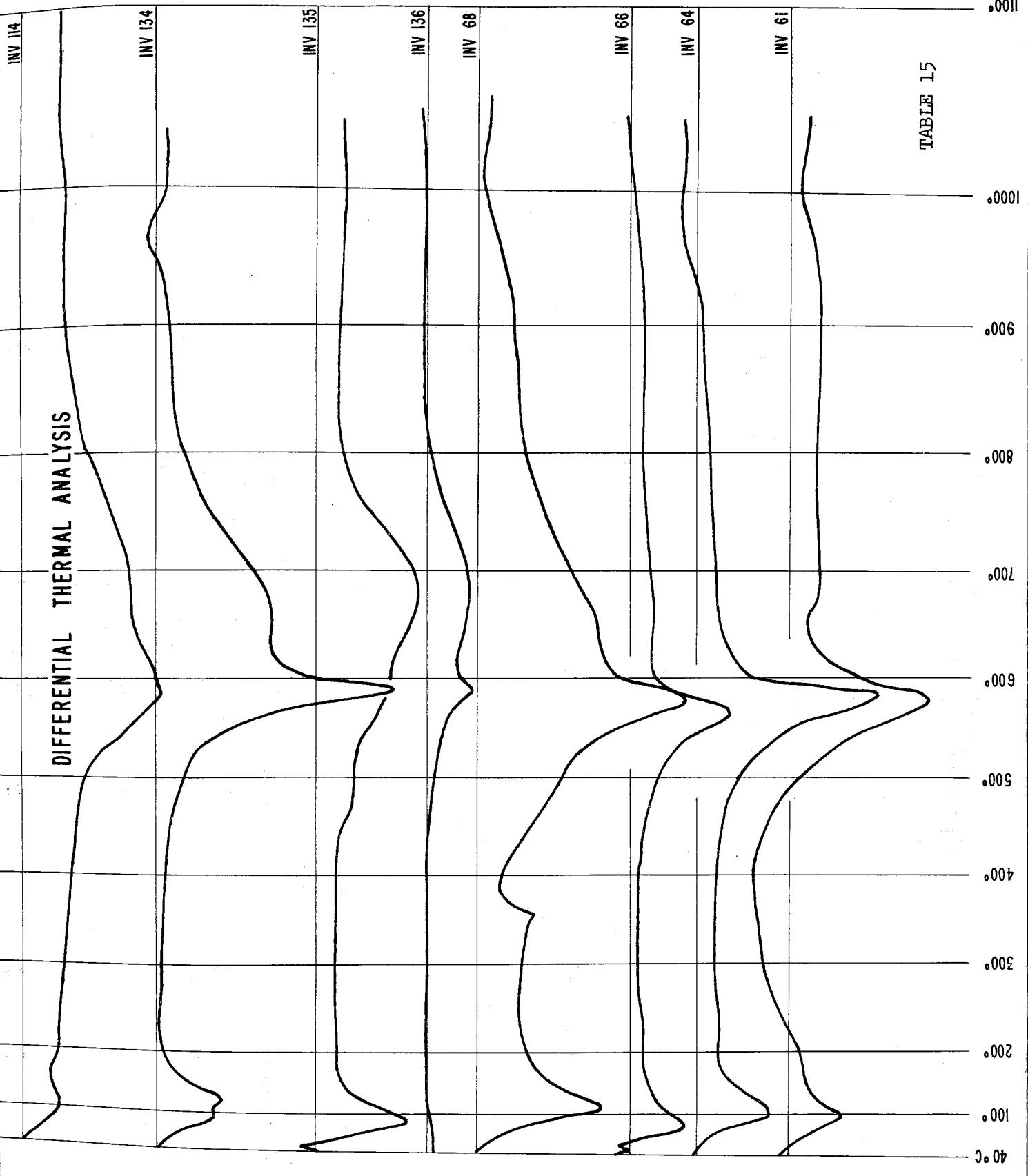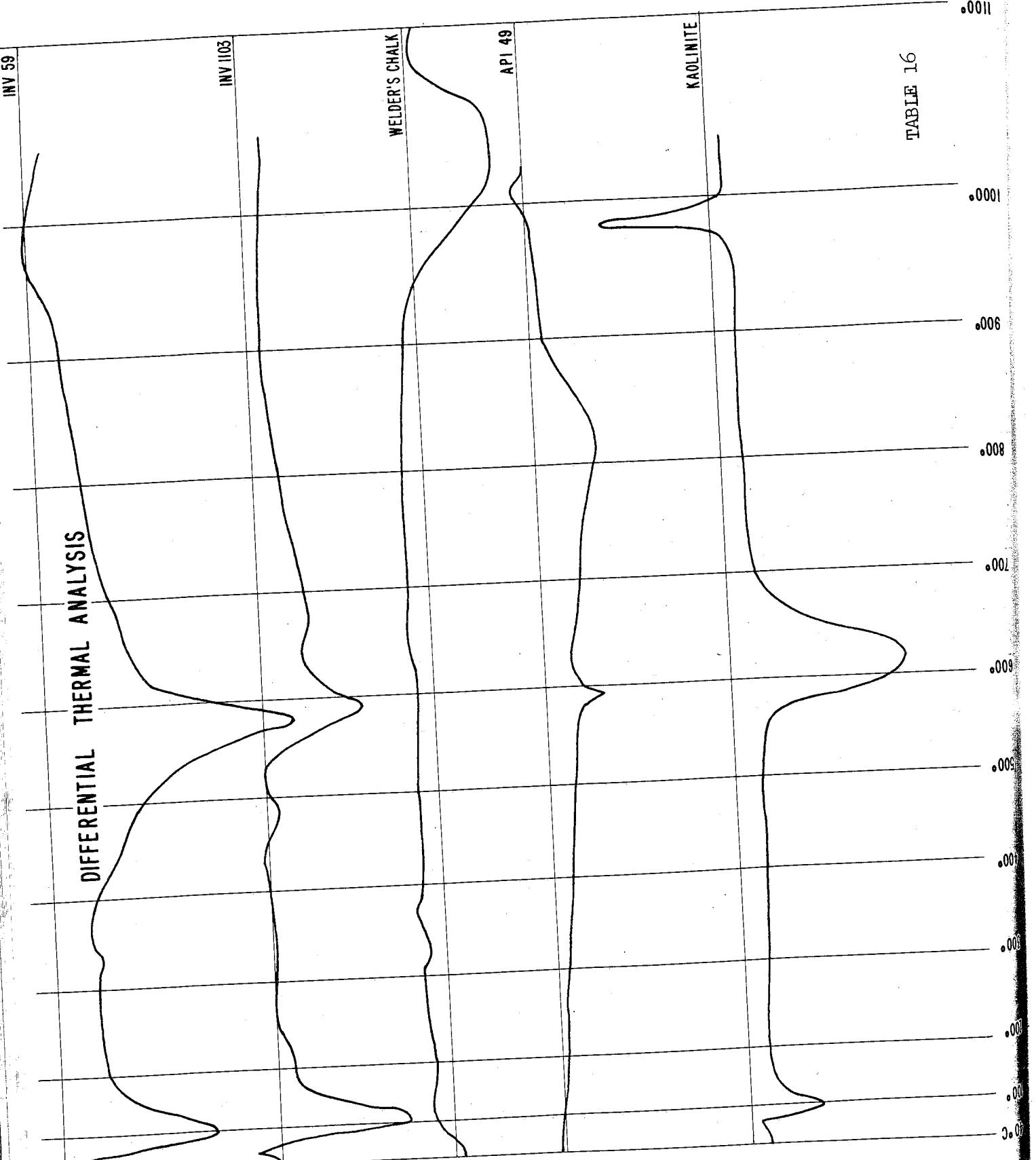
effect of this mineral coming at around 580°C rather than 610°-620°C (Table 16, "kaolinite") tends to confirm this idea. It is possible that our kaolinite was in the early stages of formation at the expense of feldspar when the process was stopped by burial of the sediments.

The endothermic effect around 100°C is due, of course, to the moisture being driven off. In sample INV 134 (Table 15) a double peak can be observed in this region which might be due to small amounts of montmorillonite present in this sample.

As we have mentioned before, we believe that the illite present here is almost a mica and as such would not leave any trace in the DTA curve. However, in samples INV 40, 41, 44, 46 and 52 (Table 14) there is an endothermic inflection around 520°C. We are not sure what may cause this inflection but it could be due to some incipient formation of illite (hydromica) even though the temperature seems a bit low for the dihydroxylation of this mineral.

THERMAL DATA

The vitrification temperature of these clays (both Bobare and Pegón-type) is cone 19 (1541°C). The melting point varies from cone 26 to cone 32 (1621°C to 1770°C). These comparatively high temperatures seem out of place in clays high in illite. However, we know from the chemical analyses that the illite involved is a low potassium one. This, coupled with the virtual absence of other fluxes, such as iron oxide and the presence of pyrophyllite contributes to give these clays their refractoriness.

PEGON-TYPE CLAYS

Chemical Composition.- The chemical composition of the Pegón-type white clays is very similar to that of the Bobare-type. The most importance difference is that they are very high in silica (Table 1 shows the quartz content as estimated from X-ray work). This high silica gives the chemical analysis a very high silica-alumina ratio, as can be seen on Table 17. Correcting this ratio for the quartz content as estimated from X-ray work we obtained an average value equal to that of the Bobare clays.

The iron content, which ranges from 0.96% to 3.19%, is much higher than in the Bobare-type clays. At least in one place, in the Curigua mine, it could be seen clearly that most of the iron must have been due to later infiltration of ferruginous solutions, since the cracks in the clays were stained a reddish color. At this mine the exploitation is done by hand and the clay breaks up in large lumps. According to what I was told there, if the stained parts are shaved off these lumps, the iron content is reduced considerably.

On the average, the calcium and magnesium content of these clays is slightly higher than the Bobare-type. But even then the content is low, never being much higher than one percent.

Due to the high quartz content of these clays, the ignition loss is also small.

X-Ray Diffraction.- The patterns of most of these clays are of very low intensity. On this feature alone they can be distinguished from the Bobare type. However, this rule does not hold true always and at times one obtains patterns indistin- guishable from the Bobare type. Of course, a number of factors influence the intensity of the peaks of a pattern. In this particular case we feel the low intensity is due mostly to poor crystallinity of the minerals involved and per- haps also the presence of amorphous material. Both the kaolinite and the illite have broad-based and round-topped peaks. The quartz and the pyrophyllite give sharp peaks although the latter has an intensity lower than the Bobare-type clays. Therefore when we apply to these clays the quantitative criteria we use in our work (Rivero Palacio, 1964b) we find that the sum of the components never goes much over 50%. Then when we try to make a mineralogic interpretation of chemical analyses it is necessary to increase the quantitative estimates of the X-ray work so much that the interpretation is meaningless. This is the reason why we give only one interpretation of a chemical analysis on Table 12 (INV 68).

The kaolinite content of these clays is much higher than the Bobare-type clays and feldspar is absent.

Differential Thermal Analysis.- In Table 15 we give four curves for these clays (INV 61, 64, 66 and 68) and in Table 16 we give another curve (INV 59). As can be seen there, the pyrophyllite very often does not show any trace in these curves. INV 68 and 61, however, show a small inflection at around 680°C probably due to this mineral. The endothermic effect of kaolinite is strong but the gamma alumina exothermic effect is barely noticeable.

The endothermic effect around 350°C in INV 68 and INV 59 might be due to the presence of gibbsite. If so, no trace of this mineral is found in the X-ray pattern. Furthermore, the very low ignition loss of these clays makes unlikely the presence of gibbsite in appreciable amounts. Goethite could cause this inflection: small amounts of it are detectable in the X-ray pattern of INV 68 but none in INV 59.

The difference between these two types of clays can be summed up as fol- lows:

Pegon Type	Bobare Type
High quartz content	Quartz content low to absent
Higher iron content	
Low intensity patterns	High intensity patterns
Feldspar absent	Small amounts of feldspar common
Kaolinite content noticeable	Kaolinite low to absent
Diffuse reflections	Sharp reflections
Good plasticity	Not plastic
Endothermic effect at about 700°C seldom present	Endothermic effect at about 700°C nearly always present

TABLE # 17

PEGON FM. WHITE CLAYS
CHEMICAL ANALYSIS

	INV 62	INV 63	INV 64	INV 65	INV 66	INV 67	INV 68	INV 69	INV 59	INV 60	INV 61	INV 142	INV 143	INV 144	INV 145	INV 140	INV 141
	QUIBOR-SANARE ROAD				MINA CURIGUA		CASERIO EL YESO	CASERIO YAY					Q.PLANCONES QUIBOR-CUBIRO ROAD				MINA EL TANQUE
Si O2	71.51	69.64	79.02	69.57	65.22	66.37	62.60	75.78	70.47	69.16	69.99	73.18	77.11	74.86	79.63	63.11	78.53
Al2 O3	18.90	21.10	12.31	21.78	26.04	23.62	25.30	15.72	19.32	22.67	22.22	17.27	15.87	18.91	13.85	27.55	14.58
Fe2 O3	3.19	1.76	2.23	1.68	1.20	1.04	3.19	0.96	3.11	1.48	2.00	2.95	1.04	1.36	0.88	1.12	1.52
Ca O	0.21	0.27	0.32	0.20	0.34	0.90	0.84	0.77	0.32	0.33	0.15	0.70	0.57	0.45	1.13	0.22	0.67
Mg O	1.16	0.68	0.55	0.31	0.76	0.51	0.68	0.50	0.72	0.76	1.04	0.42	0.50	0.44	Tr.	0.48	0.38
H2O (110°C)	1.41	1.01	1.23	0.83	0.88	1.51	1.76	0.83	1.05	1.00	0.67	1.08	0.94	0.92	0.56	1.64	0.66
H2O (1000°C)	4.90	4.42	3.64	4.58	5.53	5.53	5.61	4.68	4.93	6.61	6.32	3.76	3.50	3.77	3.50	6.51	3.34
TOTAL	101.28	98.88	99.30	98.95	99.97	99.48	99.98	99.24	99.92	102.01	102.39	99.36	99.53	100.71	99.95	100.63	96.68

AVERAGE

SILICA - ALUMINA RATIO OF CLAY MINERALS

	INV 62	INV 63	INV 64	INV 65	INV 66	INV 67	INV 68	INV 69	INV 59	INV 60	INV 61	INV 142	INV 143	INV 144	INV 145	INV 140	INV 141	AVERAGE
AS COMPUTED FROM ANALYSIS	6.4	5.6	10.9	5.4	4.3	4.8	4.2	8.2	6.2	5.2	5.3	7.2	8.2	6.7	9.7	3.9	9.1	6.5
CORRECTED FOR QTZ CONTENT	3.2	-	4.4	3.9	2.3	1.9	2.9	2.8	-	2.5	-	3.7	2.9	3.1	7.8	2.6	3.3	3.4

Comparison of the white clays with the pyrophyllitic schists of North Carolina.-
It was our intention to discuss here pyrophyllitic rocks from elsewhere in the
world to picture clearly the type of rock that might have been the source of
the white clays. However, due to shortcomings in our library facilities we only
can discuss the mineralogy of the pyrophyllitic schists of North Carolina.

These pyrophyllitic schists are located in what is locally known as the
Deep River Talc Belt, which forms part of the Carolina Slate Belt of Precambrian
age extending across the Carolinas. The pyrophyllitic deposits resulted from the
alteration of an acid volcanic tuff of rhyolitic and dacitic composition (Stucky,
1928).

Kerr et al., 1949, in API Research Project No. 49, Clay Mineral Standards,
collected three samples of pyrophyllitic material near Robbins, N.C. numbered
47, 48 and 49. In the same work a complete chemical analysis is given of sample
No. 47.

Molloy and Kerr, 1961, give a diffractometer pattern of sample API No. 47.
Combining the diffractometer pattern and the chemical analysis (Table 12) we obtain
the following composition:

Pyrophyllite	28.7%
Muscovite	13.1%
Kaolinite	8.0%
Quartz	48.3%
Moisture	0.1%
Other oxides	1.3%
	99.5%

To arrive at this composition we had to use a muscovite with 10% potassium
oxide and 3.7% water content instead of the 11.8% and 4.5% respectively called
for by the formula. The kaolinite water content was assumed to be 12.1% instead
of the 13.9% derived from the formula. The lower water content of muscovite and
kaolinite was assumed to be able to come out even with the chemical analysis
instead of having an excess of 0.6%. The lower potassium content was necessary
to obtain a higher quantity of muscovite more in accord with the relative inten-
sities of the X-ray pattern. With these modifications we arrive at a quantitative
composition that agrees well, in our estimation, with the relative intensities
shown in the X-ray patterns.

Molloy and Kerr, 1961, suggest that the reflection at 7A° of API No. 47
might be due to dickite. Although they do not give any reasons for this sugges-
tion, it seems probable that they felt that in a schist the presence of dickite
would be more likely than kaolinite. Our D.T.A. curve of API No. 49 (Table 16)
does not bear this suggestion out. The endothermic effect comes around 580°C
which is too low a temperature for dickite. Furthermore, the sharpness of this
peak does not suggest a mineral of the kaolinite group. It reminds one more of
the alpha-beta quartz inversion point. The exothermic effect around 1010°C
being of a rounded diffuse nature suggests again poorly crystallized kaolinite
and not dickite. The temperature, however, is somewhat high for the gamma
alumina phase.

Molloy and Kerr (op. cit.) in the text of their paper give the opinion that
the content of pyrophyllite of sample API No. 47 is of 70% and that the impuri-
ties, quartz, muscovite and kaolinite amount to 30%. We cannot agree with this
estimate. Quartz alone, in our estimation, amounts to about half the sample and
if we include muscovite and kaolinite the total is about 70% "impurities" and a
little less than 30% for pyrophyllite. Moreover 70% content of pyrophyllite would
require 3.5% water and the chemical analysis only gives 2.9%. Similarly, 70%
pyrophyllite would require 19.8% of alumina and the total alumina given in the
chemical analysis is 16.5%.

Our computed composition of the schist is very similar to that of the
Venezuelan white clays except that the pyrophyllitic schist presumably contains
muscovite, is high in quartz and does not seem to have any feldspar whereas the
white clays presumably contain illite, are low in quartz and do have feldspar.
Barring these differences, the rest is very similar; particularly to those spe-
cimens of white clays with low illite content.

The similarity of composition of these two rocks, one metamorphic and the
other sedimentary, is very strong. It is so strong in fact that one cannot help
but wonder what will happen when that highly imaginative breed of scientist, the
student of Lara geology, comes to realize this fact, since it is not fashionable
to talk about the geology of Lara without invoking the term "allochthonous block".
If the reader will excuse a facetious note, I suspect that the result will be to
postulate that the white clays of Lara are an allochthonous block, derived from
sediments which in turn originated from the North Carolina Precambrian: a block
of presumably Cretaceous age that arrived in Venezuela as a submarine slide dur-
ing the Tertiary Era.

PYROPHYLLITIC CLAYS FROM ELSEWHERE IN VENEZUELA

Rivero Palacio, 1963 (p. 207) discusses the presence of pyrophyllite in
Recent clays from the Samán de Apure-Arismendi-El Baúl region of central
Venezuela.

In Rivero Palacio, 1964b, the presence of pyrophyllite is described in
black clays of Middle Eocene age (Botucal Member of the Morán Formation) and
the conclusion is reached that these clays are derived from the Bobare white
clays.

In the latter paper (p. 296, 311) pyrophyllitic clays are discussed from
N.W. Portuguesa in the Paleocene Trujillo Formation and in Rivero Palacio, 1962a
(p. 286), from the same formation in the State of Lara near Guárico.

From the Casupal Formation in the State of Falcón, we have two samples
(INV 101 and 102) which contain very small amounts of pyrophyllite. That is to
say we only observe one very small reflection which could be the third order of
the basal reflection of pyrophyllite. This reflection has a spacing of
3.07Å. From the Pozón Formation in the same state, samples INV 209 and 210
also contain small amounts of pyrophyllite. Sample 209 exhibits five orders of
reflections, all very small and sample 210 shows first and third order reflec-
tions only. The presence of pyrophyllite in these two samples is well establish-
ed. Both these formations, according to the Stratigraphic Lexicon of Venezuela,
range in age from Upper Oligocene to Lower Miocene.

These four samples come from the Río Tocuyo basin. The headwaters of this river, today, are in areas of white clays. The presence of pyrophyllite in these sediments seems to indicate that some of the components of these clays were derived from the white clays of Lara which in turn indicates similarity of the modern drainage to the Miocene-Oligocene drainage. However, the bulk of the sediments of the post-Eocene of Falcón, being highly kaolinitic, could not have been derived from the white clay areas, which are high in illite and very low in kaolinite.

As mentioned in Rivero Palacio, 1964b, the Eocene towards the north of Lara and in south Falcón and Eastern Zulia is very kaolinitic. These beds could be a possible source for the post-Eocene of Falcón.

From the Paria Peninsula in the State of Sucre, we have examined one sample, INV 1103, that contains pyrophyllite in significant amounts. This sample comes from 21.4 Km. east of Yaguaraparo towards Güiria (see small location map). It was ascribed in the field to Recent (?). On Table 13 we give a mineralogical interpretation of the chemical analysis of this sample.

In the Paria Peninsula, according to González de Juana et al., 1965, lightly metamorphosed sediments are found with a thickness of over 4,500 meters underlying the also slightly metamorphosed Lower Cretaceous. The age of these sediments, presumably, is Jurassic or older. The presence of pyrophyllite in the younger sediments of this area indicates that the pyrophyllite-schist, source of the white clays, could be located here and a thorough search should be made to test this idea.

SUMMARY OF OCCURRENCE OF PYROPHYLLITIC CLAYS IN VENEZUELA

In order to give the reader a picture of not only the areal distribution of pyrophyllitic clays but their distribution in time as well, we will assume, for the purposes of this summary, that the Bobare-type white clays are of Cretaceous age (which is the personal opinion of this writer) and we will take for granted that Jefferson, 1964, is entirely correct in his assumption that the Pegón Formation is of post-Eocene age. Bearing these assumptions in mind the following situation obtains:

Pyrophyllitic clays are found throughout a large part of the Cretaceous of Lara both vertically and horizontally. For the most part the color of these clays is white or very light grey, but at times the color is dark.

In Lara and also in northwest Portuguesa, pyrophyllitic black clays are found of Middle Eocene age.

Also in Lara State, white clays are found of post-Eocene age (Pegón Formation).

In these four occurrences, the pyrophyllite is present in substantial amounts. Other occurrences are:

In the State of Falcón in buff colored clays of post-Eocene age, in very small amounts (Casupal and Pozón formations).

In recent sediments and soils of the State of Lara.

In recent sediments of the States of Portuguesa and Apure (about two hundred kilometers south of the area of white clays of Lara) in very small amounts.

In the Recent (?) of the Paria Peninsula in the State of Sucre, in considerable amounts.

All these occurrences of pyrophyllite, except the Paria Peninsula one, are genetically connected, in the opinion of this writer. They are all derived from the Cretaceous pyrophyllitic clays of Lara.

Under the assumed ages made for the white clays at the beginning of this chapter, the study of the DTA curves brings out an interesting relationship. The pyrophyllite of the North Carolina schist (API No. 49) shows the dehydroxylation temperature of this mineral to be around 810°C. The Bobare-type clays dehydroxylate at about 100°C lower and the Pegón-type clays quite frequently do not show any loss of heat where the dehydroxylation should occur, that is around 700°C. From this it seems that, if the post-Eocene clays were derived from the Cretaceous, every cycle of erosion has contributed to altering the structure of pyrophyllite so that the hydroxyl is held more and more loosely: in going from a schist to Bobare-type clays the temperature of dehydroxylation comes down 100°C and in going from Bobare- to Pegón-type the amount of heat lost is very small and quite frequently no appreciable loss of heat takes place.

REFERENCES

AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1960

X-Ray Powder Data File

_____, 1966

Standards

EVANOFF, J., ZOZAYA, D., ALCANTARA, C. and FERNANDEZ, J. C., 1957

Arcillas blancas en el Estado Lara
Bol. de Geol., vol. 4, no. 9, p. 83-93. (Venezuela).

GONZALEZ de JUANA, C., MUÑOZ, N. G., and VIGNALI, M., 1965

Reconocimiento geológico de la parte oriental de Paria
AVGMP, Bol. Inform., vol. 8, no. 9, p. 255-279.

GRIM, R. E., 1953

Clay mineralogy
McGraw-Hill Inc.

INVESTI, 1962-1966

Arcillas Industriales: 1, Bases técnicas (May, 1962); 2, Arcillas de Guayana (Oct., 1963); 3, Arcillas de Venezuela (Jul., 1966).

JEFFERSON, C. C., 1964

Post-Eoceno entre Quibor y Sanare, Estado Lara
AVGMP, Bol. Inform., vol. 7, no. 7, p. 219-223.

KERR, P. F. (Editor), 1949

Clay mineral standards
Amer. Petrol. Inst., Res. Proj. 49.

MOLLOY, M. W. and KERR, P. F., 1961

Diffractometer patterns of API reference clay minerals
Amer. Min., vol. 46, May-June, p. 583-605.

MACKENZIE, R. C. (Editor), 1957

The differential thermal investigation of clay
Mineralog. Soc., London.

MINISTERIO DE MINAS E HIDROCARBUROS, 1956

Stratigraphical Lexicon of Venezuela
Bol. de Geol., Spec. Publ. no. 1. (Venezuela).

RIVERO PALACIO, M., 1962a

Stratigraphic aspects of the mineralogy of some Venezuelan clays
AVGMP, Bol. Inform., vol. 5, no. 10, p. 283-295.

_____, 1962b

Notas mineralógicas de unas arcillas de Guayana
Univ. Centr. Ven., Geos, no. 8, p. 25-28.

_____, 1963

Mineralogía de algunas arcillas recientes de Venezuela
AVGMP, Bol. Inform., vol. 6, no. 7, p. 203-219.

_____, 1964a

Contribución al estudio de productos de desintegración de las rocas de la
    Cordillera de la Costa
Univ. Centr. Ven., Geos, no. 11, p. 27-34.

_____, 1964b

Mineralogy of the fine sediments of western Venezuela
AVGMP, Bol. Inform., vol. 7, no. 10, p. 289-314.

ROSS, C. and KERR, P. F., 1931

The kaolin minerals
U.S. Geol. Surv., Prof. Paper 165-E.

_____, 1934

Halloysite and allophane
U.S. Geol. Surv., Prof. Paper 185-G.

STUCKY, J. L., 1928

The pyrophyllite deposits of North Carolina
Nth. Carolina Dept. Conserv. and Dev., Bull. 37.