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CHEMICAL, PETROGRAPHIC, AND CERAMIC PROPERTIES OF FOUR CLAYS FROM THE DAKOTA FORMATION IN KANSAS

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ABSTRACT

Four commercial-type clays from the Dakota formation were studied by chemical and spectrochemical analysis, x-ray diffraction, electron and light microscopy, differential thermal analysis, mechanical analysis, and specific surface measurements. The basic chemical and physical properties so determined are compared with pH, apparent viscosity, and the results of empirical ceramic tests, including water of plasticity, shrinkage water, pore water, volume and linear shrinkage, fired color, pyrometric cone equivalent, saturation coefficient, apparent porosity, apparent and bulk specific gravity, and hardness at various fired temperatures.

Relationships between green properties and percentage water of plasticity and between green properties and specific surface are shown. The fired properties are shown to be more directly related to chemical and mineralogical composition. There is a correlation between percentage volume shrinkage on firing and percentage of fluxes contained in the clays. The basic properties explain the behavior of the clay materials when subjected to ceramic tests; and, conversely, easily obtained ceramic data can be used for rough determination of basic properties.

INTRODUCTION

The Dakota formation of central Kansas is the State's most important source of commercial fire clay for use in the manufacture of refractories, structural clay products, pottery (including porcelain, whiteware, stoneware, earthenware, and art ware), and similar high-grade products.

For the past 20 years the Ceramics Division of the State Geological Survey has been engaged in a detailed study of the ceramic properties of clays from the Dakota formation, and data on the behavior of more than 500 samples from about 200 localities have been collected. This work has resulted in the building of three potteries and two well-established brick plants with two more planned for construction by 1955.

Within recent years the application of powerful analytical tools, including differential thermal analysis, modern chemical and spectrochemical analysis, x-ray diffraction, and electron microscopy, to the study of clay materials has made possible much better understanding of clay mineralogy.

Variation between beds in the Dakota formation is pronounced; the deposits include kaolin, ball clay, plastic fire clay, siliceous fire clay, and highly siliceous fire clay. For the present report, four representative clays were selected for a study of the relations between their fundamental or basic properties (such as chemical and mineral composition and particle size and shape) and their ceramic behavior.

Correlations found between the basic properties of the clays and their behavior under ceramic tests are definite aids to the understanding of ceramic properties and to the application of the ceramic data to problems arising in the ceramic industry. Furthermore, the basic properties, alone or in connection with the ceramic data, can be used directly by the industry as a means of finding the cause of deviations in quality of the product, as a positive check on the quality of clays mined for ceramic use, or as a means of finding new deposits. These correlations between basic properties and the ceramic data also indicate that the easily obtained ceramic data can be used as a method for the rough determination of basic properties.

SAMPLING

The clay samples studied were obtained by channeling on the face of pits excavated for the specific purpose of clay sampling (Plummer and Romary, 1947). The samples contain only clean clay free from surface contamination and weathering.

The entire sample (60 to 70 pounds) obtained by this method was mixed thoroughly and pulverized in a 3-foot pan mill. A representative cut, a sufficient amount for the entire investigation, was taken from this sample and screened through a 20-mesh sieve. The over size was pulverized with a mortar and pestle until all the sample had passed the sieve. This cut of the sample was again split to obtain a relatively large sample for the ceramic tests and a smaller one for the basic studies involved.

The size fractions coarser than 8 microns, from 2 to 8 microns, and finer than 2 microns used in the chemical, x-ray, and differential thermal analyses were separated according to Stokes' law by repeated decantations from additional cuts of the four clay samples. It was necessary to treat sample O-5-6 with a 3 percent hydrogen peroxide solution prior to fractionation. This treatment, which was not necessary for the other three clays, may have caused slight modifications in the size fractions obtained from clay O-5-6 as compared to the other three.

METHODS USED

The four representative Dakota formation clays described were analyzed and examined by every means available in the Geological Survey laboratories. The fundamental or basic properties of the clays were determined by chemical and spectrochemical analyses of both the major and minor constituents, and by petrographic and mineralogical analyses. Pipette analysis, optical examination of thin sections, and electron micrographs were used to determine particle size and shape. Mineral composition was calculated from chemical composition, x-ray diffraction, and differential thermal analyses. The ceramic analyses are empirical tests of the clays under dynamic conditions of wetting and drying when unfired and under conditions of increasing temperature when fired.

The data are presented with a minimum of interpretation except for that needed for an understanding of the specific tests. Interpretations and correlations are discussed in a separate section of this report.

OCCURRENCE

STRATIGRAPHY

The clays described in this report were sampled from the Dakota formation, which is the lowest stratigraphic unit of the Gulfian Series of the Cretaceous System in Kansas. The relation of this formation to the underlying Kiowa shale and the overlying Graneros shale is shown in the following stratigraphic sequence.

- Cretaceous System
  - Gulfian Series
    - Graneros shale
    - Dakota formation
      - Janssen clay member
      - Terra Cotta clay member
  - Comanchean Series
    - Kiowa Shale

As shown above, the Dakota formation is subdivided into the Terra Cotta and Janssen clay members. The Terra Cotta member, which includes two-thirds to four-fifths of the total thickness of the Dakota formation, consists of massive clay, silt, and sandstone. The most conspicuous lithological feature of this member is widespread distribution of gray and red mottled clay. The Janssen member includes beds of lignite, gray to dark-gray clay, silt, and some shale and sandstone (Plummer and Romary, 1942; Moore and others, 1951).

LOCATION AND DESCRIPTION OF DEPOSITS

The four clays described were chosen from a sample file of about 1,400 Dakota formation clays. These particular clays were selected for study because they represent a wide range of types of commercially valuable clays. Clay EL-60-6 and clay O-5-6 represent two types most commonly recognizable in the Dakota formation in Kansas. Although the locations sampled were miles apart, the beds are closely related stratigraphically. Both occur in the Janssen member of the Dakota formation, and generally the dark-colored, commonly fine-grained O-5-6 type occurs immediately above the coarser, silty, light-gray EL-60-6 type. Clays representing both of these types are used in the manufacture of face brick in brick plants at Concordia and Great Bend, Kansas.

Clay O-38-4 represents a less common but important type of clay found in deposits of irregular extent near the middle of the Terra Cotta member of the Dakota formation. The environment of deposition obviously was farther removed from marine than that of the other three clays studied. The Janssen clays EL-60-6 and O-5-6 are judged to have been deposited in a littoral environment and are immediately overlain by the marine Graneros shale. Clay EL-69-2 was deposited under similar conditions near sea level immediately after the final retreat of the sea in which the marine Kiowa shale was deposited.

Clay O-38-4 is a "clean" clay, lacking superficial impurities, and is the moderately fine-grained, smooth, plastic type commonly classified as ball clay. This clay was used in the manufacture of pottery at Miltonvale and Topeka.

Clay EL-69-2 represents a type common to the lower part of the Dakota formation, occurring in association with a persistent series of beds which probably should be given the same member status as the Terra Cotta and the Janssen. Some lignite or thin lignite beds and thin pure kaolin beds commonly are associated with the EL-69-2 type clay. It is slightly less smooth and plastic than clay O-38-4, and probably is not quite clean enough to be classified as a ball clay. Actually it represents a rather common type of fire clay. This clay was used at one time in the manufacture of insulating fire brick and glazed tile blocks by Ludowici-Celadon Company at Coffeyville, Kansas.

Clay EL-60-6.—The clay identified in this report as EL-60-6 was sampled in the SE¼SW¼ sec. 19, T. 15 S., R. 9 W., Ellsworth County. Where sampled the bed is 4.1 feet thick and consists of relatively gritty, light-gray silty clay that contains lignite particles. An irregular kaolin streak at the top has a maximum thickness of 0.2 foot. The bed is underlain by 0.8 foot of lignitic silt and immediately overlain by 10 feet of gray silty to plastic refractory clay which is in turn overlain by 3.5 feet of gray clayey silt. The top of the silt bed is only a few inches below the Dakota formation-Graneros shale contact.

Clay EL-60-6 is of a type commonly found in the Janssen member of the Dakota formation. The bed from which sample EL-60-6 was taken is recognizable locally along at least 1.5 miles of outcrop.

Clay EL-69-2.—Clay EL-69-2 was sampled in the NW¼ NW¼ sec. 30, T. 15 S., R. 6 W., Ellsworth County. The bed sampled includes 10 feet of gray to light-gray clay with some yellow stain and contains lignite particles. The upper 0.5 foot of the bed is an impure kaolin. The bed is underlain by more than 10 feet of yellow sandstone and overlain by 6 feet of gray clay mottled with red, yellow, and lavender.

Although clays EL-60-6 and EL-69-2 are similar in appearance and both have a kaolin streak at the top, the EL-69-2 bed occurs in the lower part of the Terra Cotta member, a few feet above the Kiowa shale-Dakota formation contact, whereas the EL-60-6 bed occurs about 14 feet below the top of the formation.

Clay O-5-6—Clay sample O-5-6 was taken in the SW¼ NE¼ sec. 18, T. 11 S., R. 4 W., Ottawa County. This clay bed was exposed in three separate pits in which the thickness of the bed ranged from 2.8 to 5.7 feet. Channelings taken in all three pits were mixed for the test sample.

This clay is very dark gray to black, is unusually fine-grained and slick in appearance, and has a conchoidal fracture. In contrast to the majority of Dakota formation clays, which are moderately soft, clay O-5-6 is hard and rattles when handled. It contains numerous small slickensides, and in some places has the appearance of having been squeezed into irregular cavities in the overlying bed.

This clay represents one of the most persistent beds in the Dakota formation. The slick, highly plastic appearance is common, although this bed may be represented in some exposures by impure lignite or very silty lignitic clay.

Clay O-38-4.—Where clay O-38-4 was sampled in the NW¼ NE¼ sec. 8, T. 9 S., R. 2 W., Ottawa County, the bed is 6.3 feet thick. The bed occurs as a long, narrow body extending at least 2 miles north-northwest from this location, and probably about the same distance to the south-southeast also.

The clay is light gray in color and is smooth and plastic. It contains some lignite particles and a small amount of limonite stain. The overlying clay is similar but is mottled with red, brown, and yellow. The underlying clay is definitely more silty and has a gritty texture.

This clay bed occurs about 100 feet below the top of the Dakota formation, probably about the middle of the Terra Cotta member.

CHEMICAL PROPERTIES

Chemical Analyses

Chemical analyses of four portions of each clay were made: the original clays, the minus 2-micron fraction, the 2- to 8-micron fraction, and the plus 8-micron fraction. The analyses consisted of quantitative determinations for major elements present. Sulfide sulfur, sulfate sulfur, and phosphorus pentoxide were determined for all the original clays and for some of the fractions. Generally, only traces were noted. The procedures used to determine silica, alumina, iron oxide, titanium dioxide, calcium oxide, magnesium oxide, sodium and potassium oxides, and loss on ignition are accepted procedures for research accuracy. A brief description of these methods is given.

PROCEDURES

Silica.—Analysis for silica was begun by fusion with sodium carbonate followed by double dehydration with hydrochloric acid. The crude silica obtained was ignited to 1200° C., then treated with hydrofluoric and sulfuric acids. The residue was ignited, weighed, and the loss of weight calculated as silica.

Alumina.—The entire ammonium hydroxide group was double precipitated after removing silica with hydrofluoric and sulfuric acids. The R_2O_3 precipitate was ignited to 1200° C., cooled, and weighed. The other elements were subsequently removed, leaving alumina by difference.

Calcium oxide.—Calcium was determined by double precipitation with ammonium oxalate from the R_2O_3 filtrate. The calcium oxalate was titrated with ceric sulfate and calculated to calcium oxide. The combined filtrates were used to determine magnesium.

Magnesium oxide.—The combined filtrates from the calcium determination were treated with nitric and hydrochloric acids to destroy excess oxalate and ammonium salts. The magnesium was then double precipitated with diammonium phosphate. The final weighing was as magnesium pyrophosphate.

Loss on ignition.—The determination of loss on ignition represents the net change of weight occurring between 140° C. and 1000° C. It generally represents a net loss of weight and includes such elements and compounds as carbon (organic matter), sulfide sulfur, carbon dioxide, and water of hydration.

Iron and titanium.—The procedure used for iron and titanium was a gravimetric procedure utilizing cupferron (Runnels, Utter, and Reed, 1950). The R_2O_3 precipitate was put into sulfuric acid solution after fusion with potassium bisulfate. The iron and titanium (along with zirconium, vanadium, copper, and tin if present) were then precipitated with cupferron, leaving alumina (and phosphorus pentoxide and gallium oxide). The combined precipitate was ignited and weighed. Total iron was then determined, reported as Fe_2O_3, and subtracted from the cupferron precipitate, leaving titania (RO_2 plus R_2O_5) by difference.

Potassium and sodium oxide.—The alkali metals were determined with a model 52-C Perkin-Elmer flame photometer using acetylene and air. Solution was accomplished by treatment with hydrofluoric and sulfuric acids.

DISCUSSION OF DATA

Table 1 shows the results of the chemical analyses. Comparison of the analyses of the four clays indicates some of the basic differences observed and which are discussed in the other sections of this report. All the minus 2-micron fractions show a marked in-

TABLE 1.—*Chemical analyses of original clays and the various size fractions*

	EL-60-6				EL-69-2				O-5-6				O-38-4			
	Whole clay	<2 microns	2-8 microns	>8 microns	Whole clay	<2 microns	2-8 microns	>8 microns	Whole clay	<2 microns	2-8 microns	>8 microns	Whole clay	<2 microns	2-8 microns	>8 microns
Silica (SiO_2)	73.26	45.50	65.75	96.22	66.80	49.04	73.37	93.38	62.14	51.04	83.50	95.47	64.23	49.21	82.63	94.57
Alumina* (Al_2O_3)	17.86	37.09	22.93‡	1.66‡	20.94	32.83	15.91‡	3.27‡	24.27	31.47	9.26‡	1.69‡	22.84	32.55	10.15‡	2.19‡
Titania** (TiO_2)	1.25	1.54	1.92	0.97	1.24	0.94	1.81	0.83	1.09	0.81	1.96	1.13	1.29	1.19	1.61	1.23
Total iron (Fe_2O_3)	0.65	1.23	0.57	0.13	1.40	2.17	0.97	0.44	2.16	2.87	0.77	0.48	1.51	2.29	0.57	0.26
Calcium oxide(CaO)	0.14	0.09	0.07	0.04	0.24	0.16	0.13	0.09	0.54	0.52	0.14	0.07	0.28	0.30	0.10	0.08
Magnesium oxide(MgO)	0.15	0.12	0.15	0.10	0.65	0.86	1.27	0.04	0.54	0.65	0.43	0.01	0.63	0.78	0.72	0.03
Potassium oxide(K_2O)	0.06	0.05	0.05	0.05	1.98	2.30	1.85	0.41	0.72	0.75	0.53	0.28	1.59	1.93	1.03	0.20
Sodium oxide (Na_2O)	0.05	0.08	0.04	0.03	0.16	0.19	0.18	0.07	0.15	0.16	0.15	0.06	0.20	0.25	0.13	0.05
Phosphorus pentoxide (P_2O_5)	tr	tr	N.D.	N.D.	tr	tr	N.D.	N.D.	nil	tr	N.D.	N.D.	tr	tr	N.D.	N.D.
Sulfate sulfur (SO_3)	tr	0.14	N.D.	N.D.	tr	0.12	N.D.	N.D.	tr	0.05	N.D.	N.D.	tr	0.09	N.D.	N.D.
Loss on ignition† (L.O.I.)	6.48	13.73	8.41	0.60	6.70	10.89	5.19	0.99	8.41	11.09	3.17	0.62	7.33	10.60	3.21	0.83
Sulfide†† sulfur(S)	0.02	N.D.‡‡	N.D.	N.D.	0.12	N.D.	N.D.	N.D.	nil	N.D.	N.D.	N.D.	nil	N.D.	N.D.	N.D.
Total	99.90	99.57	99.89	99.80	100.11	99.50	100.68	99.52	100.02	99.41	99.91	99.81	99.90	99.19	100.15	99.44

* Contains gallium (Ga_2O_3) and MnO_2 when present.

** Contains ZrO_2 and V_2O_5 when present. Gravimetric method.

† Net loss of weight from 140° C. to 1000° C.

†† Included in L.O.I. for total.

‡ Contains P_2O_5 when present.

‡‡ Not determined.

crease in alumina and a corresponding decrease in silica. The other fractions reflect the free silica. There is a sharp increase in titanium in the 2- to 8-micron fraction and iron decreases, suggesting that most of the titanium is present as a dioxide and not as ilmenite. The other elements such as magnesium and the alkalies reflect the clay mineral composition and vary according to the concentration of the clay. Tables 2, 3, 4, and 5 show the various fractions calculated on a weighted basis. Totals calculated from the various fractions show fair agreement with the analyses of the whole clays. The most deviation occurs in sample O-5-6.

Discrepancies between percentages obtained by adding the various fractions and analyses of the whole sample are owing, at least in part, to not sampling the same percentage of the various fractions as determined by particle size analysis.

TABLE 2.—*Weighted composition of the sized fractions of clay EL-60-6*

	<2 microns, 35 percent	2-8 microns, 16 percent	>8 microns, 49 percent	Total of fractions	Whole clay
SiO_2	15.9	10.5	47.1	73.5	73.3
Al_2O_3	13.0	3.7	0.8	17.5	17.8
TiO_2	0.5	0.3	0.5	1.3	1.3
Fe_2O_3	0.4	0.1	0.1	0.6	0.6
CaO	0.03	0.02	0.02	0.1	0.1
MgO	0.03	0.03	0.05	0.1	0.2
K_2O	0.03	0.02	0.02	0.1	0.1
Na_2O	0.03	......	0.02	0.05	0.1
L.O.I.	4.8	1.3	0.3	6.4	6.5

TABLE 3.—*Weighted composition of the sized fractions of clay EL-69-2*

	<2 microns, 49 percent	2-8 microns, 23 percent	>8 microns, 28 percent	Total of fractions	Whole clay
SiO_2	24.0	16.9	26.2	67.1	66.8
Al_2O_3	16.1	3.6	0.9	20.6	20.9
TiO_2	0.4	0.4	0.2	1.0	1.2
Fe_2O_3	1.1	0.2	0.1	1.4	1.4
CaO	0.1	0.02	0.03	0.2	0.2
MgO	0.4	0.3	0.01	0.7	0.7
K_2O	1.1	0.4	0.1	1.6	2.0
Na_2O	0.1	0.05	0.02	0.2	0.2
L.O.I.	5.3	1.2	0.3	6.8	6.7

TABLE 4.—*Weighted composition of the sized fractions of clay 0-5-6*

	<2 microns, 62 percent	2-8 microns, 23 percent	>8 microns, 15 percent	Total of fractions	Whole clay
SiO_2	31.6	19.2	14.3	65.1	62.1
Al_2O_3	19.5	2.1	0.3	21.9	24.3
TiO_2	0.5	0.5	0.2	1.2	1.1
Fe_2O_3	1.8	0.2	0.1	2.1	2.2
CaO	0.3	0.02	0.01	0.3	0.5
MgO	0.4	0.1	......	0.5	0.5
K_2O	0.5	0.1	0.04	0.6	0.7
Na_2O	0.1	0.04	0.01	0.2	0.2
L.O.I.	6.9	0.7	0.1	7.7	8.4

TABLE 5.—*Weighted composition of the sized fractions of clay 0-38-4*

	<2 microns, 60 percent	2-8 microns, 29 percent	>8 microns, 11 percent	Total of fractions	Whole clay
SiO_2	29.5	24.0	10.4	63.9	64.2
Al_2O_3	19.6	3.0	0.2	22.8	23.1
TiO_2	0.7	0.5	0.1	1.3	1.3
Fe_2O_3	1.4	0.2	0.03	1.6	1.5
CaO	0.2	0.03	0.01	0.2	0.3
MgO	0.5	0.2	.....	0.7	0.6
K_2O	1.1	0.3	0.02	1.4	1.6
Na_2O	0.2	0.03	......	0.2	0.2
L.O.I.	6.4	0.9	0.1	7.4	7.3

SPECTROCHEMICAL ANALYSES

Spectrographic analyses are generally divided into three types: qualitative, semiquantitative, and quantitative. A qualitative analysis makes no attempt to give a concentration value for any constituent, except occasionally to classify the constituents present as major, minor, or trace. The definitions of these terms are not fixed. In semiquantitative analysis the concentrations are determined definitely, but owing to the fact that many of the variables inherent in spectrography are not controlled, the accuracy of the method is generally conceded to be not better than 50 percent of the amount reported. In quantitative analysis the accuracy ranges from about 20 percent in the easier and less closely controlled methods to as high as 4 percent under the most ideal conditions with variables very closely controlled. The method used in this study was the "internal standard" quantitative method, using a general internal standard. An accuracy of 7 to 10 percent should be expected from this method.

SAMPLE PREPARATION

The original clays and the minus 2-micron fractions were analyzed spectrographically. The chemical analyses show that the minus 2-micron fractions differ widely in composition from the original clays. As appreciable compositional variation has a decided effect on the spectrographic sensitivities of the various elements, the samples were divided into two groups, by particle size. The elements chosen for internal standards were iron and germanium, the iron to be used for the high-melting, high-boiling elements Mn, V, Cr, Mo, Ni, and Ga; for the low-melting, low-boiling elements Pb, Zn, Sn, and Cu, germanium was used. Iron was already present in all the samples. The amount of Fe_2O_3 necessary to bring the concentration of iron in each original clay to the concentration in the sample highest in iron (clay O-5-6 which contained 2.12 percent Fe_2O_3) was dried, weighed, and added to each of the other original clays. The Fe_2O_3 necessary to bring the iron in the minus 2-micron fractions to a concentration identical with that in the minus 2-micron fraction of clay O-5-6 (2.63 percent) was added to these fractions. To 1 gram of each of the samples 1 percent germanium as the oxide GeO_2 and 1 gram of pure anhydrous Li_2SO_4 (to act as spectrographic buffer) were added. The 2 grams of each powder were then intimately ground and mixed in a mullite mortar to a particle size of about minus 150 mesh.

STANDARD PREPARATION

Separate matrices were made up for the two groups of samples. The first, as standard for the original clays, made up to the average major composition of the original clays, had a composition as follows.

SiO_2	2.6640 grams
Al_2O_3	0.8636
Fe_2O_3	0.0848
CaO	0.0400
GeO_2	0.0526
Total	3.7050

This mixture was equivalent to 4.0000 grams of the average original clay, the remainder being the loss the average original clay sustained on ignition to 1000° C.

The second clay standard, for the minus 2-micron fractions, had a composition as follows.

SiO_2	1.9480	grams
Al_2O_3	1.3316	
Fe_2O_3	0.1052	
CaO	0.0400	
GeO_2	0.0576	
Total	3.4824	

This mixture was equivalent to 4.0000 grams of the average minus 2-micron fraction, the remainder being loss on ignition.

To each of these two matrices 4.0000 grams pure anhydrous Li_2SO_4 was added and the mixtures ground together. Because the four original clays varied rather widely from the average composition, as did the minus 2-micron fractions, from their average, it was decided, in the interest of greater accuracy, to reduce compositional variations by reacting the oxide mixtures. Accordingly, the two raw matrices were heated at 900° C., and the resulting sinter crushed and reground to about minus 150 mesh. To 1.9275 grams of the total clay matrix and 1.8706 grams of the minus 2-micron fraction (1.0000 gram equivalent for each) 0.0100 gram (1.00 percent) each of V, Cr, Mn, Ni, Pb, Sn, Mo, and B, and 0.0010 gram (0.10 percent) Cu was added. Portions of the original matrices were used to make successive dilutions until standards of 0.1 percent, 0.05 percent, and 0.010 percent of each of the elements V, Cr, Mn, Ni, Pb, Sn, Mo, and B and 0.01 percent, 0.005 percent, and 0.001 percent Cu were available for each of the two groups.

SPECTROGRAPHIC EQUIPMENT

The instrument used was a 1.5-meter Applied Research Laboratories grating-type spectrograph powered by a 250 volt D.C. arc source. The film on which the spectra were recorded was Eastman Spectrum Analysis no. 1, which after exposure was developed for 3 minutes in Eastman D-19 developer, short-stopped for 10 seconds in 3 percent acetic acid solution, and fixed in Kodak rapid liquid fixer with hardener. After fixing, the film was given a 1-minute tap-water wash, and a 30-second distilled water wash, after which it was rinsed with fresh distilled water, the excess water removed with a sponge, and the film dried on an infra-red forced-air dryer. When dry, the film was placed in an A.R.L. densitometer-comparitor and the densities of the element lines read. The line pairs used for this study were as follows.

Mn: 2576.1 A,	Fe: 2584.6 A
V : 3185 A,	Fe: 3205 A
Cr : 4289.7 A,	Fe: 4294.3 A
Mo: 3170.3 A,	Fe: 3205 A
Ni : 3414.8 A,	Fe: 3413.1 A
Ga: 2943 A,	Fe: 2941.6 A
Cu: 3274 A,	Ge: 3269.5 A
Pb: 2833 A,	Ge: 3269.5 A
Sn: 3262.3 A,	Ge: 3269.5 A

PROCEDURE

Fourteen milligrams of clay-buffer mix was packed into a standard concave, center-post platform electrode formed from quarter-inch National Carbon Company standard electrode-grade graphite rod. The counterelectrode was a similarly formed graphite rod. Three samples of each clay were arced consecutively, without changing the position of the film, thus superimposing the 3 ignitions on the film as 1 spectrum. For this study, 8 spectra for each sample were made, making a total of 24 ignitions on each clay. Each ignition was made at 8 amperes for 60 seconds, with the rotating sector at 10 percent, the grating doors set at 3.4, or about 50 percent transmission, a slit-width of 50 microns, and an electrode-counter-electrode distance of 4 mm. The same procedure was followed with each of the standards in which concentrations of the various elements were known. A curve showing the ratio of intensity of the various element lines to the internal standard line of the pair was drawn, and the intensity ratios of the line pairs in the clay samples were read on these curves. The averages of the eight determinations on each element of each clay, along with the mean deviation of the eight determinations and the percent mean deviation are shown in Table 6. Zinc, zirconium, germanium, strontium, barium, silver, cobalt, cadmium, and the lanthanides were not present. Boron could not be determined because of interference of silicon.

DISCUSSION OF RESULTS

In a quantitative spectrochemical analysis by the internal standard method, compensation for many variables is automatic. One, however, for which it is impossible to compensate, is the amount of basic difference which exists between the physico-chemical

TABLE 6.—*Spectrochemical analyses of clays**

	O-5-6		O-38-4		EL-60-6		EL-69-2	
Elem.	Whole clay	<2 microns	Whole clay	<2 microns	Whole clay	<2 microns	Whole clay	<2 microns
Mn	0.0069	0.0065	0.0070	0.0069	0.0073	0.0067	0.0072	0.0078
M.D.**	0.0006	0.0004	0.0006	0.0008	0.0006	0.0006	0.0004	0.0006
P†	8.5	6.0	8.5	11.5	8.0	9.0	5.5	7.5
V	0.0125	0.0178	0.0131	0.0183	0.0076	0.0119	0.0177	0.0231
M.D.	0.0008	0.0030	0.0013	0.0025	0.0008	0.0016	0.0031	0.0030
P	6.5	17.0	10.0	13.5	10.5	13.5	17.5	13.0
Cr	0.0102	0.0121	0.0105	0.0124	0.0071	0.0083	0.0105	0.0177
M.D.	0.0004	0.0004	0.0005	0.0005	0.0002	0.0001	0.0004	0.0016
P	4.0	3.5	5.0	4.0	3.0	1.0	4.0	9.0
Mo	0.0033	trace‡	ND††	0.0047	0.0029	0.0046	0.0027	0.0050
M.D.	0.0001			0.0003	0.0002	0.0003	0.0002	0.0005
P	3.0			6.5	7.0	6.5	7.5	10.0
Ni	0.0050	0.0054	0.0038	0.0042	0.0029	0.0034	0.0033	0.0055
M.D.	0.0003	0.0006	0.0002	0.0002	0.0004	0.0006	0.0004	0.0005
P	6.0	11.0	5.5	5.0	14.0	17.5	12.0	9.0
Ga	0.0049	0.0038	0.0038	0.0033	0.0036	0.0037	0.0034	0.0031
M.D.	0.0006	0.0007	0.0003	0.0005	0.0005	0.0005	0.0005	0.0003
P	12.0	18.5	16.0	15.0	14.0	13.5	14.5	9.5
Cu	0.00135	0.0058	0.0018	0.0053	0.00037	0.0039	0.00103	0.0085
M.D.	0.00028	0.0009	0.0010	0.0013	0.00012	0.0007	0.00032	0.0022
P	20.5	15.5	55.5	24.5	32.5	18.0	31.0	26.0
Pb	trace	trace	trace	trace	trace	trace	trace	ND
Sn	trace	trace	trace	trace	0.002	trace	trace	trace

*Amounts shown are the averages of 8 groups of 3 separate samples each, or a total of 24 samples per determination per clay or clay fraction.

**M.D. (mean deviation) is the average deviation from the mean value shown.

†Precision value obtained from the ratio of the mean deviation to the mean value obtained, expressed as percent.

††Not detected.

‡Trace is defined in this study as less than 0.001 percent but present in detectable amounts.

properties of the "unknown" element and the internal standard element and the effect of variation of the matrix upon this difference. In a study which involves only one element in a number of closely similar samples, a careful and exacting selection of the internal standard element may be made. When several elements are being determined for a group of rather widely differing samples, compromise conditions must be accepted. If iron is chosen as the compromise internal standard, it cannot be the ideal choice for an element such as gallium. The behavior of the two elements in the electric arc will be dissimilar, and these differences may be intensified by the effect exerted by the major constituents on the behavior of the more minor constituents. A high-silica clay, for example, may cause the iron lines to be darker, relative to the gallium, than a high-alumina clay. Therefore, a compromise internal standard introduces inaccuracies which may be exaggerated by the other differences between samples. This was probably the case in the determination of Cu (with an average precision of about 28 percent, scarcely better than a semiquantitative analysis), Ga (with an average precision of about 14 percent), and to a lesser extent, V (with an average precision of about 12 percent). Determinations of Ni, Cr, Mo, and Mn seem to have greater precision in this general-type analysis (with an overall precision average of 7.4 percent) using iron as the internal standard.

In order to show more clearly the enrichment or depletion of the minor elements in the minus 2-micron fraction, calculations were made to show the amount of each element present based upon the percentage of minus 2-micron fractions present in the original clays. The percentage increase or decrease of the various elements was then computed. These figures are shown in Table 7.

Considering these results, a few general statements can be made. Vanadium, chromium, and nickel (to a lesser degree) are enriched in the minus 2-micron fractions. Manganese and gallium show depletion. This depletion is directly opposed to normal theory. Gallium, especially, is supposedly associated with aluminum and was expected to be enriched in the minus 2-micron fractions. The copper determination is known to be erroneous; the explanation is that in separating the minus 2-micron fractions (particle size analysis) a brass agitator was used in conjunction with a dilute ammonium hydroxide suspension of the clay.

Although the molybdenum concentration seemed to be similar to the other elements the calculations show it to range from minus 71 percent to plus 84 percent. This variation was too erratic to indicate any definite trend.

PETROGRAPHIC AND MINERALOGICAL PROPERTIES

PARTICLE SIZE DATA

A mechanical analysis of each sample was made by pipette method, using NH_4OH as a dispersing agent. Pipette samples were taken at single phi intervals from 4 to 11 phi. The results are shown

TABLE 7.—*Comparisons of the proportions of the minor elements present in the minus 2-micron fractions to the amount (percent by weight) of minus 2-micron fraction in each of the four clays*

		<2-micron fraction				
Elements present	Element in whole clay, percent*	Element present, percent*	Percent of whole clay represented**	Weighted amount of element, percent†	Relative percentage of element present††	Enrichment of element in percent‡
			EL-60-6			
Mn	0.0073	0.0067	35	0.0023	31	— 11
V	0.0076	0.0119	35	0.0042	55	+ 57
Cr	0.0071	0.0083	35	0.0029	41	+ 17
Mo	0.0029	0.0046	35	0.0016	55	+ 57
Ni	0.0029	0.0034	35	0.0012	41	+ 17
Ga	0.0036	0.0037	35	0.0013	36	+ 3
Cu	0.00037	0.0039	35	0.0014	378	+980
			EL-69-2			
Mn	0.0072	0.0078	49	0.0038	53	+ 8
V	0.0177	0.0231	49	0.0113	63	+ 29
Cr	0.0105	0.0177	49	0.0087	83	+ 69
Mo	0.0027	0.0050	49	0.0024	90	+ 84
Ni	0.0033	0.0055	49	0.0027	82	+ 67
Ga	0.0034	0.0031	49	0.0015	44	— 10
Cu	0.00103	0.0085	49	0.0032	311	+739
			O-5-6			
Mn	0.0069	0.0065	62	0.0040	58	— 6
V	0.0125	0.0178	62	0.0110	89	+ 44
Cr	0.0102	0.0121	62	0.0075	73	+ 18
Mo	0.0033	0.001	62	0.0006	18	— 71
Ni	0.0050	0.0054	62	0.0033	67	+ 8
Ga	0.0049	0.0038	62	0.0024	49	— 21
Cu	0.00135	0.0058	62	0.0036	267	+352
			O-38-4			
Mn	0.0070	0.0069	60	0.0041	59	— 2
V	0.0131	0.0183	60	0.0110	84	+ 40
Cr	0.0105	0.0124	60	0.0074	70	+ 17
Mo	ND	0.0047	60	0.0028	....	...
Ni	0.0038	0.0042	60	0.0025	66	+ 10
Ga	0.0038	0.0033	60	0.0020	53	— 12
Cu	0.0018	0.0053	60	0.0032	178	+197

*From spectrographic analysis.

**From particle size data.

†Calculated: percent element present times percent whole clay represented.

††Calculated: weighted percent in minus 2-micron fraction divided by percent element in whole clay.

‡Calculated: percent of whole clay represented minus relative percentage present divided by percent of whole clay represented.

in Table 8. For purposes of analysis, size fractions finer than 2 microns and from 2- to 8-microns were obtained by sedimentation and repeated decantation at time intervals and depths determined by Stokes' law. The accuracy obtained was somewhat less than that of the mechanical analyses themselves. Particle size distributions finer than 11 phi (0.5 micron) were estimated by measurements of particles in electron micrographs. Cumulative size frequency curves derived from pipette analyses and measurements on electron micrographs are shown in Figure 1. It was necessary to treat clay O-5-6 with H_2O_2 to prevent flocculation so the results may not be strictly comparable with those from the other three clays.

Clay EL-60-6 is coarsest and most poorly sorted of the four clays. The sorting, recorded as the phi percentile deviation, is 4.45. The distribution shows a single mode in the coarse silt to very fine sand region, and the remainder of the sample is rather evenly distributed throughout the curve. The median diameter is 7.13 phi (7.1 microns).

Clay EL-69-2 is somewhat finer grained and shows a principal mode at about 7 phi (8 microns). The median diameter is 8.93 phi (about 2 microns).

According to the pipette data, clay O-5-6 is the finest grained of the four clays (median diameter 10.2 phi, or 0.85 microns) and its distribution seems to be bimodal: one mode is at about 8.5 phi (2.8 microns), and another at nearly 11 phi (0.5 micron). The curve

TABLE 8.—*Particle size distribution, percent by weight, by pipette analysis*

Phi	Microns	EL-60-6	EL-69-2	O-5-6	O-38-4
<4	>62	13.8	4.8	0.4	....
4-4.5	62-44	6.1	2.6	1.9	....
4.5-5	44-31.2	7.1	3.2	1.9	....
5-6	31.2-15.6	11.7	7.0	4.8	4.3
6-7	15.6-7.8	10.1	10.4	6.1	6.5
7-8	7.8-3.9	8.7	11.4	10.2	13.7
8-9	3.9-1.95	7.9	11.2	12.3	15.1
9-10	1.95-1	7.2	8.7	10.2	11.0
10-11	1-0.5	6.5	8.7	13.7	9.4
>11	<0.5	20.9	32.1	38.5	40.0
Md[1]		7.13	8.93	10.20	9.95
PD[1]		4.45	4.25	3.95	3.60

[1] From cumulative curves (Fig. 1).

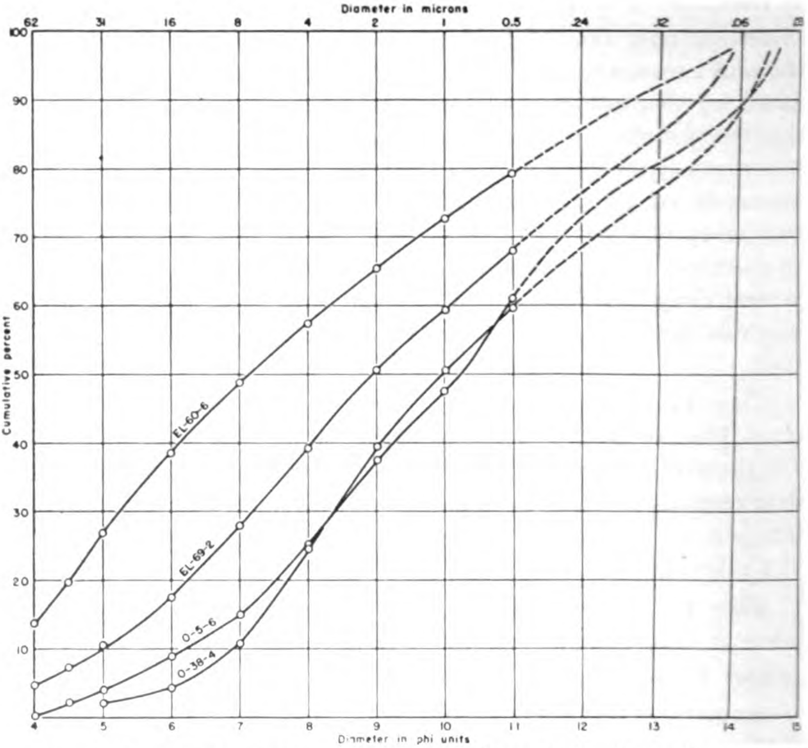

Fig. 1.—Cumulative particle size distributions of the four clays. Solid lines from pipette data; dashed lines from electron micrograph measurements.

from the electron micrograph data suggests a third mode at 14 phi (0.06 micron) but this value may not be reliable.

Clay O-38-4 is nearly as fine grained as clay O-5-6 (median diameter 9.95 phi, about 1 micron) but the curve is less complex. The principal mode is at about 8 phi (4 microns). Electron micrograph data suggest another mode at 13.5 phi (0.09 micron). The sorting is better than that of the other clays (phi percentile deviation, 3.60).

SPECIFIC SURFACE

The specific surface of the four clays was calculated in order to determine the relationship between particle size and shape and the green properties of the clays such as drying shrinkage, water of plasticity, and shrinkage water. Inasmuch as the somewhat elusive property of clays termed "plasticity" is largely determined by the amount and manner in which water is held within the clay material, it is assumed that the specific surface of a clay is a reliable quantitative index of its plasticity.

The specific surface was obtained from the following formula:

$$S = \frac{2(1 - 2x)}{\rho D x}$$

where S = specific surface (square meters per gram of sample)

D = mean diameter (microns)

x = ratio of thickness to length

ρ = density of sample (2.62 grams per cc)

The procedure for the determination of specific surface was modified slightly from that used by Johnson and Lawrence (1942) and by Whittaker (1939).

The mean diameter was determined from the particle size analyses described elsewhere in this report. The ratio of thickness to length was determined by measuring a large number of particles on electron micrographs. Separate determinations were made on kaolinite, illite (montmorillonite and mixed-layer clay minerals were not distinguished from illite), and quartz, on the assumption that the kaolinite flakes all show 120° angles. Estimated percentages of each of these mineral constituents were used in calculating a weighted average. The thickness to length ratio (x) was determined separately on the minus 2-micron fraction and the 2- to 8-micron fraction. Electron micrographs were not available for the plus 8-micron fraction, but the ratio (x) for the quartz in the 2- to 8-micron fraction was applied to the plus 8-micron fraction. The percentage of each of these fractions was also used in calculating weighted averages.

The specific surface values obtained are listed in Table 9.

Table 9.—*Specific surface (S) for the four clays investigated*

Sample no.	Specific surface, square meters per gram
EL-60-6	3.07
EL-69-2	7.24
O-5-6	11.74
O-38-4	8.19

THIN SECTIONS

Photomicrographs of thin sections from the four clays are shown in Plates 1 and 2.

The thin section from clay EL-60-6 contains scattered quartz grains (some as large as 150 microns in long diameter) in a matrix of pale brownish clay having low birefringence (Pl. 1A, 1B). Some elongate areas of the clay show good preferred orientation, and their birefringence seems to be slightly greater than that of pure kaolinite. Large curved "books" of kaolinite are scattered throughout the thin section; the largest of these is about 90 microns long and 40 microns wide in the plane of the thin section. A few small grains of zircon and tourmaline are present. No feldspar is observed, but some small areas of clay having uniformly low birefringence may possibly be feldspar grains that have completely altered to kaolinite.

The thin section from clay EL-69-2 also has many large quartz grains in a clay matrix. The clay contains many fine, highly birefringent shreds (presumably illite), oriented in all directions and scattered throughout the less birefringent kaolinite. No kaolinite books are visible, and there are a few small spots of dark-brown organic matter (Pl. 1C, 1D).

Clay O-5-6 contains much more organic matter than the other three clays (Pl. 2A, 2B). The quartz grains are smaller and less abundant than those of clays EL-60-6 and EL-69-2. The clay matrix has more highly birefringent areas than that of clay EL-60-6, but they cannot be resolved so easily into distinct flakes or shreds as can those of clay EL-69-2. These may be the mixed-layer mineral and montmorillonite detected by x-ray diffraction. The clay shows excellent local preferred orientation, but its direction varies throughout the slide and extinction in any one small area is undulatory.

Clay O-38-4 contains fewer and smaller quartz grains than the other three clays. The matrix seems nearly uniform or homogeneous throughout the thin section, and many small highly birefringent shreds are observed under high magnification (Pl. 2C, 2D).

PLATE 1. Photomicrographs of thin sections, x 175. **A**, Clay **EL-60-6, plane** polarized light. **B**, Clay EL-60-6, crossed nicols. Note **slightly birefringent** area of clay near upper left-hand corner. **C**, Clay EL-69-2, **plane polarized** light. Note shredlike character of matrix. **D**, Clay EL-69-2, **crossed nicols.**

Orientation of the shreds seems fairly good in two directions. A small quantity of organic matter is present as scattered dark-brown spots.

ELECTRON MICROSCOPY

Early examination of the clays was done with an RCA EMU-2B microscope operated by C. C. McMurtry at the Department of Oncology, University of Kansas Medical Center. Later electron micrographs were made in a Philips EM-100 microscope. The 2- to 8-micron fractions and the minus 2-micron fractions were examined. Samples were prepared by drying a drop of clay suspension on a collodion substrate and shadowing with chromium from an angle of about 20 degrees. Representative electron micrographs are shown in Plate 3.

Most particles in the 2- to 8-micron fractions are relatively thick in comparison with their length and width and have irregular angular shapes. These are probably predominantly quartz. Some coarse irregular particles, particularly in clay EL-69-2, are shown by their shadows to be thin flakes; these may be 2:1 layer lattice silicates (illite and mica). The coarse fraction from clay EL-60-6 contains many large accordion-shaped kaolinite books; the largest of those observed in the electron microscope is a curved book about 10 microns long with individual flakes nearly 4 microns in diameter (Pl. 3D). Kaolinite books were not observed in the other three clays.

The fraction finer than 2 microns from clay EL-60-6 consists almost entirely of well-developed pseudohexagonal flakes of kaolinite. The fine fraction from clay EL-69-2 contains some irregularly shaped flakes, as well as large numbers of hexagonal flakes (Pl. 3C). The most common flakes of clays O-5-6 and O-38-4, although hexagonal, are smaller than those of clay EL-60-6. Cottony aggregates, typical of Ca-montmorillonite, were not observed in any of the clays, but some, particularly clay O-5-6, contain minute particles finer than 0.5 micron which may possibly be montmorillonite or mixed-layer mineral (Pl. 3B). A few fields contain one or two small elongate particles which may possibly be halloysite. Some

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PLATE 2. Photomicrographs of thin sections, x 175. **A**, Clay O-5-6, plane polarized light. Note quantities of dark organic matter. **B**, Clay O-5-6, crossed nicols. **C**, Clay O-38-4, plane polarized light. **D**, Clay O-38-4, crossed nicols.

FIG. 2.—Diffractometer patterns from raw clay samples, packed in specimen holders. Nickel-filtered copper radiation. **A**, Macon kaolinite (A.P.I. H-4); **B**, clay EL-60-6; **C**, clay EL-69-2; **D**, clay O-5-6; **E**, clay O-38-4.

micrographs show dense cubic crystals which may be anatase. Most of them are of the order of one-half micron in diameter.

X-RAY DIFFRACTION DATA

Diffraction patterns were made with a GE XRD-3 Geiger-Mueller counter spectrogoniometer. The patterns were run at a speed of 0.2° 2θ per minute, using a 1° beam slit, 2° detector slit, and nickel-filtered copper radiation at 50 kv and 15 ma. The patterns, reproduced in Figures 2 to 7, show the characteristics of the critical reflections. Diffraction patterns from a sample of Macon kaolinite (A.P.I. H-4) are included for comparison.

The clays were ground to pass a 62-micron screen and packed into a specimen holder with a shallow opening 1⅝ inches long. Care was taken to produce random orientation by packing the clay into the specimen holder with the edge of a spatula and forming the final flat surface with rough paper. Patterns from the raw clays

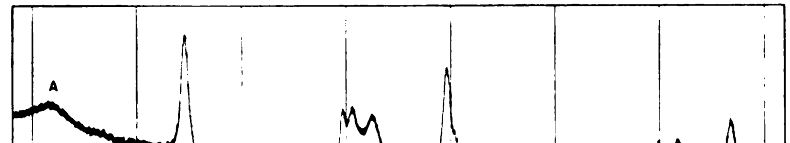

FIG. 3.—Diffractometer patterns from fractions finer than 2 microns, packed in specimen holders. Nickel-filtered copper radiation. **A**, Macon kaolinite; **B**, clay EL-60-6; **C**, clay EL-69-2; **D**, clay O-5-6; **E**, clay O-38-4.

and the fraction finer than 2 microns are shown in Figures 2 and 3. Oriented samples of the fraction finer than 2 microns were used for study of the basal reflections from the clay minerals. They were prepared in the standard way by allowing the clay to settle onto a glass microscope slide from a water suspension. After the clay was dried at room temperature a diffraction pattern was obtained (Fig. 4). The slide was then treated with glycerol and another diffraction pattern was run.

All four clays produced reflections for kaolinite, quartz, and a suggestion of a trace of feldspar. Other minerals found in one or more of the clays include illite, muscovite, "fire-clay mineral," mixed-layer minerals, montmorillonite, and possibly anatase.

Rough semiquantitative estimates of the mineral percentages were made, and although these are reported to the nearest 5 percent, their accuracy may be much less. The chemical analyses, differential thermal curves, and electron micrographs were taken into consideration in estimating percentages.

CLAY EL-60-6

Diffraction patterns for clay EL-60-6 give reflections for quartz, kaolinite, and a trace of feldspar. The clay is judged to contain about 50 percent quartz and 45 percent kaolinite. The fraction finer than 2 microns contains almost 95 percent kaolinite and about 1 percent quartz.

The kaolinite reflections are sharp and clearly defined, including the group of reflections from 4.46 A to 3.56 A and the two prominent groups, each of which contains three reflections with spacings 2.55, 2.52, 2.49 and 2.37, 2.33, 2.28 A. The 4.34 A reflection is stronger than that at 4.44 A. The first order basal spacing (001) is 7.2 A. These data indicate that the mineral is kaolinite rather than fire clay (Brindley, 1951, pp. 50-51, 71). The pattern from clay EL-60-6 closely resembles that from the Georgia kaolinite, except for quartz reflections, which are not present in the pattern from the Georgia clay.

The fraction finer than 2 microns, oriented on a glass slide, shows a weak but definite reflection at 14.4 A (Fig. 4A). This reflection, which does not shift in the glycerated clay and is destroyed by heat treatment, may be attributed to a chlorite admixture. The Georgia kaolinite produces a similar low-angle reflection, and the

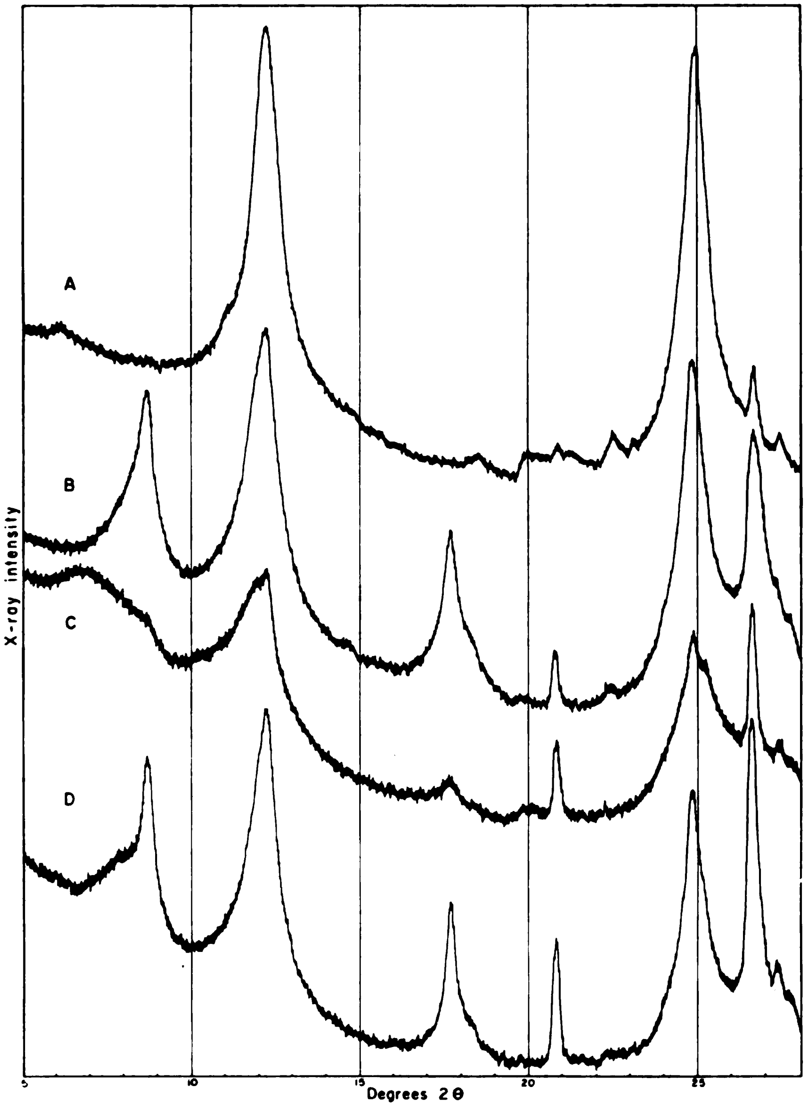

Fig. 4.—Diffractometer patterns from fractions finer than 2 microns, oriented on glass slide. A, Clay EL-60-6; B, clay EL-69-2; C, clay O-5-6; D, clay O-38-4.

common presence of such impurities in kaolinite has been mentioned by Glass (1952, p. 211) and Keller (1952, p. 225). Part of the minus 2-micron fraction which had been heated for 30 minutes at 600° C. showed a reflection at 3.52 A. This reflection is tentatively assigned to anatase, for nearly 2 percent of a titanium mineral is suggested by the chemical analysis of this fraction, and electron micrographs show a few cubic crystals. No 10 A basal reflections from hydrous mica are observed in the diffraction pattern from the heat-treated clay.

CLAY EL-69-2

Clay EL-69-2 consists primarily of quartz (35 percent), kaolinite (35 percent), and illite and muscovite (25 percent). It also contains more feldspar than clay EL-60-6, and a small quantity of a mixed-layer clay mineral.

The 2- to 8-micron fraction contains more than 50 percent quartz, about 20 percent kaolinite, and less than 30 percent illite, muscovite, and mixed-layer clay. The fraction finer than 2 microns contains approximately 60 percent kaolinite (which gives a broad first-order basal reflection with slight asymmetry suggesting a small quantity of "fire-clay mineral," about 25 percent illite, about 10 percent mixed layer clay, and about 3 percent quartz. An oriented preparation of the minus 2-micron fraction shows the 10 A reflection to be asymmetrical also. The reflection is symmetrical after saturation with glycerol, but the small quantity of mixed-layer material present does not produce an individual reflection at a lower angle (Fig. 5).

CLAY O-5-6

Clay O-5-6 is shown by diffraction patterns to contain about 30 percent quartz, 40 percent "fire-clay mineral" and kaolinite, 25 percent micaceous clay minerals (including illite, hydrous mica with basal spacing greater than 10 A, and montmorillonite), and a suggestion of feldspar.

This clay, which contained appreciable quantities of organic matter, had been treated with H_2O_2 to make size fractionation possible. This treatment seemingly modified the micaceous clay minerals, so that the minus 2-micron fraction and the 2- to 8-micron fraction may not be representative of these fractions in the original clay. The 2- to 8-micron fraction contains approximately 70 percent

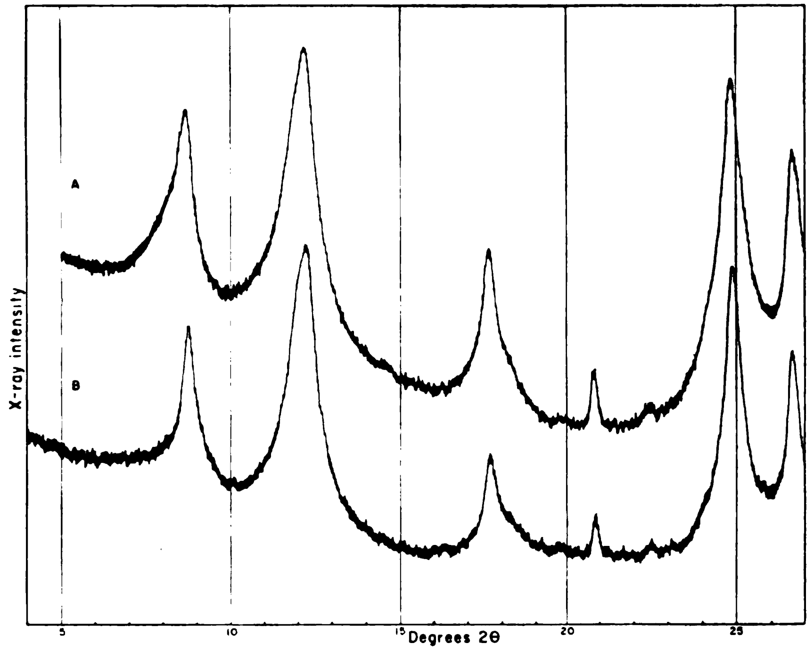

Fig. 5.—Diffractometer patterns from fraction finer than 2 microns, clay EL-69-2, oriented on glass slide. Nickel-filtered copper radiation. **A**, Air dried; **B**, glycerated. Note change in 10 A reflection.

quartz, 15 percent kaolin, and less than 15 percent illite, montmorillonite, and mixed-layer mineral.

The fraction finer than 2 microns contains less than 5 percent quartz, about 55 percent "fire-clay mineral" and kaolinite (there is considerably more fire-clay mineral than kaolinite in this fraction), and about 35 percent montmorillonite, illite, and mixed-layer mineral.

The following descriptions of the spectrogoniometer patterns refer to clay which was not treated with H_2O_2 and was not fractionated. The dry unoriented clay produces a broad kaolin mineral reflection at about 7.3 A and a very broad indistinct basal reflection at 12.6 A. After treatment of the clay with glycerol, this reflection had shifted to 14.2 A but was still broad and indistinct. There is also a weak 10 A reflection from the glycerol-treated clay. Clay allowed to settle in water onto a glass slide and dried at room temperature shows the kaolin basal reflection to be a double one with maxima at

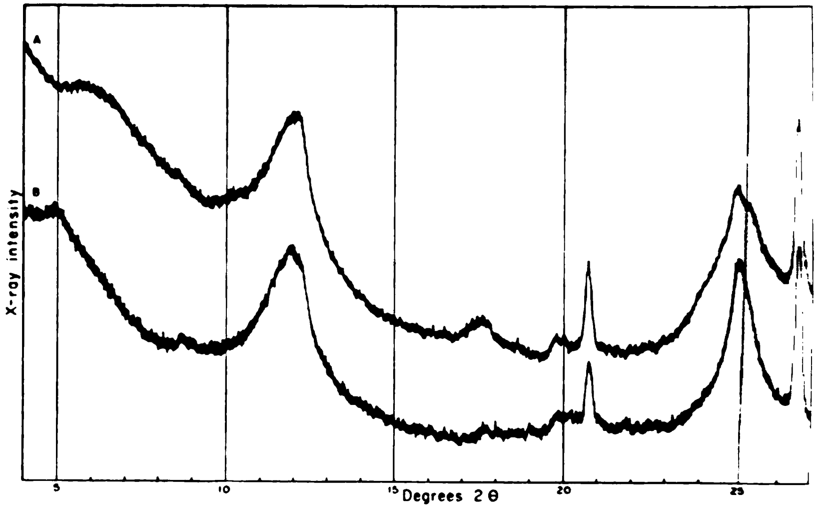

Fig. 6.—Diffractometer patterns from fraction finer than 2 microns, clay O-5-6, oriented on glass slide. Nickel-filtered copper radiation. A, Air-dried; B, glycerated.

7.4 and 7.2 A. There is also a broad band from 10 A to about 18 A with a maximum at 15.4 A. Saturating the oriented clay with glycerol causes the 15.4 A maximum to move to about 18 A and isolates the 10 A reflection, but the 18 A reflection is not sharp, and mixed layer material is obviously present also (Fig. 6). No higher order reflections for the montmorillonite are produced.

Seemingly, treatment with distilled water (and a few drops of NH_4OH) modified the micaceous clay mineral so that there is an 18 A reflection after glycerol treatment, whereas clay which had not been in distilled water did not react to the glycerol. It is possible that the organic matter in the clay had formed a complex which was destroyed by distilled water.

CLAY O-38-4

Clay O-38-4 contains about 40 percent kaolinite, 35 percent quartz, 20 percent illite and muscovite, and a trace of feldspar. There is a slight but definite indication of a mixed-layer mineral.

Plate 3. Electron micrographs of clay particles, shadowed with chromium. A, Clay O-38-4, fraction finer than 1 micron, x15,000. B, Clay O-5-6, fraction finer than 2 microns, x11,800. Note hexagonal flakes and scattered small particles. C, Clay EL-69-2, fraction finer than 2 microns, x 4,800. Note large irregular flakes. D, Kaolinite book from clay EL-60-6, 2- to 8-micron fraction, x 10,600.

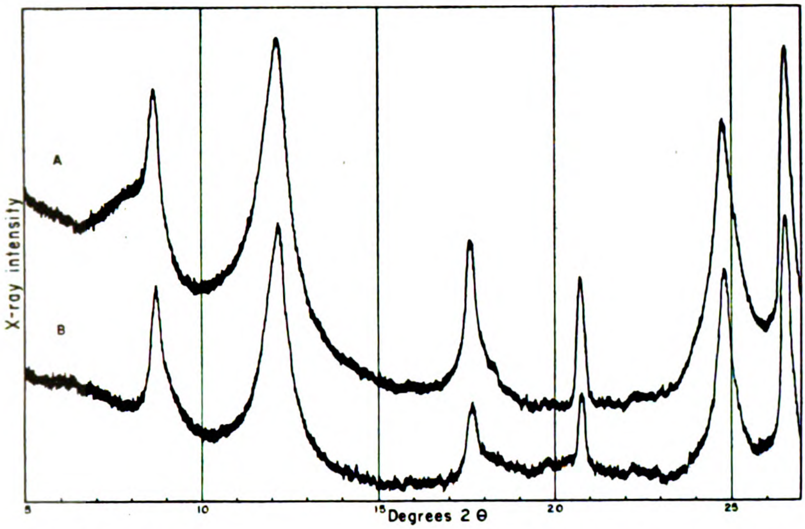

FIG. 7.—Diffractometer patterns from fraction finer than 2 microns, clay O-38-4, oriented. Nickel-filtered copper radiation. **A**, Air dried; **B**, glycerated.

The 2- to 8-micron fraction contains about 70 percent quartz, about 10 percent illite and muscovite, less than 20 percent kaolin and a trace of a mixed-layer mineral.

The fraction finer than 2 microns contains about 65 percent kaolinite, 25 percent illite and mixed-layer mineral, and little more than 5 percent quartz.

The (001) kaolinite reflection at 7.2 A is broad but only slightly asymmetrical, suggesting a very small quantity of fire-clay mineral.

The 10 A reflection is shown on the pattern from the oriented sample to be produced by a mixed-layer mineral as well as illite. Saturating the clay with glycerol shifts part of this reflection to 14.2 A from 11 A or less (Fig. 7), but there are no higher order reflections.

SUMMARY OF PETROGRAPHIC DATA

The petrographic characters of the four clays are summarized below.

Clay EL-60-6, the coarsest textured of the four, is also mineralogically the simplest. It consists almost entirely of rather coarse quartz grains and large to small kaolinite books and flakes. It also seems to contain traces of a chlorite mineral, anatase, and feldspar.

Clay EL-69-2, which is nearly as coarse textured as clay EL-60-6, contains most of its quartz in the silt sizes. Besides quartz and small flakes of kaolinite, it contains about 25 percent illite and muscovite and a small quantity of dark-brown organic matter. Slight asymmetry in the illite and kaolinite basal reflections indicates the presence of small quantities of mixed-layer mineral and "fire-clay mineral" in addition to the illite and kaolinite. The illite occurs as small shreds or flakes distributed in a matrix of kaolinite.

Clay O-5-6 contains appreciable quantities of "fire-clay mineral," some kaolinite, and less illite than clays EL-69-2 and O-38-4. It also contains montmorillonite, a mixed-layer mineral, and much more organic matter than the other clays. It is the finest grained of the four clays, and its particle-size distribution is not unimodal. The quartz grains are predominantly of very fine silt size. The birefringent clay does not occur as visibly distinct shreds in the thin section, although it has good preferred orientation.

Clay O-38-4 is also a fine-grained clay, containing about 40 percent kaolin (only a small proportion of which is "fire-clay mineral"), 30 percent quartz, 25 percent illite and mixed-layer mineral, and a small quantity of organic matter. Most of the kaolinite is in the fraction finer than 2 microns. This clay contains less total quartz but more quartz in the minus 2-micron fraction than the other three clays.

DIFFERENTIAL THERMAL ANALYSES

EQUIPMENT AND METHODS

A variety of apparatus for differential thermal analysis has been described rather extensively in the literature. The apparatus consists essentially of control and recording equipment, furnace, sample holders, and thermocouples. The apparatus used in the Geological Survey laboratory includes a Leeds and Northrup Model S Micromax recorder operating in conjunction with a controller, timer, and Variac transformer by means of which the temperature of the furnace can be increased at a uniform rate. The equipment permits variations in heating rate from 0° to 25° C. per minute. The furnace temperature is recorded on the Micromax instrument.

The furnace is the vertical platinum-wound type with an inside diameter of slightly more than 1 inch. The sample and reference material holder is made from alumina, and the differential thermocouple junctions are placed in the approximate center of the two 3/16-inch wells. These two junctions and that of the furnace temperature thermocouple are placed at an equal distance from the furnace walls in order to insure equal heat distribution. Platinum and platinum - 10 - percent - rhodium thermocouples are used throughout.

The differential thermocouple output is preamplified ahead of the Leeds and Northrup Speedomax which records the differential curves. A high degree of amplification of the circuit is possible. The apparatus used is similar to those described by Kerr and Kulp (1948), Kerr, Kulp, and Hamilton (1949), Lambe (1951), and McConnell and Early (1951).

All the analyses reported in this paper were run at an amplification low enough to keep the maximum peaks on the chart paper. Inasmuch as a uniform amplification was deemed necessary in order to facilitate comparisons, rather small peaks were produced on the thermal curves of samples high in quartz. The rate of heating of the furnace was 10° C. per minute for all samples.

RESULTS OF DIFFERENTIAL THERMAL ANALYSES

Three differential thermal analyses were run on each of the clays investigated—on the whole or unfractionated clay, the minus 2-micron fraction, and the 2- to 8-micron fraction. Reference analyses of the A.P.I. standard clay, H-4, Macon, Georgia, kaolin (Kerr, Kulp, and Hamilton, 1949), and a commercial sample of Champion and Challenger ball clay from the H. C. Spinks Clay Company, Paris, Tennessee, were run for comparison and are included in the illustrations (Figs. 8, 9, 10).

The differential thermal curves produced by the four Kansas clays and the two reference samples are dominantly those of kaolinite. This is true despite the fact that illite, montmorillonite, and mixed-layer clay minerals total nearly as much as the kaolinite in sample EL-69-2 and represent a considerable proportion of samples O-5-6 and O-38-4 and the Champion and Challenger ball clay. This dominance of the kaolinite curves is due to the fact that endothermic and exothermic reactions produced by heating kaolinite represent much greater energy absorption and output than those produced by heating the other clay minerals.

The differential thermal curves of the original (unfractionated) clays, including the Tennessee ball clay, are shown in Figure 8. For sample EL-60-6 only the characteristic endothermic and exothermic curves of kaolinite were produced. A broad exothermic curve below 400° C. on the thermogram for sample EL-69-2 indicates organic material, probably lignite. A broadening of the endothermic curve slightly below 600° C., and slight endothermic reaction at 900° C. are effects probably produced by illite and mixed-layer clay minerals. The thermogram for sample O-5-6 shows a small but definite endothermic curve at about 200° C. and an inflection at 700° C. indicating a small percentage of montmorillonite. The broad endothermic peak extending from about 450° to 660° C. is probably a composite effect of kaolinite, illite, and mixed-layer minerals. A high-temperature endothermic peak below 900° is too slight to be ascribed definitely to clay-mineral reactions. The exothermic reaction with a relatively sharp peak at about 410° C. was produced by organic material. It is probable, however, that the sharp inflection in the curve can be ascribed to a small amount of pyrite. The thermal curve produced by clay O-38-4 is quite similar to those produced by clays EL-69-2 and O-5-6. The reactions characteristic of kaolinite are dominant, and probably mask the 500° to 650° C. endothermic curve for illite and the slight exothermic reaction above 900°. Illite is indicated by a small endothermic peak at 900°. A broad, shallow exothermic reaction extending from about 250° to 425° was probably produced by a small percentage of organic material. The sharp inflection at 400° may have been caused by a very small percentage of pyrite. A slight endothermic reaction near 200° is indicative of montmorillonite, but this clay mineral was not detected by x-ray analysis.

Differential thermal curves from the minus 2-micron fractions of the four clays and from an unfractionated sample of Macon, Georgia, kaolin (A.P.I. standard H-4) are shown in Figure 9. The differential curves for the finer fractions differ from those for the whole clays chiefly in the increased areas under the peaks, with the exception of the exothermic reactions for organic material. In this case the peaks are greatly reduced or absent. This difference is especially noticeable on the curves for clays EL-69-2 and O-5-6. The organic matter in clay O-5-6 was removed with H_2O_2 before fractionation, but clay EL-69-2 was not treated with H_2O_2 and the absence of a strong exothermic reaction for organic material indicates that it was concentrated in the coarser fractions.

The differential thermal curves for the 2- to 8-micron fractions of three of the clays (Fig. 10) differ markedly from those of the

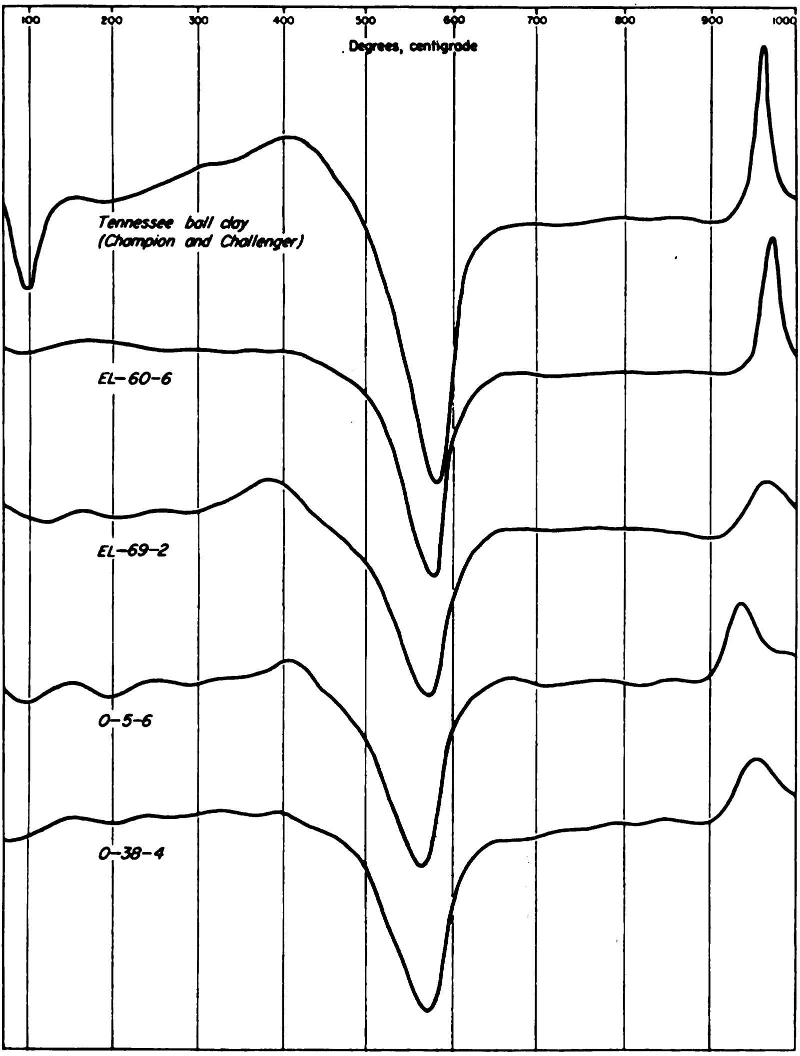

FIG. 8.—Differential thermal curves of the four Kansas clays and a Tennessee ball clay.

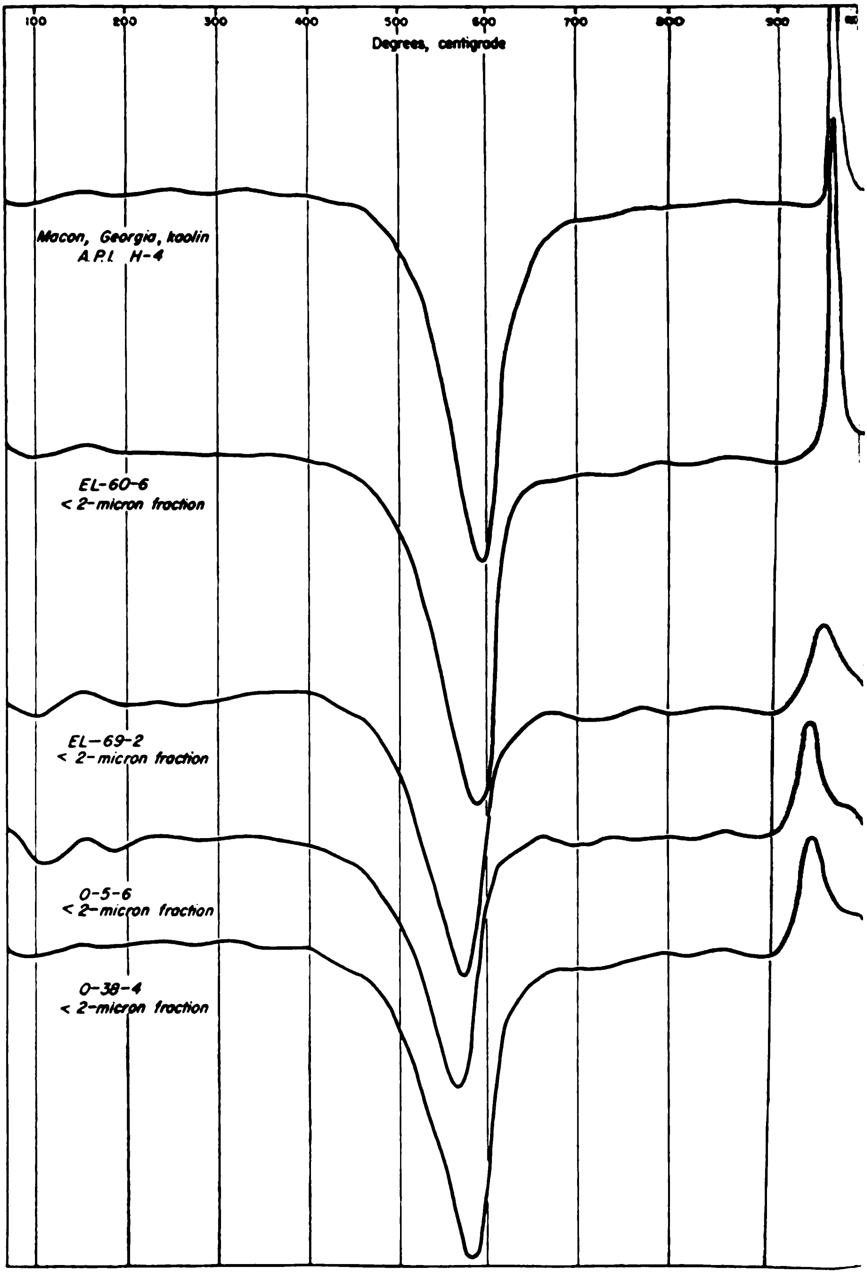

Fig. 9.—Differential thermal curves of the minus 2-micron fraction of the four Kansas clays and Macon, Georgia, kaolinite.

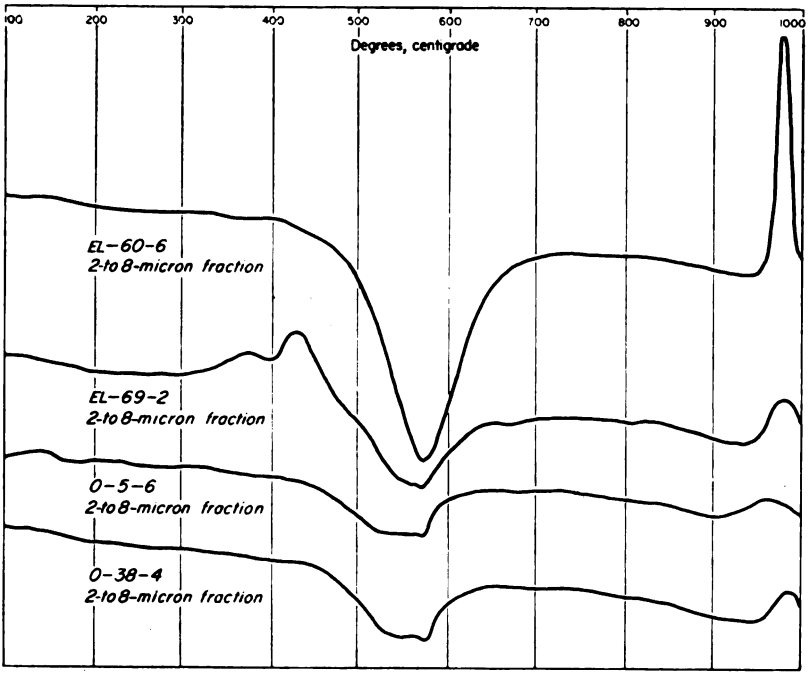

FIG. 10.—Differential thermal curves of the 2- to 8-micron fraction of the four Kansas clays.

finer fractions and of the whole clays. The 2- to 8-micron fraction of clay EL-60-6, however, produces a curve that is essentially the same as that for the whole clay, although the endothermic peak for kaolinite is broader, and indicates a greater percentage of kaolinite. The thermogram for clay EL-69-2 has a strong exothermic peak from 300° to 400°C. showing a concentration of organic material and perhaps some pyrite in the 2- to 8-micron fraction whereas the other three clays do not show this concentration. The characteristic peaks for kaolinite are small for all the clays except EL-60-6, and these three clays (EL-69-2, O-5-6, and O-38-4) produced a small but definite inflection at the *alpha* to *beta* quartz inversion. The fact that this inversion occurs at about 575° C. on the curves indicates that all other temperatures are approximately correct.

Peak temperatures and areas are given in Table 10. The endothermic kaolinite peaks occurred at higher temperatures on the thermograms of the minus 2-micron fractions than on those of

TABLE 10.—*Data from thermal analysis curves*

	EL-60-6	EL-69-2	O-5-6	O-38-4	H-4	C&C
Endothermic peaks						
Peak temperatures, degrees C.						
Unfractionated clay	580	565	565	575	600	583
2-8-micron fraction	582	560	550	555		
<2-micron fraction	590	575	570	590	575	
Peak areas, square cm.						
Unfractionated clay	21.80	19.19	21.65	21.13	39.14	24.13
2-8-micron fraction	24.49	10.09	7.05	8.77		
<2-micron fraction	34.90	28.38	26.52	33.24	25.65	
Exothermic peaks						
Peak temperatures, degrees C.						
Unfractionated clay	970	965	935	950	930	963
2-8 micron fraction	977	982	960	982		
Minus 2-micron fraction	960	950	952	940	965	
Peak areas, square cm.						
Unfractionated clay	5.06	2.13	2.53	2.97	9.14	5.10
2-8-micron fraction	6.65	1.50	0.57	1.46		
<2-micron fraction	7.43	2.52	3.36	4.28		

either the whole clay or the 2- to 8-micron fractions. With the exception of clay EL-60-6 the same peak occurred at lower temperatures on the 2- to 8-micron fractions. The exothermic peaks, on the other hand, occurred at the lowest temperatures on the minus 2-micron fractions, and at the highest temperatures on the 2- to 8-micron fractions. Areas under both the endothermic and exothermic peaks are roughly proportional to the concentration of kaolinite in the samples. These areas are larger for the 2- to 8-micron fraction of clay EL-60-6 than those for the whole clay, but are markedly smaller for the same size fraction of the other three clays. In every case the minus 2-micron fraction produced peaks enclosing the largest areas.

An attempt was made to use the peak areas as a means of estimating the percentage of kaolinite contained in each clay and clay fraction. It was possible to estimate the order of magnitude, but accurate quantitative estimates are not possible unless a complicated series of known clays is used. Particle size, perfection of crystallization, and the influence of the other clay minerals would have to be taken into account. In a general way the curves for the Macon, Georgia, kaolin and clay EL-60-6, and for the Champion and Challenger ball clay and the other three clays show quantitative agreement. The quantitative aspects of the differential thermal curves will be compared with other data in another section.

CERAMIC PROPERTIES

METHODS OF TESTING

STANDARD OR ROUTINE TESTS

The procedure and methods used in this investigation followed as closely as was considered advisable the standards recommended by the Committee on Standards of the American Ceramic Society (Watts and others, 1928) and American Society for Testing Materials (1952) standard methods of testing for apparent porosity, water absorption, apparent specific gravity, and bulk density of burned refractory brick (A.S.T.M. designation C 20-46); water absorptions and saturation coefficient (A.S.T.M. designation C 67-50); and pyrometric cone equivalent (A.S.T.M. designation C 24-46).

The amount of water, determined by previous tests, required for optimum workability was mixed with the minus 20-mesh dry clay and the mixture stored for several hours in closed containers. After this the clay was thoroughly mixed and wedged.

Test bars approximately 1⅛ inches square in cross section and 7 inches long were hand-molded from the prepared clay. The bars were marked immediately with a 14 cm tram (for linear shrinkage measurements) and weighed both in air and suspended in kerosene to determine plastic weights and volumes. After the test bars were completely dried they were again measured and weighed in air and suspended in kerosene to determine dry weights and volume. From these plastic and dry data, water of plasticity, shrinkage water, pore water, volume shrinkage, and linear shrinkage were calculated.

Because test bars from all four clays were fired together, the effects of heat treatment are completely comparable. The bars were fired at a slow rate in a Globar-heated electric furnace. At the end of the firings the kiln temperature was held at near the maximum for at least 1 hour so that the pyrometric cones were "soaked down" and uniform penetration of heat was assured.

The test bars were fired to five temperatures, cone 05 (approximately 1030° C.), cone 02 (approximately 1095° C.), cone 4 (approximately 1165° C.), cone 8 (approximately 1225°C.), and cone 10 (approximately 1260° C). After each firing the test bars were weighed, then saturated in cold water for 24 hours and again weighed to determine the cold-water absorption. The same procedure was repeated after immersion in boiling water for 5 hours, then cooling, to determine the boiling-water absorption. Volumes were determined from the difference between the weight of the saturated test bar in air and suspended in water. Measurements of linear shrinkage were also made. From the above data linear and volume shrinkages, absorptions, saturation coefficient, apparent porosity, apparent specific gravity, bulk specific gravity, and ignition loss were determined. The saturation coefficient is the ratio of absorption determined by 24-hour submersion in cold water to that after 5 hours submersion in boiling water. The saturation coefficient is a more reliable index to the resistance of burned clay products to freezing and thawing and other weathering agents than any other method that has been devised.

A separate and independent test was run on all four clays as a check on the accuracy of the first series. The test bars were fired to cone 4 only, however.

REFRACTORIES TESTS

Standard 9 by 4½ by 2½-inch fire-clay bricks were prepared from clays EL-60-6 and O-5-6 by the dry press method using 2,000 psi pressure in forming the bricks. Carefully graded grog (calcined and crushed clay) was mixed with the plastic clay. In the preparation of the EL-60-6 batch 70 percent grog was used, and in the O-5-6 batch 80 percent grog was used. The bricks were fired to cone 13 and cone 14 in a down-draft, gas-fired kiln.

pH AND VISCOSITY

Both the pH and the viscosity of the four clays and of Champion and Challenger ball clay from Tennessee were determined on suspensions containing 100 grams of clay and 250 grams of distilled water. The clay suspensions were thoroughly agitated with an electric stirrer. The pH values were determined with a Beckman Model H2 glass electrode pH meter. Apparent viscosities were determined with a Brookfield Model LVF Synco-Lectric viscosimeter (Oliver, 1948). The same suspensions were used for both determinations.

CERAMIC DATA

STANDARD OR ROUTINE TESTS

The data on ceramic tests of these clays (Table 11) show an obvious relationship to the properties of the clays observed in the field and during the process of preparing the test bars. Clay EL-60-6 is a coarse-grained, "lean," relatively nonplastic clay, whereas clay O-5-6 is a fine-grained, "fat" highly plastic clay. Clays EL-69-2 and O-38-4 are also fine-grained, plastic clays, but less so than clay O-5-6. These two clays are very much alike in this respect, but O-38-4 is slightly more plastic than EL-69-2 and EL-69-2 is the coarser of the two. The water of plasticity, shrinkage water, and volume shrinkage on drying accurately reflect these differences. The "fatter," finer grained, and more plastic the clay the higher the water of plasticity, shrinkage water, and volume shrinkage. The order from lean to fat, and from low to high percentages for the above properties is EL-60-6, EL-69-2, O-38-4, and O-5-6. These are empirical characteristics universally observed by workers in clay, but which can be verified by more scientific means. "Plasticity" is a property of clays that is not only difficult to measure accurately, but is in fact incompletely defined. Particle size, however, is a measurable quantity. Specific surface is also measurable and is definitely related to particle size and shape and to the plasticity, or perhaps more accurately the workability of the clays. This relation will be discussed in a separate section.

The differences noted above are also reflected in the shrinkages and absorptions of the clays when fired to cone 05, but above this temperature other factors such as the fusibility of the clay become increasingly effective. The higher temperature characteristics of the clays will be discussed in relation to the chemical composition in the section on interpretation and correlation. Although the pyrometric cone equivalent of clay EL-60-6 (cone 28-29) is slightly lower than that for clay O-5-6 (cone 30), within the range of the ceramic tests the fine-grained O-5-6 clay is affected more by increasing temperatures than the coarse-grained EL-60-6 clay (Table 11). The same relation can be observed in the fired data on the other two clays, but it is less obvious. The causes for these differences are complex and will be discussed in the last section, but it should be noted in connection with the presentation of the ceramic data that coarse-grained clays like EL-60-6, made up almost entirely of

TABLE 11.—*Data on standard ceramic tests of the four clays investigated*

	EL-60-6	EL-69-2	O-5-6	O-38-4
PLASTIC AND DRY PROPERTIES				
Water of plasticity, percent	16.31	22.65	26.94	22.89
Shrinkage water, percent	5.63	10.85	15.55	11.62
Pore water, percent	10.68	11.80	11.39	11.27
Volume shrinkage, percent	10.91	20.61	30.19	22.55
Linear shrinkage (measured), percent	3.51	5.90	8.08	5.33
Linear shrinkage (calculated from vol. shrink.), percent	3.51	6.44	9.20	7.02
FIRED PROPERTIES				
Pyrometric cone equivalent	28-29	23-29	30	27
Fired color at				
Cone 05 (1030°C.)	Ivory	Light buff	Light buff	Cream
Cone 02 (1095°C.)	Nearly white	Cream	Dark cream	Dark cream
Cone 4 (1165°C.)	Off white	Cream	Light buff	Dark cream
Cone 8 (1225°C.)	Off white	Dark cream	Dark cream	Yellow cream
Cone 10 (1260°C.)	Off white	Light gray	Yellow tan	Yellow gray
Cone 16 (1450°C.)	Light cream			
Volume shrinkage, percent at				
Cone 05	1.07	2.46	6.90	5.78
Cone 02	1.15	8.67	11.54	12.54
Cone 4	1.46	15.79	18.28	19.19
Cone 8	3.17	21.35	19.37	23.92
Cone 10	4.39	19.59	21.20	23.60
Cone 16	2.22			
Linear shrinkage (measured), percent at				
Cone 05	0.09	0.57	1.73	1.50
Cone 02	0.00	2.64	3.33	3.70
Cone 4	0.37	4.84	5.58	5.83
Cone 8	0.93	6.16	5.70	6.90
Cone 10	1.11	5.59	6.41	6.77
Cone 16	0.37			
Linear shrinkage (calculated from vol. shrink.), percent at				
Cone 05	0.36	0.83	2.36	1.97
Cone 02	0.39	2.98	4.00	4.37
Cone 4	0.49	5.57	6.51	6.86
Cone 8	1.07	7.69	6.93	8.71
Cone 10	1.49	7.01	7.64	8.58
Cone 16	0.75			

Absorption (24 hours cold water), percent at					
Cone 05		14.85	13.74	13.27	12.95
Cone 02		14.96	10.30	10.59	9.28
Cone 4		14.49	5.95	5.75	4.56
Cone 8		13.43	0.83	2.62	0.02
Cone 10		13.04	0.91	0.52	0.02
Cone 16		11.79			
Absorption (5 hours boiling water), percent at					
Cone 05		16.92	14.41	14.06	13.66
Cone 02		17.08	10.93	11.10	9.78
Cone 4		16.74	6.17	5.97	4.85
Cone 8		15.87	1.20	3.20	0.15
Cone 10		15.35	2.17	1.02	0.14
Cone 16		14.97			
Saturation coefficient at					
Cone 05		0.88	0.95	0.94	0.95
Cone 02		0.88	0.94	0.95	0.95
Cone 4		0.87	0.96	0.96	0.94
Cone 8		0.85	0.69	0.82	0.13
Cone 10		0.85	0.42	0.51	0.20
Cone 16		0.79			
Apparent porosity, percent at					
Cone 05		30.97	26.51	26.71	26.23
Cone 02		21.23	21.42	22.20	20.15
Cone 4		30.80	13.08	12.90	10.82
Cone 8		29.84	2.72	7.01	0.35
Cone 10		29.01	4.71	2.30	0.03
Cone 16		27.70			
A. Apparent specific gravity B. Bulk specific gravity at					
Cone 05	A.	2.65	2.50	2.59	2.60
	B.	1.83	1.84	1.90	1.92
Cone 02	A.	2.66	2.49	2.57	2.58
	B.	1.83	1.96	2.00	2.06
Cone 4	A.	2.65	2.44	2.48	2.50
	B.	1.84	2.12	2.16	2.23
Cone 8	A.	2.68	2.33	2.36	2.37
	B.	1.88	2.27	2.19	2.36
Cone 10	A.	2.66	2.28	2.30	2.36
	B.	1.89	2.17	2.25	2.35
Cone 16	A.	2.56			
	B.	1.85			
Hardness as to steel at					
Cone 05		Softer	Softer	Softer	Softer
Cone 02		Softer	Softer	As hard	As hard
Cone 4		Softer	Harder	Harder	Harder
Cone 8		Softer	Harder	Harder	Harder
Cone 10		Softer	Harder	Harder	Harder
Cone 16		Softer			

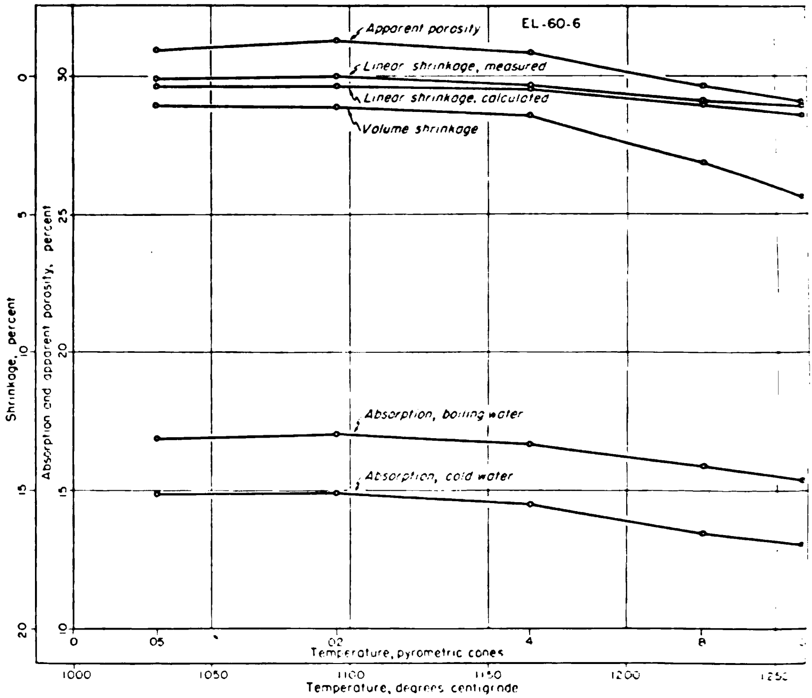

FIG. 11.—Graph showing changes in fired properties with increasing temperature for clay EL-60-6.

pure kaolinite and pure quartz and containing a very small percentage of fluxes, shrink in firing and show a decreasing porosity largely because the quartz-kaolin proportion approaches a eutectic. Clay O-5-6, on the other hand, contains a much larger percentage of the fluxes such as calcium, magnesium, and the alkalies, but is more refractory because it contains a higher percentage of kaolinite. At the comparatively low temperatures used in these tests the fluxes were active in clay O-5-6 and produced incipient fusion, shrinkage, and decreased porosity. The reaction between the relatively nonrefractory mixture of quartz and kaolinite in clay EL-60-6 produces decided fluxing action only at much higher temperatures.

The fired properties of the four clays are shown graphically in Figures 11 to 15. The relation of the various properties is much more obvious in the graphic representation than it is in Table 11. The curves for the shrinkage characteristics are plotted in reverse

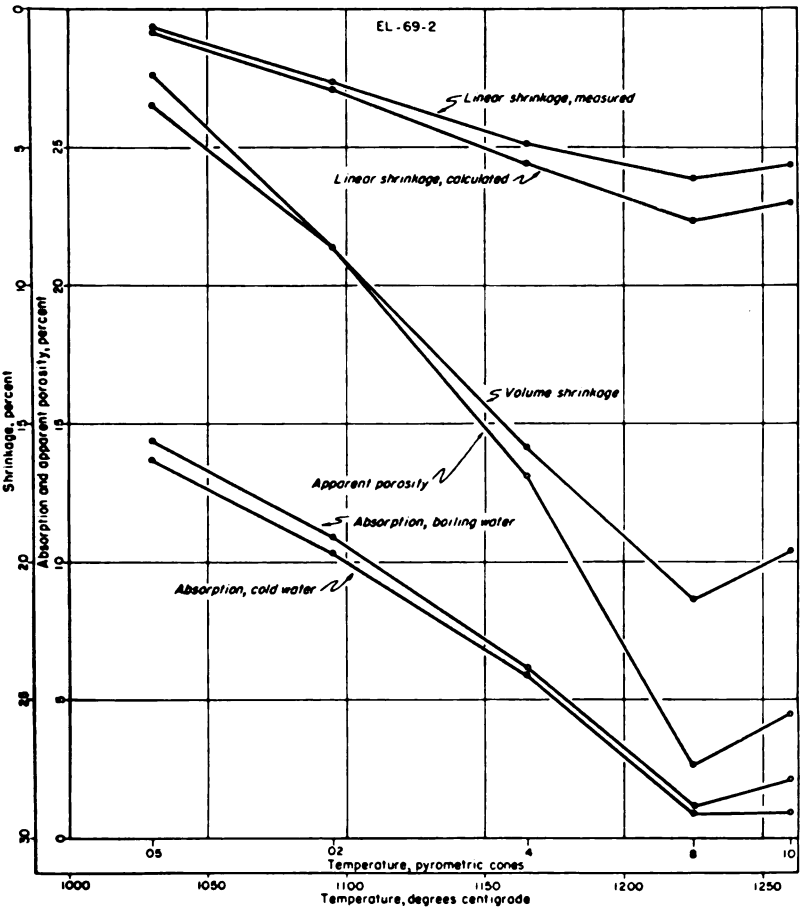

Fig. 12.—Graph showing changes in fired properties with increasing temperature for clay EL-69-2.

in order to facilitate comparison with absorption and porosity. It will be noted that the general trends of all fired properties of each clay are comparable, showing that they are in fact interrelated properties. In Figure 15 the apparent porosity percentages of all four clays are shown graphically. The apparent porosity was chosen from the various fired characteristics because it is calculated from both the absorption and the volume shrinkage and therefore is representative of all the fired properties of each clay. It will be noted that clays EL-69-2, O-5-6, and O-38-4 are very similar, and

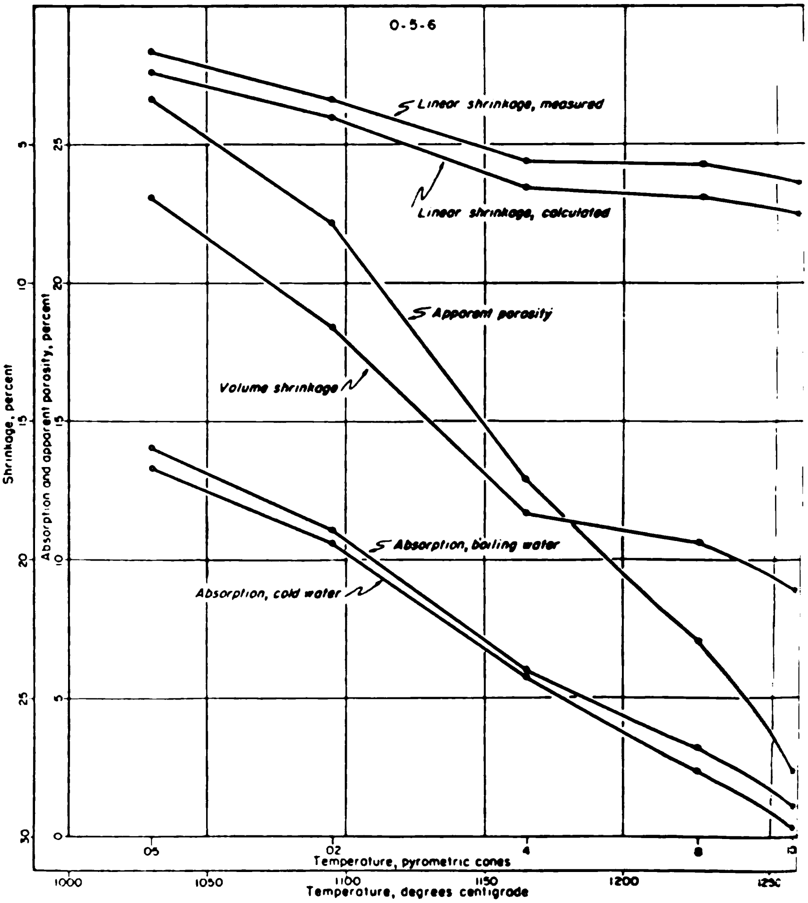

FIG. 13.—Graph showing changes in fired properties with increasing temperature for clay O-5-6.

that EL-60-6 is in a class by itself. This difference is apparent in all the work that was done on these four clays.

The ceramic test data on clays EL-69-2 and O-38-4 indicate a fairly uniform change in fired properties with increasing temperature up to cone 8. At this temperature clay O-38-4 is almost completely vitrified and clay EL-69-2 is nearly vitrified. At cone 10 the data on both of these clays indicate slight overfiring whereas clay O-5-6 is approaching vitrification at that temperature but is not overfired. The data for clay EL-60-6 produce a quite different pattern (Fig. 11) with only slight differences in fired properties at the temperatures shown. Clay EL-60-6 was fired to cone 16 (about 1450° C.) although the others were fired no higher than cone 10. At cone 16 the EL-60-6 test bars expanded slightly, but were slightly less porous than they were at cone 10, indicating that a decided decrease in porosity would be attained at a considerably higher temperature.

In addition to a separate run on all four clays including a cone 4 firing only, another separate run was fired to cone 10 only. Data on this test indicate that the evidence of overfiring shown in Table 11 and in Figures 12 and 15 was the result of the conditions of

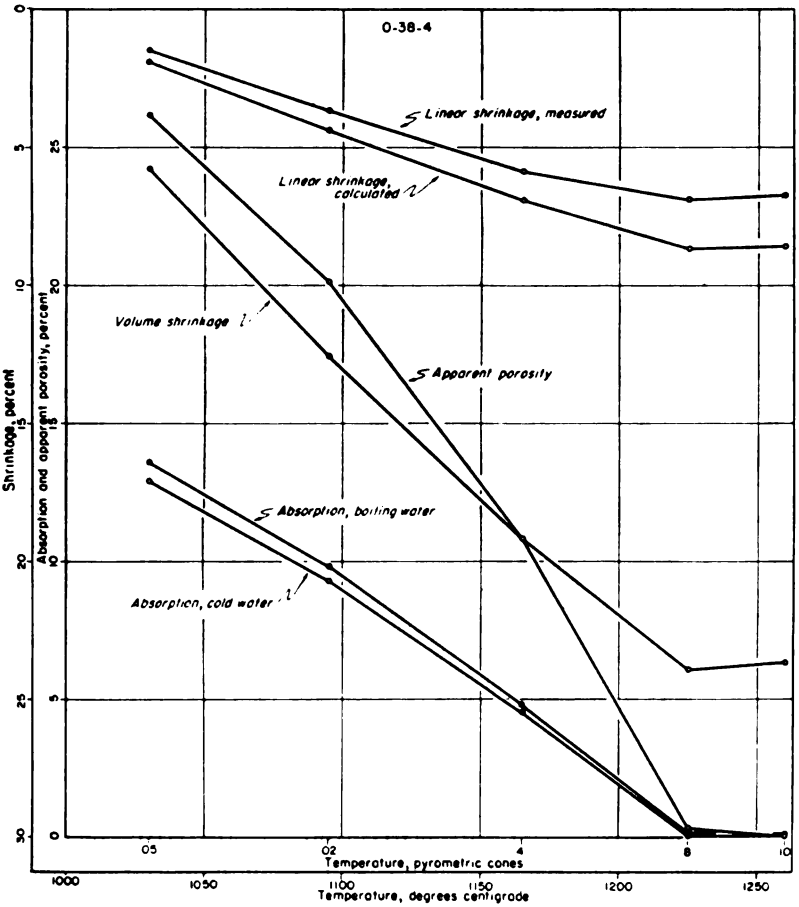

FIG. 14.—Graph showing changes in fired properties with increasing temperature for clay O-38-4.

firing. The check run was fired very slowly, with the result that shrinkages increased and absorptions and porosity decreased from the cone 8 to the cone 10 temperature. In the graphic representation of the data for clay EL-69-2 (Fig. 12) the upturn from cone 8 to cone 10 would have been represented by a decrease in the rate of change if the check data had been used.

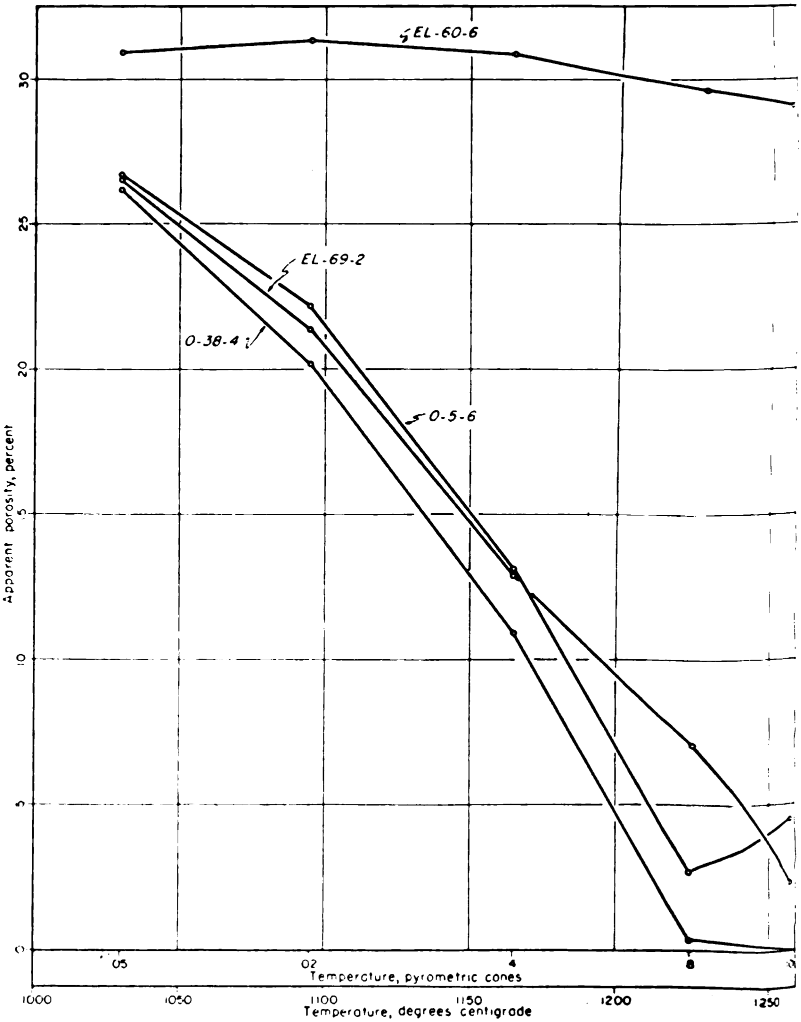

Fig. 15.—Graph showing changes in porosity with increasing temperature for the four clays.

TABLE 12.—*Ceramic data on the minus 2-micron fractions of the four clays*

	EL-60-6	EL-69-2	O-5-6	O-38-4
Water of plasticity, percent	36.67	45.95	31.97	33.75
Linear drying shrinkage, percent	5.82	6.95	6.38	6.38
Firing shrinkage (cone 4-5), percent	11.91	12.03	8.51	9.58
Cold water absorption (cone 4-5), percent	3.85	1.00	1.00	1.00

Partial ceramic tests were also run on the minus 2-micron fractions of all four clays. This material is not only fine-grained, but consists almost entirely of clay minerals. As should be expected the percent water of plasticity was much higher on these tests. The linear drying shrinkage, however, is decidedly higher for the finer fraction only for clay EL-60-6. The shrinkage on the fine fraction of clay EL-69-2 is slightly higher, but on the fine fractions of clays O-5-6 and O-38-4 the shrinkage is lower. Firing shrinkages at cone 4-5 were much higher, and the absorptions indicated that the test bricks were near vitrification at that temperature. Test data on the minus 2-micron fractions are shown in Table 12.

REFRACTORIES TESTS

Standard 9 by 4½ by 2½ inch fire-brick shapes were made from clays EL-60-6 and O-5-6 containing 70 percent and 80 percent, respectively, of hard-fired grog. The bricks were fired in an A.S.T.M. standard reheat furnace to cone 13 and cone 14. Data on these are given in Table 13.

A characteristic of grogged clays is that they can be fired to much higher temperatures without bloating or other indications of overfiring than is possible with the ungrogged clay. These two clays show the same characteristics; however, the decrease in percentage absorption with increased temperature is much higher for clay O-5-6 than for clay EL-60-6.

TABLE 13.—*Data on grogged refractory shapes*

	Boiling water absorption, percent	
Sample no.	Cone 13	Cone 14
EL-60-6	22.80	22.71
O-5-6	13.26	11.16

pH AND APPARENT VISCOSITY DATA

The pH and viscosity determinations are discussed as a unit because the tests were run on the same suspensions containing 100 grams of clay to 250 grams of water. The results of the tests are given in Table 14.

The pH and apparent viscosity of the first three clays in Table 14 are rather uniform and more or less normal. Usually the pH of Dakota formation clays is somewhat higher. The much higher pH of clay O-38-4 is typical for freshly sampled Dakota formation clays, whereas the lower pH obtained on the preceding three is typical for samples that have been in storage for a long time. This explains the low values obtained on three of the clays, but O-38-4 has been in storage for an equal length of time so its pH is anomalous. The viscosities of the first three clays can be readily understood. Samples EL-69-2 and O-5-6 contain a relatively high percentage of fine-grained clay, whereas EL-60-6 has a higher quartz content, and the particle size of both the quartz and the clay mineral is coarse.

The low values obtained for apparent viscosity on clay O-38-4 can be explained by the fact that the pH is on the alkaline side. The extremely high apparent viscosity shown for the Champion and Challenger ball clay is difficult to explain in view of the normal pH obtained. This high viscosity is particularly puzzling in view of the fact that casting bodies containing this Tennessee ball clay are easily deflocculated by the addition of electrolytes. Under similar conditions clay O-38-4 is also easily deflocculated but tends to be thixotropic. Clay EL-60-6 deflocculates very easily, but the other two are not only difficult to deflocculate, but tend to be thixotropic as well.

TABLE 14.—*pH and apparent viscosity of clay slips at various time intervals*

	pH			Apparent viscosity (centipoises)	
	Time elapsed after mixing			Time elapsed after mixing	
Sample no.	15 minutes	24 hours	3 days	4 hours	3 days
EL-60-6	3.68	3.84	3.85	18	19
EL-69-2	3.80	3.92	3.88	25	40
O-5-6	4.20	4.30	4.40	36	40
O-38-4	7.20	7.20	7.25	6	7
*C. & C.	4.00	4.38	4.43		338

*Tennessee ball clay.

INTERPRETATION AND CORRELATION OF DATA

The four samples that are the subject of this study have been designated as clays, although the samples contain from 25 to more than 50 percent quartz. The term "clay material" which Grim (1953) uses to describe any fine-grained, natural, earthy, argillaceous material is preferable from the standpoint of accuracy despite the fact that the clay minerals present in the samples must be considered as the dominant factors in attempting to account for the physical and chemical properties of the clays.

The particle size and shape of the clay minerals, the quartz and other so-called nonplastics, and the adsorbed ions and soluble salts determine the clay-water behavior of the clays in respect to such physical properties as plasticity and shrinkage on drying. The effect of heat on the clays, especially in the higher temperature range, is determined to a limited extent by particle size and shape, but largely by the chemical composition of the minerals present. The objectives of this study have been, therefore, to determine the kind and relative percentage of the clay minerals, quartz, and other constituents, by means of x-ray, differential thermal, and chemical analyses, and by examination with the optical and electron microscope; particle size by sedimentation methods; and particle shape by means of the optical and electon microscopes. A further objective of the investigation was the determination of the clay-water characteristics of the clays such as water of plasticity, plasticity, and drying shrinkage; and determination of the effect of heating to relatively high temperatures as measured by shrinkage, water absorption, and (correlatively) porosity. In the following paragraphs we shall attempt to show the interrelation of the fundamental properties, and the relation of the fundamental to the ceramic properties.

INTERRELATED METHODS OF DETERMINING MINERAL COMPOSITION

The kind and percentage of clay minerals and of quartz, feldspar, and muscovite were determined by a combination of methods. In fact, reliable estimates can be achieved only by correlation and interpretation of a variety of data, which have been reported under separate headings.

X-ray diffraction furnished an accurate qualitative basis for estimates of mineral content of the clays (Figs. 2-7). Differential thermal analyses, electron micrographs, and optical examination supplemented the x-ray data. These data also furnished the basis for semiquantitative estimates which were correlated with the chemical composition in order to obtain greater accuracy. In calculating from the chemical composition, chemical analyses of relatively pure illite, montmorillonite, and mixed-layer (illite-montmorillonite) clay having intermediate compositions were used. The theoretical composition of kaolinite was used because it does not have the range of composition characteristic of the other clay-mineral groups. The rough quantitative estimates for the original or whole clay, the 2- to 8-micron fraction, and the minus 2-micron fraction for each of the four clays, reported to the nearest 5 percent, are given in Table 15.

The quantitative estimates of mineral content of the clay obtained from the x-ray diffraction data alone agreed within 5 percent with those calculated from the chemical composition, and some of the percentages obtained by the two methods were in much closer agreement.

Although the differential thermal analysis curves indicate accurately the various clay minerals present in the samples, their usefulness is limited so far as quantitative estimates are concerned.

TABLE 15.—*Estimated percentages of the minerals found in the whole clay and in two fractions*

	Minerals present, percentage						
Sample no.	Kaolinite	Illite	Mixed-layer	Montmorillonite	Muscovite	Feldspar	Quartz
			EL-60-6				
Whole clay	45						50
2-8-micron	55						40
<2-micron	95						1
			EL-69-2				
Whole clay	35	20	5		5	trace	35
2-8-micron	20	20	5		<5		50
<2-micron	60	25	10				< 5
			O-5-6				
Whole clay	40	5	15	10		trace	30
2-8-micron	15	<10	< 5	< 5			70
<2-micron	55	10	15	10			< 5
			O-33-4				
Whole clay	40	20	< 5		trace	trace	35
2-8-micron	15	<10	< 5		trace		70
<2-micron	65	<25	< 5				5

chiefly because the intensity of the endothermic and exothermic reactions produced by the different clay minerals differ greatly. Furthermore, both kaolinite and illite, the major clay-mineral constituents of the clays studied, produce endothermic reactions within the range of 400° to 700° C.; therefore, accurate quantitative distinctions can be made only with the aid of an elaborate series of standards. Clay EL-60-6, composed almost entirely of kaolinite and quartz, was in fair quantitative agreement with the Macon, Georgia, kaolin, and the other three clays showed a quantitative relation with each other and with the Champion and Challenger ball clay.

It was possible to determine, however, that the areas obtained under the endothermic peaks ranging from 400° to 650° C. (Figs. 8-10) rather accurately represent the percentage clay-mineral composition. Assuming that the mineral composition of the clays determined from x-ray diffraction data and chemical analyses was accurate, and using the percentages obtained before "rounding off" to the nearest 5 percent (Table 10), the expected relative size of the endothermic peaks was calculated by the following method. Speil and others (1945) tabulated peak areas for various clay minerals as determined with the same apparatus under identical conditions. The area under the 620° C. endothermic peak for kaolinite was found to be 61 square cm under the conditions of their tests, whereas under the same conditions the 605° C. peak area for illite was 16.25 square cm. From data obtained by us a comparable area for mixed-layer clay (illite-montmorillonite) was assumed to be 10 square cm. Using the above described estimated percentages of the various clay minerals in the samples, the theoretical areas were computed by multiplying the percentage of kaolinite by 61, the percentage of illite by 16, and the percentage of mixed-layer clay minerals by 10. Montmorillonite was not included because it does not produce an endothermic peak within the temperature range considered. The computed areas were somewhat larger than those obtained by us due to differences in amplification. The areas of the endothermic peaks determined experimentally are compared to the calculated ones in Table 16. Values for the standard clays previously mentioned were also included, although fewer data were available for calculating the percentage of clay minerals present in the standard clays. The percentage alumina in the various clays is also compared to the areas of the endothermic peaks in Table 16.

The ratios of calculated to measured areas of the endothermic peaks for the four Kansas clays show that the differential thermal curves rather accurately reflect the percentage clay-mineral composition of the clays. The maximum deviation from the average is only 3.8 percent. Although there is a marked difference in the two standard kaolins, the average of the two is only 0.6 percent higher than the average for the four Kansas clays. The ratios for the two Tennessee ball clays are similar to each other, but markedly higher than those for the Kansas clays.

The close agreement of the ratios of calculated to measured areas of the endothermic peaks indicates that factors such as particle size and perfection of crystallization have little influence on the size of the peaks. Clays EL-60-6 and O-5-6, for example, range from large, very well-formed crystals to very small, imperfect ones, yet the ratios are in close agreement.

The ratios of measured areas of endothermic peaks to the alumina content of the clays are similar only for clays having similar clay-mineral compositions. This is to be expected, of course, because complete correlation could be obtained only if the percentage of alumina found in each clay mineral were directly proportional

TABLE 16.—*Areas of endothermic peaks compared to calculated areas and to percentages of alumina*

Sample no.	Measured area of endothermic peak, sq.cm.	Calculated area of endothermic peak, sq.cm.	Alumina, percentage	Ratio, calculated to measured areas	Ratio, measured area to alumina
EL-60-6	21.80	27.45	17.80	1.259	0.817
EL-69-2	19.19	25.05	21.18	1.305	1.104
O-5-6	21.65	26.70	24.29	1.233	1.122
O-38-4	21.13	28.10	23.09	1.330	1.093
C. & C.*	24.13	37.23	27.86	1.543	1.155
Tenn. No. 5**	26.88	39.80	29.96	1.481	1.115
H-4 kaolin†	39.14	56.73	37.20	1.449	0.950
Bell kaolin††	52.84	59.78	38.40	1.131	0.727
Average of H-4 & Bell kaolins	45.99	58.25	37.80	1.290	0.823
Average of 4 Kansas clays				1.282	1.034

*Ball clay furnished by H. C. Spinks Clay Co., Paris, Tenn.
**Ball clay furnished by Kentucky-Tennessee Clay Co., Mayfield, Ky.
†Macon, Georgia, Kaolin. A.P.I. standard sample.
††Georgia kaolin furnished by the Bell Foundry, St. Louis, Mo.

to the areas of endothermic peaks produced by them. It will be noted that for clays in which kaolinite is practically the only clay mineral (H-4 kaolin, Bell kaolin, and clay EL-60-6) the ratios compare fairly well. The same similarity can be noted for the other three Kansas clays and the two ball clays, all five of which have similar clay mineral assemblages.

CORRELATION OF FUNDAMENTAL AND CERAMIC PROPERTIES

The clay minerals under consideration in this study are composed essentially of minute flake-shaped particles. These flakes in the montmorillonites are relatively small and thin; the kaolinite flakes have a wide range in size and shape, but on the average are larger than those of the montmorillonites. Most of the illite flakes are larger than the average kaolinite flakes, and on working with water have a greater tendency to remain in aggregates than flakes of either montmorillonite or kaolinite. On working with water the water film between the clay particles acts as a lubricant and bond, producing the plasticity which is the physical property most characteristic of clays. The clays made up of relatively smaller and thinner flakes also possess a greater total surface, and will therefore retain a greater amount of water and have greater plasticity and bond strength than those made up of larger, thicker flakes. Ion exchange capacity and the presence of soluble salts also affect these properties.

The effects produced by heating or firing clays depend on the mineralogical changes produced by increasing temperatures and the formation of a glassy phase. Kaolinite, consisting only of alumina and silica, above 600° or 700° C. is relatively refractory. Montmorillonite, which usually contains fluxes such as magnesium within the molecule and calcium and sodium as adsorbed ions, is much less refractory than kaolinite. The illites, which contain magnesium, potassium, and iron, are usually the least refractory; quartz acts as a flux to kaolinite at high temperature; and feldspar, muscovite, and iron compounds are also fluxing materials at somewhat lower temperatures. The relation of the individual properties of the various clay minerals to the green or unfired characteristics of the clays is discussed in some detail by Grim (1939, 1939a) and Grim and Bradley (1940).

Those familiar with ceramic tests are well aware that the various properties revealed by the tests are closely interrelated. If the green or unfired properties of the four clays are compared (Table 11) it will be noted that a clay with a low percentage water of plasticity (EL-60-6 for example) has also a low percentage of shrinkage water and low volume and linear shrinkages. A clay such as O-5-6 having a high percentage of water of plasticity has proportionately high percentages shrinkage water and volume and linear shrinkages. The pore water, on the other hand, does not correlate perfectly with the other properties, although the tendency is in the direction of correlation.

The fired properties of clays are also interrelated (Table 11. Figs. 11-15). With increasing temperatures clays normally show increased shrinkage. As the clays shrink the open pores decrease proportionately, thus decreasing absorption at a rate corresponding to the rate of shrinkage. The green or unfired properties of the clays can be considered as one unit, and the fired properties as another but related unit; therefore, the comparison of ceramic data with the more fundamental properties is simplified.

RELATION OF UNFIRED PROPERTIES TO SPECIFIC SURFACE

The plastic and dry, or unfired properties of a clay are directly related to its specific surface. Specific surface, expressed as square meters of surface per gram of sample, should be considered a composite of two properties of a clay: mean diameter of the clay particles and the shape of the clay particles. As stated above, the plasticity of clay is produced by the water film between the clay particles. Drying the plastic clay removes the water film and at a certain point in the drying process the clay particles touch. The amount of water removed up to that point is the shrinkage water. The remainder of the water used to produce plasticity is held in the pores or interstices formed by the imperfect orientation and "fit" of the clay particles. This is given as percentage pore water in Table 11. Volume and linear shrinkage, which are by definition completely correlative, occur only while the shrinkage water is being removed by drying.

The relation of specific surface to the unfired properties of the four clays is shown graphically in Figure 16. The volume shrinkage and shrinkage water are shown to be a linear function of specific surface for the four clays studied, and the water of plasticity shows a close correlation. Harman and Fraulini (1940) have

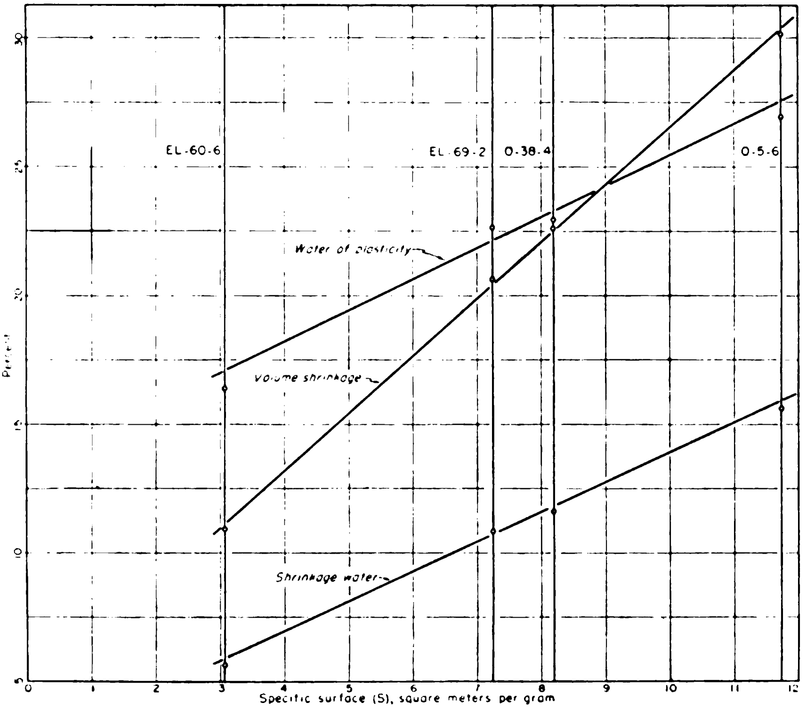

Fig. 16.—Graph showing correlation of specific surface to plastic and drying properties of the four clays.

shown that the shrinkage of kaolinite is a linear function of base-exchange capacity. Thus with clays composed dominantly of kaolinite, or kaolinite and quartz, the volume shrinkage on drying or the shrinkage water can be used as an indication of specific surface and base-exchange capacity. Clays such as EL-69-2, O-5-6, and O-38-4 would not show complete correlation between specific surface and base-exchange capacity because of the presence of the illite group of clay minerals and the montmorillonites and because of the considerable variation in these clay minerals, especially those produced by differences in exchangeable cations present. For these three clays the correlation should be fairly good, however, because of general similarity and the dominance of kaolinite.

Whitaker (1939) has shown in his work with kaolinite that plasticity is directly related to total surface and inversely related to particle size. He expressed the relation of plasticity to specific surface in the formula: $\log S = AP + \log B$, where S equals square centimeters of surface area per 100 grams of clay; P equals the product of yield and strain; and A and B are constants. He has also shown that drying shrinkage increases, in general, with decreasing particle size, and that drying strength also increases with decreasing particle size until a maximum is reached. Norton (1942) also commented on the influence of particle size and shape, the types of clay minerals, and the soluble salts and adsorbed ions on the plastic and drying properties of clays.

EFFECT OF CHEMICAL AND MINERAL COMPOSITION ON FIRED PROPERTIES

In the temperature range within which shrinkage occurs in clays, particle size and shape have little influence on the fired properties. Within this range increased shrinkage and decreased porosity with increasing temperature are caused by the formation of new minerals, and the ultimate formation of a glassy phase due to the fluxing action of some of the components of the clay minerals and to accessory minerals such as limonite, hematite, calcite, and dolomite. Minerals of the illite and montmorillonite groups contain ferric iron replacing the aluminum, and alkalies and alkali earths either within the lattice or as adsorbed ions (Grim and Bradley, 1940). Within the lower temperature ranges K_2O and Na_2O are the most active fluxes. Calcium, magnesium, and iron oxides are active at somewhat higher temperatures, although in combination with the alkalies they are quite active at relatively low temperatures.

In Figure 17 the percentage volume shrinkage between cone 05 and cone 8 (about 1030° to 1225° C.) has been plotted against the percentages of fluxes contained in the clays and the molecular ratios of the fluxes to the alumina (Table 17). The cone 05 to cone 8 range was chosen because shrinkage calculated from dry size is deceptive. Some of the shrinkage in the early stages of heating reflects particle size, shape, and packing rather than chemical fluxing action. Cone 8 was used as the top temperature because abnormal bloating occurred in some of the clays at cone 10. Figure 17 shows a general correlation between the amount of fluxes present and volume shrinkage on firing. The total percentage of alkalies plotted against volume shrinkage results in a curve which is shown in relation to a segment of an elipse. Whether or not the

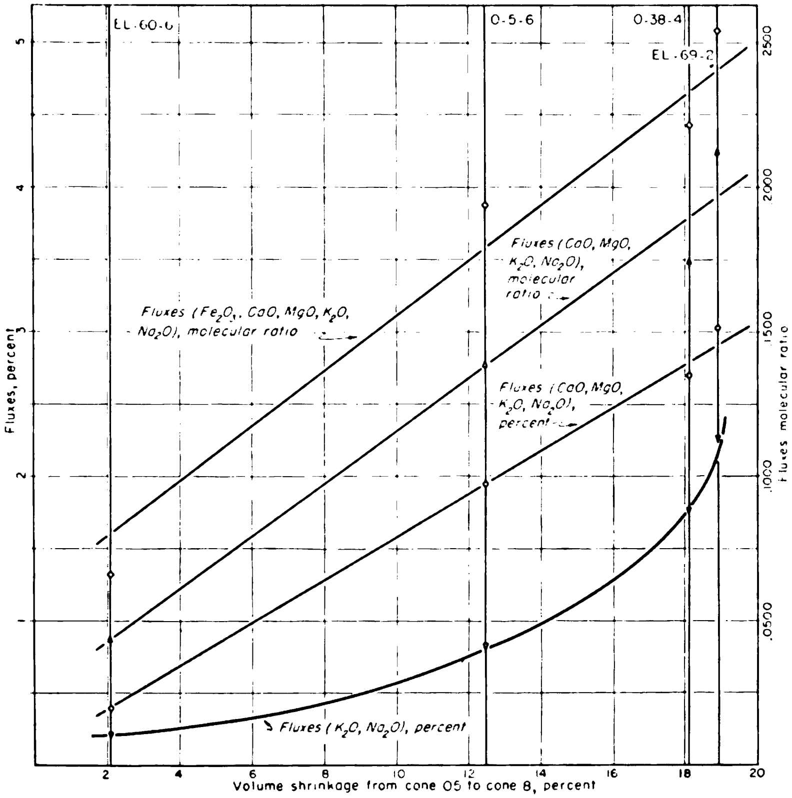

Fig. 17.—Graph showing correlation between fired volume shrinkage and fluxes.

shape of the curve has any significance is not known, but there is evidence that the rate of increase in volume shrinkage declines with increasing content of the alkalies. This same type of deviation occurs for the total of CaO, MgO, K_2O and Na_2O, although the relation is less clear. With Fe_2O_3 included with the fluxes, the deviations are even more pronounced, although the general relation is still clear.

CONCLUSIONS

The basic properties of these clays are chemical composition, mineral composition, and particle size and shape. It is assumed that if the exact percentage and chemical composition of each of the minerals present were known, the chemical composition of the

TABLE 17.—*Empirical molecular formulas of the four clays, with alumina calculated to unity*

RO	R_2O_3	RO_2
	EL-60-6	
0.0034 K_2O		
0.0046 Na_2O	1.0000 Al_2O_3	6.9863 SiO_2
0.0143 CaO	0.0235 Fe_2O_3	0.0893 TiO_2
0.0212 MgO		2.0596 H_2O
	EL-69-2	
0.1022 K_2O		
0.0127 Na_2O	1.0000 Al_2O_3	5.5769 SiO_2
0.0209 CaO	0.0428 Fe_2O_3	0.0613 TiO_2
0.0784 MgO		
		1.8101 H_2O
	O-5-6	
0.0319 K_2O		
0.0101 Na_2O	1.0000 Al_2O_3	4.3452 SiO_2
0.0403 CaO	0.0567 Fe_2O_3	0.0571 TiO_2
0.0563 MgO		
		1.9601 H_2O
	O-38-4	
0.0723 K_2O		
0.0137 Na_2O	1.0000 Al_2O_3	4.5720 SiO_2
0.0214 CaO	0.0406 Fe_2O_3	0.0688 TiO_2
0.0667 MgO		
		1.7392 H_2O

whole clay could be calculated. The real problem involved is that of identifying the clay minerals with sufficient exactness. Fairly accurate estimates of the percentage of each of the clay mineral groups present can be made. Kaolinite, which has a definite chemical composition, can be identified with relative ease, but the montmorillonite and illite groups include many members, each of which has a different chemical composition. Exact identification of members is difficult and often impossible. The correlation obtained in this study between (1) mineral identification and estimated percentages and (2) chemical composition, is due in part to the fact that the major constituents, kaolinite and quartz, have a definite chemical composition. It is also probable that the assumption of an "average" composition for each of the clay mineral groups was justified. The use of x-ray diffraction, the electron microscope, the petrographic microscope, and differential thermal analysis constitutes a concerted attack on the problem of mineral identification.

A lack of agreement from one method to the other indicates error in a determination. The chemical analyses represent a positive check on the other methods, although it is one that is difficult to apply.

Particle shape and size determinations will correlate with those for specific surface inasmuch as they are different aspects of the same physical properties. Particle size and shape (or specific surface) is in turn directly related to the characteristic size and shape of the minerals found in the sample.

The basic or fundamental data should be considered as one class of information about the clay material, and the ceramic data another class. The relation between these two classes of data is of considerable importance. The basic data explain the behavior of the clay materials under the conditions of ceramic tests, and can be used as a guide to control ceramic properties. Sometimes the determination of one or more of the basic properties can be used as a positive check on the quality of clays mined for ceramic use, or as a means of finding a new clay deposit.

Very little use has been made of the fact that easily obtained ceramic data can be used as a method for the rough determination of basic properties. In many cases an estimate of the relative proportion of the minerals present in a clay material can be made from a careful study of ceramic data. The close correlation between drying shrinkages, shrinkage water, and specific surface has been shown. In materials having approximately the same clay mineral assemblage the ion-exchange capacity of the materials is indicated by the same properties. There is also a clear relation between the fluxes present in the clays and firing shrinkage, absorptions, and porosity. This factor is largely a reflection of the kind and proportion of clay minerals present but it is modified by the quantity and particle size of the quartz that is usually found in clay materials.

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