

The constitution of some Egyptian clays.

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Introduction.

THE Egyptian clays under consideration are obtained from two different localities. The Aswan clays are mainly concentrated in the neighbourhood of Aswan town in Upper Egypt and the Sinai kaolins from the Sinai Peninsula. The Aswan clays, namely: red Aswan clay, white Aswan clay, and siliceous Aswan clay, are transported clays, while Aswan kaolin is a residual clay. The Sinai kaolins are of obscure origin but most probably are transported clays. As is shown later, these are alunite-bearing clays not previously recorded in Egypt.

Petrographic examination.

Megascopic investigation of hand-specimens of the raw clays followed by petrographic examination of thin sections and of elutriated fractions, showed that quartz is the main constituent beside the clay minerals. It is abundant and of very small particle-size, and is evenly distributed in all the elutriated fractions. Iron compounds as well as some mica also occur. The red colour in some of these clays, especially in the red Aswan clay, is mainly due to iron compounds. Sinai kaolin, an alunite-bearing clay, shows coarser quartz grains and small gypsum veinlets.

The determination of free quartz.

Since all these clays contained quartz in appreciable amounts, a quantitative determination was necessary. This was first carried out using the method of estimation devised by Trostel and Wynne, 1940 [1]. The results obtained from three Egyptian clays using this method are as follows:

White Aswan clay.	Red Aswan clay.	Sinai kaolin.
20.8%	16.6%	7.8%

There are certain limitations regarding the accuracy of the method,

since microscopic investigations showed that the finer quartz fractions passed through the paper during filtration and thus a rather low value may be obtained. A centrifugal separation ought therefore to be made. A further defect, which may give rise to misleading results, arises from the dissolving effect of sodium hydroxide on any silica present in a chalcedonic form.

A more reliable quantitative determination of the free quartz was achieved by making use of the small thermal effect of the $\alpha \rightarrow \beta$ transition at 573° C. The amount of quartz was determined by measuring the heat evolved in this reversible transformation using a sensitive galvanometer. This method has been perfected by Grimshaw, Westerman, and Roberts, 1948 [2], and one of us (G. M. G.) was privileged to use their apparatus for the purpose of this investigation. The following results were obtained for the percentages by weight of free quartz in the Egyptian clays:

Siliceous Aswan clay.	Aswan kaolin.	White Aswan clay.	Red Aswan clay.	Sinai kaolin.
56 %	47 %	20 %	18 %	8 %

These results may be compared with the corresponding results obtained by the Trostel and Wynne method.

Identification of the clay minerals

The clay minerals present in these clays are of extremely small particle-size and could not be identified microscopically. For their industrial application, the determination of the kind of clay mineral present is important. The clay mineral component, as illustrated by Grim, 1939 [3], is the chief factor determining the physical properties of the clay; even a minor clay mineral constituent may play an important part in the characteristics of the raw clay material.

For such identification, several methods were used, some helping to place the clay in its group (e.g. the kaolin group of minerals) and others to identify the particular clay mineral.

Chemical analysis.

This is of rather limited value since the different clay minerals of a group have similar compositions. Nevertheless it seems to indicate broadly the type of clay mineral present. Chemical analysis has been limited to the determination of SiO_2 , Al_2O_3 , and water. Subtracting the

percentages of free quartz from the total silica we obtain the following results:

	Total SiO ₂ %.	Free quartz %.	Combined SiO ₂ %.	Al ₂ O ₃ %.	H ₂ O %.
White Aswan clay...	50.54	20	30.54	32.0	10.05
Red Aswan clay ...	53.53	18	35.53	27.0	11.05
Sinai kaolin ...	29.10	8	21.10	36.0	14.00

When these percentages of combined SiO₂, Al₂O₃, and H₂O are reduced to their molecular proportions, the ratios of Al₂O₃:SiO₂:H₂O are as follows:

	Al ₂ O ₃	SiO ₂	H ₂ O
White Aswan clay ...	1	1.6	1.8
Red Aswan clay ...	1	2.2	2.1
Sinai kaolin ...	1	1	2.2

Generally the figures obtained are not inconsistent with the kaolin group of minerals. It is seen, however, that SiO₂ in the Sinai kaolin is very low, while the Al₂O₃ and H₂O contents are high. This is simply due to the occurrence of alunite beside the clay mineral, as will be shown later.

Cationic exchange measurements.¹

As shown by Hendricks, 1945 [4], the cationic exchange properties of clays are of considerable value in placing them in their groups. For the Egyptian clays the total exchangeable cations were found by electro-dialysis and by the ammonium acetate leachate method of Bray and Willhite, 1929 [5]. The results are as follows, expressed in milligram equivalents per 100 grams of the clay material:

White Aswan clay.	Red Aswan clay.	Sinai kaolin.
4.7	7.1	2.6

The cation exchange capacity was then determined by the method of Schollenberger and Dreibelbis, 1930 [6]. Results in milligram equivalent per 100 grams of the clay material are given below:

White Aswan clay.	Red Aswan clay.	Sinai kaolin.
8.8	12.3	9.6

These results suggest that the main clay minerals are of the kaolin group, which is in accordance with the previous chemical analysis.

¹ 'Cationic exchange' was suggested as better than 'base exchange' at the International Geological Congress, London, 1948, by Dr. J. S. Hosking.

Identification of the kaolin clay minerals.

To identify the individual kaolin clay minerals present, three different methods were used, namely (1) the rates of dehydration on heating, (2) differential thermal analysis, (3) X-ray powder analysis.

(1) The rates of dehydration on heating.

The loss of combined water on heating clays has long been a subject of investigation. In carrying out the test, a sample of 1 to 2 grams is

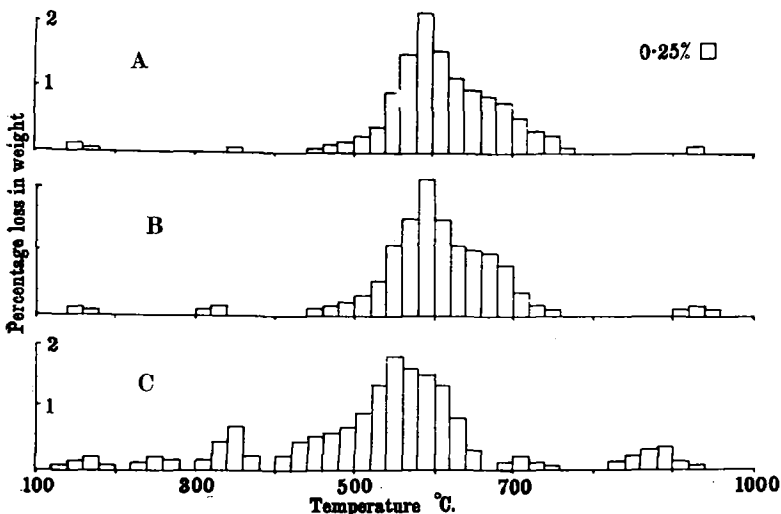


FIG. 1. Differential weight-loss diagrams. A, British standard kaolinite. B, European standard kaolinite. C, Utah halloysite.

suspended in an electrically-heated tube furnace by means of a platinum wire attached to one arm of a sensitive balance. The temperature of the furnace was measured by a platinum/platinum 13 % rhodium thermocouple placed with its junction opposite the middle of the suspended sample. The rate of heating was regulated to 10° C. per minute. Dry air was passed through the furnace at a rate of 5 litres per hour. The weight loss was recorded every 20° C. or after periods of 2 minutes. This technique was first applied to clay minerals of higher purity and later to the Egyptian clays. The results obtained were plotted as differential weight-losses against temperature in a diagrammatic manner.

(a) *Standard kaolinite and halloysite.*—Both the British standard kaolinite (china-clay 'Supreme') (fig. 1 A) and the European standard kaolinite (Zettlitz kaolinite) (fig. 1 B), show the beginning of a continuous weight-loss at 440° C., with a maximum weight-loss at 580° C. to 600° C.

In the case of Utah halloysite (fig. 1 c) the beginning of this continuous loss starts at 400° C., i.e. 40° C. lower than for kaolinite, and

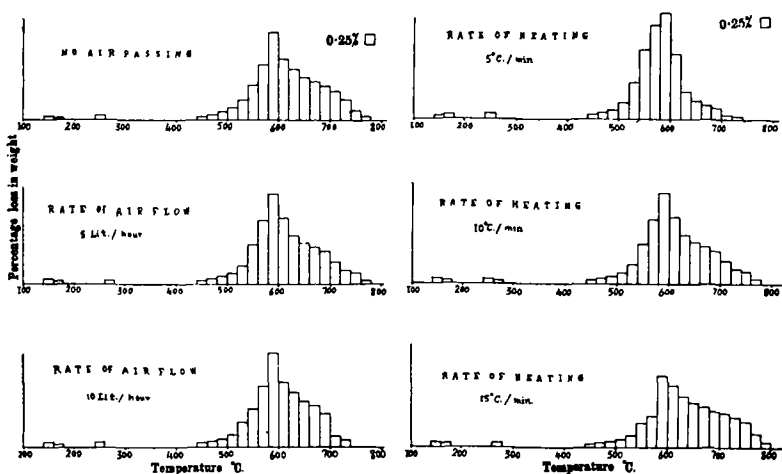


FIG. 2

FIG. 3

FIG. 2. Effect of variation of the rate of air-flow on the general shape of the differential weight-loss diagrams.

FIG. 3. Effect of variation of the rate of heating on the general shape of the differential weight-loss diagrams.

has its maximum at 540° C. to 560° C. In addition, as previously mentioned by Ross and Kerr, 1934 [7], it also shows a low-temperature water-loss up to 300° C. (The loss between 300° C. and 400° C. is due to a gibbsite impurity in the Utah halloysite sample.)

It is worth noting that neither the beginning of the continuous weight-loss, nor its maximum, is influenced by variation in the experimental conditions used, e.g. the variation of the rate of air-flow or the rate of heating. Figs. 2 and 3 show that such variations may only cause a change in the general shape of the diagram.

(b) *Aswan kaolin and siliceous Aswan clay.*—For these clays figs. 4 A and 4 B show the beginning of the continuous loss at 440° C. with its maximum at 580° C. to 600° C. in agreement with kaolinite. The

noticeable bulging on the right side of the Aswan kaolin diagram may be due to the presence of another clay mineral of the kaolin group, such as dickite.

(c) *White Aswan clay and red Aswan clay.*—In figs. 4 C and 4 D both clays show the beginning of a continuous loss in weight at 400° C. and

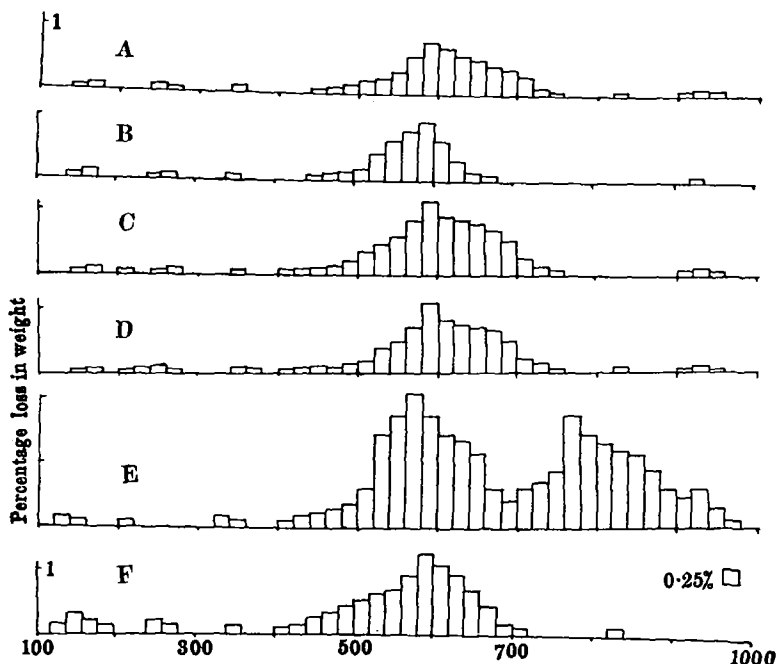


FIG. 4. Differential weight-loss diagrams. A, Aswan kaolin. B, Siliceous Aswan clay. C, White Aswan clay. D, Red Aswan clay. E, Sinai kaolin containing alunite. F, Sinai kaolin fireclay mineral.

a lower water-loss in the temperature range up to 300° C. and therefore resemble halloysite. On the other hand, the water seems to be more strongly held than in halloysite, since the maximum of the continuous weight-loss occurs at 580° C. to 600° C., resembling kaolinite. In other words, the left-hand side of the diagrams resemble halloysite and the right-hand sides resemble kaolinite. It thus seems that either there is a mixture of both minerals in these clays or we have here a case of a distinct mineral of an intermediate nature between kaolinite and halloysite, such as has been recently found by thermal analysis and by X-rays to occur in many British fireclays.

(d) *Sinai kaolins*.—Fig. 4 E shows the dehydration data for the Sinai kaolin which is later shown to contain alunite. Since both the clay mineral and the alunite lose water within the same temperature range it was found difficult to draw a definite conclusion about the kind of clay mineral present. It is, however, worth noting that this method of investigation in this case is very helpful in indicating the presence of alunite in clays from the loss of weight due to the evolution of sulphur trioxide between 700° C. and 1000° C. Identification of the clay mineral in Sinai kaolin was achieved by examining a second sample which did not contain alunite. This showed (fig. 4 F) the intermediate clay mineral previously found in white and red Aswan clays.

(2) *Differential thermal analysis*.

Thermal analysis using the differential technique has been widely used in distinguishing between individual members of clay groups, especially those of the kaolin group. Kaolinite and halloysite are characterized by a sharp and pronounced exothermic reaction at 980° C., while the kaolin mineral in many British fireclays shows a less sharp and rounded exothermic peak at 950° C. On the other hand, kaolinite, the fireclay mineral, and halloysite have endothermic peaks at 580° C., 555° C. to 565° C., and 550° C. respectively, as indicated by Grimshaw, Heaton, and Roberts, 1945 [8]. Thermal analysis of the Egyptian clays was carried out using their apparatus and applying their techniques. The following results were obtained:

(a) *Siliceous Aswan clay and Aswan kaolin* (figs. 5 A and 5 B).—The endothermic peak *b* in both cases suggests the presence of kaolinite. An extra deflection *d*, fig. 5 B, is observed with Aswan kaolin, which may be due to the presence of small amounts of dickite. The sharpness of the exothermic peak *c*, fig. 5 B, in the case of Aswan kaolin supports this kaolinite hypothesis, but the roundness of the exothermic peak *c*, fig. 5 A, of the siliceous Aswan clay may indicate a poor kaolinite or a mineral falling between kaolinite and the type of mineral found in fireclays.

(b) *White Aswan clay and red Aswan clay* (figs. 5 C and 5 D).—Both show a pronounced lower temperature peak, *a*, a V-shaped endothermic peak, *b*, and a rounded exothermic peak, *c* at 950° C. These results all suggest a fireclay mineral type. But the V-shaped endothermic peaks *b* occur in both at 575° C., which is a high temperature for the fireclay type of mineral shown by Grimshaw, Heaton, and Roberts, 1945 [8]. This may be taken either as an indication of the presence

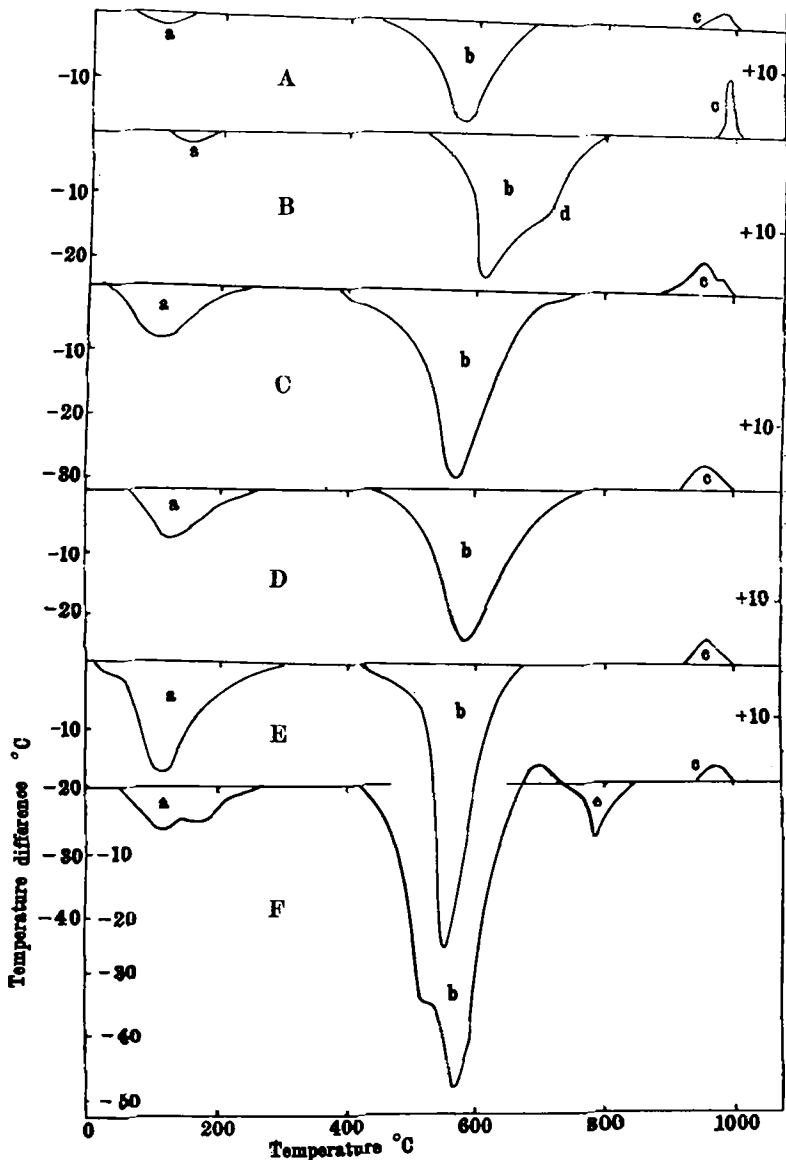


FIG. 5. Differential thermal analysis curves. A, Siliceous Aswan clay. B, Aswan kaolin. C, White Aswan clay. D, Red Aswan clay. E, Sinai kaolin fireclay mineral. F, Sinai kaolin containing alunite.

of some kaolinite or another fireclay mineral approaching the characteristic thermal behaviour of the kaolinite. This gives rise to a second exothermic peak at 980° C. in the white Aswan clay. This double-peak effect is, however, missing in red Aswan clay.

(c) *Sinai kaolins* (figs. 5 E and 5 F).—The curve of this Sinai kaolin, which is free from alunite, is shown in fig. 5 E. It is identical with the typical fireclay minerals detected by Grimshaw, Heaton, and Roberts, 1945 [8]. But when alunite is present, fig. 5 F, it is rather difficult to identify definitely the kind of clay mineral present. This is due to the influence of the water from the alunite which has its maximum peak at 570° C. However, the roundness of the exothermic peak, *c*, fig. 5 F, could be taken as an indication of a fireclay mineral. But this in some cases may give misleading results, due to the fact that when alunite is present with clays it has a reducing effect on their exothermic peaks. The endothermic peak, *e*, is also due to alunite.

(3) *X-Ray powder analysis.*

Since all the Egyptian clays under consideration contain appreciable amounts of quartz, purer clay mineral specimens were prepared from a suspension of the clay materials in distilled water after they had been allowed to settle for several hours.

The X-ray diffraction patterns were obtained using the 20 cm. semi-focusing camera, which was briefly described by Brindley and Robinson, 1946 [9] in connexion with their work on the structure of kaolinite. The results were as follows:

(a) *Aswan kaolin*.—Its pattern shows kaolinite and some mica. Dickite is not encountered and if present, as suggested by thermal analysis, the amount is less than about 5 %.

(b) *Siliceous Aswan clay*.—It is a very poor kaolinite. It could be even placed intermediate between kaolinite and the kaolin mineral which occurs in fireclays.

(c) *White Aswan clay and red Aswan clay*.—These were identified as typical fireclays. They are identical with the fireclay mineral described by Brindley and Robinson, 1947 [10] which occupies an intermediate position between kaolinite and halloysite. This was previously presumed from the studies of the rates of dehydration on heating and from the differential thermal analysis.

(d) *Sinai kaolins*.—The clay mineral was identified as the typical fireclay mineral, together with natroalunite in the sample containing alunite. It is of interest to note that alunite has been reported by

some authors to be associated with kaolinite and by others to be associated with halloysite.

Conclusion and discussion.

Although this investigation began with the object of identifying the clay mineral component in certain Egyptian clays, the final results are of wider interest. X-ray data, thermal analysis data, and dehydration data agree in showing that the principal clay mineral in a number of these clays is intermediate in character between kaolinite and meta-halloysite, and in fact it shows all the characteristics of the type of clay mineral recently discussed by Brindley and Robinson, 1947, and by Grimshaw, Heaton, and Roberts, 1945. Since the recognition of this intermediate type of kaolin clay is quite recent, it will be useful in the first place to consider what light the present results throw on this fireclay type mineral.

The X-ray photographs fully agree with those of Brindley and Robinson, 1947, and the thermal data confirm those of Grimshaw, Heaton, and Roberts, 1945. The dehydration data, however, add to our knowledge of this mineral in that they show that the fireclay type contains combined water which is lost at the low temperatures up to 300° C.

Brindley and Robinson, 1946 [11] have already suggested that most natural metahalloysites still contain residual inclusions of water. The similarity of the fireclay mineral to metahalloysite in this respect therefore suggests that there may also be some water inclusions, though perhaps fewer, in the fireclay mineral. However, although from chemical analyses water was noticed in excess of the $2\text{H}_2\text{O}$, yet such an excess has always been interpreted as hygroscopic moisture due to the fact that the clay is not of high purity.

However, it is worth noting that the fireclay mineral occurs in transported clays in Egypt. It may be that during transportation of kaolinite, water enters between the kaolinite blocks causing a displacement and giving rise to the fireclay type mineral.

It may be that these fireclay type minerals form a series in thermal behaviour, ranging from the poor kaolinite type fireclay mineral to a typical fireclay mineral.

Finally, as regards identification and elucidation of the character of the fireclay minerals, it is considered that a combination of X-ray data, differential thermal analysis data, and differential dehydration analysis is preferable, although each separately is sufficient to identify the fireclay mineral.

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