CLAY MINERAL STUDIES BY USING ELECTRON MICROSCOPY AND X - RAY DIFFRACTION TECHNIQUES

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SUMMARY

X-ray diffraction and electron microscopy were utilized to investigate the nature of some kaolinite samples collected from different localities from Kalabsha regions. About 14 clay samples were investigated by these techniques. The samples were finely ground and investigated as such in their natural condition or heat treated at different temperatures ranging from room temperature up to 1100°C. A well calibrated furnace was used for this heat treatment.

For the X-ray diffraction work, the diffractometer technique was used. Both, Cuk$_{\alpha}$ radiation and CoK$_{\alpha}$ radiation were used, slow scanning method was applied in case of crystallite size measurements. For the electron microscope work, the suspension method was utilized. Transmision micrographs were taken at different microscope magnification and also slected area diffraction micrographs were undertaken. Gold foil was used as an internal standard for the diffraction work.

The experimental results of this work could be summarised as follows :

1 - The Egyptian clays taken from different locations from the Kalabsha region are true kaolinite samples.

2 - The kaolinite clays were classified into 4 groups according to the type of impurities present in these samples. The main impurities which were found in the clays are namely, anatase, α-quartz, rutile, and diaspore.

3 - The X-ray diffraction work showed that most of these clay samples are having good crystalline kaolinite and the crystallinities varied from one sample to another, depending on the type of impurities present.

4 - The relative grain size of the kaolinite crystals measured by the line broadening method was found to decrease by increasing the temperature of the thermal heat treatment applied on the sample.

5 - The reduction in particle size when measured by the electron microscope and by applying the Feret's Statistical method was found to be none linear with temperature the results showed that the particle size became minimum at 450°, the temperature which is just before the temperature of the amorphous phase.

6 - The morphological shape of the kaolinite crystal was found to change by changing the temperature of the thermal heat treatment applied on the samples. The results showed also that kaolinite crystal preserve its net work structure even in its amorphous phase up to 600°C.

7 - The phases produced by thermal heat treatment were found to be the same in all the 14 samples irrespective of the type of the impurities present with them. Also the temperature at which the kaolinite samples became amorphous was the same in all cases , i.e. the type of the impurities present with the clay have no effect what so ever on either the phases produced or the temperature of the transformation.

CHAPTER I

INTRODUCTION

I.1- Introduction :

Clays are important materials in industry . Kaolinite is one of the most characteristic types of clays which are basic raw materials used in ceramic, porcelain, and non-ceramic production such as in manufacturing papers, filters, absorbants, Textiles, midicine, and rubber industries. In some countries, kaolinite represents an important part of the national economy. In Arab Republic of Egypt there are several localities of kaolinites which centered mainly in the Sinai peninsula and near Aswan. Due to this, it was of great national interest to study some samples of Egyptian kaolinites, in order to gain knowledge about this very important material.

I.2- Nature of Kaolinite :

Kaolin may be formed in nature either by weathering of K - and Na - feldspares from magnetic and metamorphic rocks or by a hydrothermal attack of carbonic and sulfuric acid solutions on feldspars and mica. All these minerals occurs in many kinds of rocks (granite, gneiss, parphyr, ...etc). So that the resulting kaolinite is wide spread. On the other hand kaolinite may be formed by silicification of hydrogillite silicic acid

Kaolinite deposite consisting of poorly ordered kaolinite and defiled with varying amounts of carbon and coal-like products together with mica, are called "fire clay". Samples of poorly ordered kaolinite in which the carbon and the mica components are absent are called "ball clay".

I.3- Structure of kaolinite mineral :

The structure of kaolinite was first suggested in general outlines by Pauling (1930). It was worked out in some detail by Gruner (1932) and later revised by Brindley and Robison (1946), and Brindley (1951). The structure is composed of a single silica tetrahedral sheet and single alumina octahedral sheet combined in a unit so that the tips of the silica tetrahedrons and one of the layers of the octahedral sheet form a common layer, Fig. 1. The dimensions the sheets of tetrahedral units and of the octahedral units are closely similar in their a and b dimensions, and consequently composite octahedral - tetrahedral layers are readily formed. Only minor changes in interatomic distances are necessary, and there would seem to be little tendency for the unit to bend in the stacking arrangement of kaolinite, although large crystals would be unlikely.

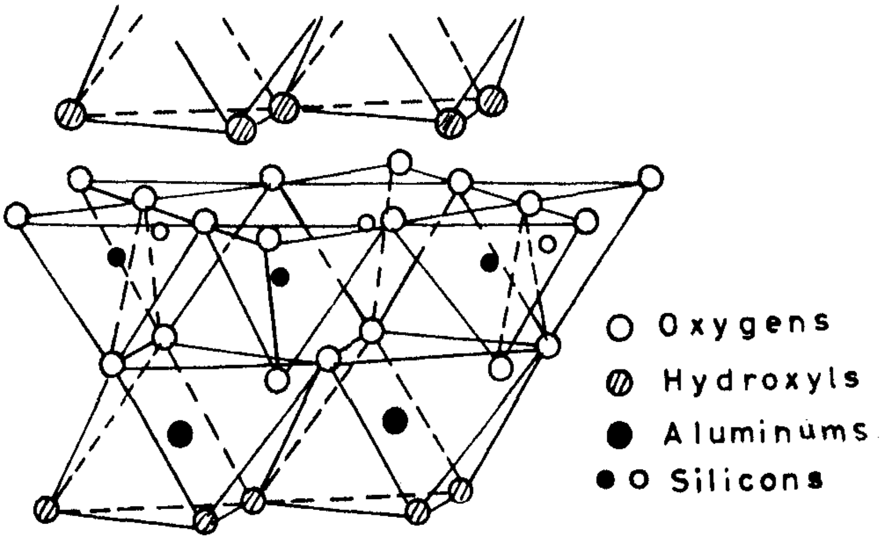

Fig. (1) Diagramatic sketch of the structure of the kaolinite layers.

In the layer common to the octahedral and tetrahedral groups, two thirdsof the atoms are shared by silicon and aluminium, and then they become O instead of OH. Only two-thirds of the possible possitions for aluminium in the octahedral sheet are filled, and there are three possible planes of regular population of the octahedral layer with aluminiums. The aluminium atoms are considered to be so placed that each two are separated by an OH above and below, thus making hexagonal distribution in a single plane in the center of the octahedral sheet. The OH groups are plsced so that each OH is directly below the perforation of the hexagonal net of oxygens in thetetrahedral sheet.

The charge distribution in the layers is as follows :-

6 O^{--}	12 -	
4 Si^{+4}	16 +	
4 O^{--} + 2 $(OH)^{-}$	10 -	(Layer common to the tetrahedral and octahedral sheets)
4 Al^{3+}	12 +	
6 $(OH)^{-}$	6 -	

The charges within the structural unit are balanced and the structural formula is $(OH)_8\ Si_4\ Al_4\ O_{10}$. The theoritical composition expressed as oxides is SiO_2 46.5; Al_2O_3 39.5, H_2O 13.96 %. The analysis of many samples of kaolinite have shown that there is very small amount of subistitution of iron or titanium for aluminium in relatively poorly crystalline variety (Ross and Kerr, 1931).

The minerals of kaolinite group consist of units of the type just discribed in the a and b directions forming a stacked sheets above each other in the c direction.

In case of kaolinite itself Brindley (1951), investigated the stacking of the unit layers. The mineral is triclinic, a = 5.15°A; b = 8.94°A ; c = 7.38°A; α = 91.8°; β = 104.5°, and γ = 90°. Successive unit layers are so arranged that oxygen atoms and OH groups of adjacent layers approach one another in pairs. Because of the superposition of O and OH planes in adjacent units, the units are held together fairly tightly by hydrogen bonding between the layers. The plane between the unit layer is a cleavage plane, which is not so pronounced in kaolinite.

Grimshaw, Heaton, and Roberts (1946); Brindley and Robison (1946); and Grim (1947), reported the presence of a kaolinite mineral of lower crystallinity than that of well-crystallized material just noted. Brindley and his colleagues (Brindley, 1951; Ross and Kerr, 1931; and Brindley and Robison, 1946) have investigated in detail some examples of rather