JÁNOS GROFCSIK

MULLITE, ITS STRUCTURE, FORMATION AND SIGNIFICANCE

AKADÉMIAI KIADÓ
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by

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The phase that certainly stamps a ceramic product made of fired alumino-silicates (e. g. fireclay refractories, pottery, ceramic whiteware, etc.) is *mullite*. This recognition has given a start to comprehensive investigations into the formation and the structure of this mineral. The extent of this research work is reflected in the vast literature relating to mullite; a close inspection, however, will reveal the lack of a summing up, because the statements of the different authors bring sharp contradictions to light. This situation has suggested the elaboration of a comprehensive work on the problem of mullite.

The book gives a critically systematized review of the results obtained by a number of research workers and examined in the light of the authors' own conclusions.

The scope of the monograph covers the properties

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CONTENTS

PREFACE

The rapid progress achieved lately in the field of silicate investigation has put an end to the empirism that had prevailed for thousands of years and has superseded the classic methods of chemistry formed in the second half of the past century. Many ceramic products consist of several phases. Certain characteristics are concomitant to distinct phases, such as mullite, cristobalite, periclase, etc. The phase that most certainly stamps a ceramic product made of fired alumino-silicate is mullite. This recognition has given a start to comprehensive investigations into the formation and structure of this mineral. The extent of this research work is reflected in the vast literature relating to mullite (see the list of references accompanying the present study). A close inspection of the literature will reveal the lack of a summing up: most of the papers give results of experiments and often the statements of the different authors bring sharp contradictions to light.

Except for a few books on silicate chemistry and ceramics, giving brief summaries of the results up to their publication, no comprehensive work covering all aspects of the mullite problem has been published so far. Such surveys can be found, for instance, in C. Koeppel's *Feuerfeste Baustoffe*, published in 1938; H. Salmang's *Die physikalischen und chemischen Grundlagen der Keramik*, reprinted several times, and particularly in W. Eitel's excellent work *The Physical Chemistry of Silicates*, an ample study, covering many details, published in 1954 (after two German editions and a reprint).

The situation outlined above has suggested the elaboration of a comprehensive work on the problem of mullite.

A few words about the composition method of the present monograph: as far as possible, we relied on papers published in journals rather than on books. Whenever it was practicable, original publications were used, since abstracts published in various digests proved inadequate for our purposes and not suitable for critical examination. The perusal of the original papers has furnished the opportunity of controlling the bibliographical references and of correcting numerous misprints that had become, so to speak, hereditary in the literature. Abstracts were used only when originals were not available.

In the spelling of some names we were confronted with difficulties. For the names of Japanese authors we have adopted the Hepburn system in Roman characters, both in the text and in the reference list. The names of Soviet authors are given in Roman characters in the text, as adopted by *Chemical Abstracts* (sole exception: the Cyrillic letter й has been transcribed as i in the middle and omitted at the end of names), but preserve their original Russian spelling in the reference list. This has led to certain discrepancies when works of Soviet authors published in foreign languages are mentioned (for instance Khizh is spelt Chish when in connection with works published in German) but their identification is ensured by cross-references in the author index.

The reference list was closed on 31st December 1959.

We hope that our study, giving a systematized review of the results obtained by research workers and examined in the light of the authors' own conclusions, will further the development of the investigation of mullite, equally essential for theory and practice.

The criticism of scientific works even in the light of development naturally implies a certain amount of subjectivism and some of the critical views may prove wrong in the future. The line of scientific development does not always go unbroken. There is much truth in Eitel's words: "Many fields of silicate investigation are not yet far enough advanced to make clear judgment possible; they are a wilderness in which only the machete of this or that investigator has cut a first gap. Maybe some of these pioneers have been in error in their effort to attain a true answer to the unknown and achieve factual accomplishment. Fortunately, however, we may hope that, even in the most intricate jungle of theories and hypotheses, the day will come when it will be apparent which direction is the correct one."

These are our principal thoughts that accompany the present work to the reader.

Budapest, March 1960

I. Grofcsik

PART ONE

THE PROPERTIES, QUALITATIVE DETECTION AND QUANTITATIVE DETERMINATION OF MULLITE

CHAPTER 1

THE PROPERTIES OF MULLITE AND OF ANHYDROUS ALUMINO-SILICATES

Mullite, which has a chemical formula of $3Al_2O_3 \cdot 2SiO_2$, crystallizes in the orthorhombic system, usually in the form of elongated needle-shaped crystals; its density is 3.03 g/cu.cm, its hardness (according to Mohs) 7.5.

Mullite is rare in nature; its most important place of occurrence is the Isle of Mull, West Scotland, where it has been formed under exceptional conditions, very similar to those required for the production of artificial mullite. As a consequence of incomplete weathering the Mesozoic mother-rock has yielded an alkali- and alumina-bearing clay-shale, which, in time, under the influence of mountain-building forces, got buried, but not too deep. Later magma of andesitic composition broke through, the temperature of which was sufficiently high to vitrify the shale, but not high enough to melt it down. This andesitic magma, bearing vitreous shale-particles 1—2 feet thick in a suspended state, approached the surface and, having cooled rapidly, formed a dike. These conditions (high Al_2O_3 content, high temperature, relatively low pressure) were roughly similar to those reproduced in the experiments aiming at achieving the artificial synthesizing of mullite. Under such conditions stable corundum and mullite were formed from the shale and were quenched by later, rapid cooling.

Although rare in nature, mullite is very common in artificial products. Porcelain, fireclay-products, high-alumina refractories, etc. all contain mullite as one of their most valuable constituents.

Mullite is the only stable crystalline compound in the Al_2O_3—SiO_2 system; under normal atmospheric pressure or at any pressure exceeding it by a few hundreds only, this compound is produced from every anhydrous or water-containing alumino-silicate.

Naturally, the pressure has a slight influence on the phase distribution of the system. This is (Miyashiro 1949) why mullite is so common in artificial products and rare in natural rocks formed usually under high-pressure conditions. Other alumino-silicates such as *andalusite*, *sillimanite* and *kyanite (disthen)* are formed under high pressure. The stability relations of the high-pressure parts of the Al_2O_3—SiO_2 system have not yet been fully revealed; it can be considered, however, as a fact (Clark, Robertson and Birch 1957; Schuiling 1957, 1958) that *andalusite* is stable under relatively low pressure and low temperature, *kyanite* under high pressure and low temperature, *sillimanite* under high pressure and high temperature.

TABLE I

Some properties of anhydrous alumino silicates
(Searle and Grimshaw 1959)

	Sillimanite		Andalusite		Kyanite		Mullite	
Formula	$Al_2O_3 \cdot SiO_2$		$Al_2O_3 \cdot SiO_2$		$Al_2O_3 \cdot SiO_2$		$3Al_2O_3 \cdot 2SiO_2$	
Crystal system	Orthorhombic		Orthorhombic		Triclinic		Orthorhombic	
Specific gravity $g \cdot ml^{-1}$	3.08		3.18		3.59		3.03	
Hardness, Mohs ...	7.5		7.5		changing		7.5	
Index of refraction	1.66		1.65		1.75		1.65	
Birefringence	0.022		0.010		0.011		0.012	
Optical character ..	pos.		neg.		neg.		pos.	
Crystal habit	fibrous		prismatic		plates		acicular	
Positions and intensities of three strongest X-ray reflections	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
	3.39	10	4.58	10	1.95	10	3.42	10
	2.20	9	1.48	10	1.38	10	2.21	8
	1.52	7	2.17	8	3.20	10	1.53	8

Table I gives some important characteristics of mullite and of the high-pressure alumino-silicates just mentioned. The Table has been compiled according to the critically evaluated data of Searle and Grimshaw (1959). As clearly shown also by these data, mullite and sillimanite are very similar.

According to Bowen and Greig (1924) mullite melts incongruently at 1810 °C. The temperature of the incongruent melting point of mullite was revised by Morris and Schole (1935) and found at 1827 °C. Toropov and Galakhov (1953, 1958) found a melting point of *congruent* nature at 1910 °C.

The *dielectric constant* of mullite is, according to Keyser (1940) and Kirillova (1959), approximately 6.

Some important technical properties measured and compiled by Bárta and Bartuška (1957) are:

bending strength	$4.2 \cdot 10^4$ kg/cm^2
modulus of shearing stress	$5.6 \cdot 10^5$ kg/cm^2 (0 °C) $2.5 \cdot 10^5$ kg/cm^2 (1200 °C)
modulus of elasticity	$3.51 \cdot 10^5$ kg/cm^2
heat conductivity	0.01 cal/sec · cm · °C
specific eletric resistance	$10^6\ \Omega \cdot$ cm (600 °C) $10^4\ \Omega \cdot$ cm (1400 °C)

Mullite has a characteristic X-ray pattern, which, however, is very similar to that of sillimanite. The almost identical positions of the strongest reflections of mullite resp. sillimanite are obvious from Table I. The other reflections of the two minerals give patterns close to one another, but well crystallized and pure samples of the two minerals are easily distinguished also by X-ray powder patterns. For the complete pattern and the method of mullite-sillimanite differentiation cf. Chap. 2.

CHAPTER 2

DETECTION AND QUANTITATIVE DETERMINATION OF MULLITE

Any scientific analysis requires the doubtless detection and exact quantitative determination of the material to be investigated. Consequently, the first task in examining the mullite problem, is to determine *the mullite content of a mix containing several minerals*, i.e. to make qualitative and quantitative distinctions between the *mineral constituents*.

The following methods are, at least theoretically, suitable for the detection and the quantitative determination of mullite:

1. *Optical methods*, by which the material can by identified and its volume percentage measured quantitatively under a suitable magnifying apparatus. In industrial materials, however, mullite is present in the form of tiny crystals, so the magnifying device must be an optical or electron *microscope*.

2. *X-ray methods* are suitable for detecting and determining mullite itself. This method makes use of the characteristic X-ray pattern of mullite which greatly differs from the patterns of almost every relevant mineral. The *intensity* of mullite reflections is — according to fundamental X-ray principles — proportional to the *concentration* of mullite in the mixture; the measurement of the absolute intensity of the X-ray lines involves difficulties (in case of a camera with photographic evaluation) because the line intensity is affected by a number of external factors, e.g. by the structure of the X-ray film, by the conditions of sample preparation or of the photographic developing process, etc. Thus the X-ray method of mullite determination requires a special technique.

3. Some other physical properties, e.g. *dilatation*, characteristic *infrared spectrum* or other physical features have also been used as a basis of detection or quantitative determination.

4. *Chemical methods* of determination use the differences in solubility existing between mullite and other minerals present. Solubility differences, however, are strongly affected by other factors, independent of the quality of the minerals, e.g. by their particle size and other properties.

Mullite can readily be distinguished on the basis of its optical, crystallographical and other properties, described in Table I from nearly all other minerals. It is easy to distinguish *mullite* and *corundum* (a very frequent constituent) by X-ray methods, for the characteristic reflection of $d_{hkl} = 1.53$ kX is always present in mullite X-ray patterns and no corundum reflection has a lattice spacing near to this value; the same can be said of the $d_{hkl} = 1.38$ kX reflection of corundum (Keyser and Degueldre 1954). The main problem of exact and safe identification is to distinguish sillimanite from mullite. This is a difficult problem as all physical characteristics of the two minerals, including their X-ray patterns, are almost completely identical.

A) THE DIFFERENTIATION OF MULLITE AND SILLIMANITE

Mullite cannot be differentiated from sillimanite by its macrophysical properties, because the slight differences in specific weight, refractive index, optic angle, etc. are influenced by very low quantities of foreign materials, to such an extent that they completely loose their characterizing value.

The X-ray method of identification seems to be more promising. The X-ray patterns of pure mullite and sillimanite are given in Table II following the measurements of Grofcsik (1957).

TABLE II

X-ray patterns of mullite and sillimanite

Mullite		Sillimanite	
d_{hkl} [kX]	Intensity	d_{hkl} [kX]	Intensity
5.34	7	5.34	7
3.77	3	3.80	3
3.400	10	3.394	10
—	—	3.351	3
2.885	3	2.888	3
2.683	6	2.667	6
2.536	7	2.536	7
2.417	4	2.424	4
2.290	3	2.287	3
2.202	7	2.197	7
2.118	5	2.108	5
1.888	4	1.870	4
1.840	4	1.831	4
1.713	5	1.784	3
—	—	1.704	5
1.692	5	1.678	3
1.600	5	1.595	5
1.578	2	1.568	3
1.525	7	1.519	7
1.463	1	1.453	5
1.444	5	1.443	3
1.425	1	1.419	3
1.406	4	1.395	4
1.348	4	1.341	4
1.337	4	—	—
1.330	5	—	—
1.318	4	1.309	4
1.280	5	1.276	4
1.266	5	1.258	5
1.241	4	1.250	4
—	—	1.233	4
		—	—

Reflections of characteristic value are the following (spacings in kX).

Muillte	Sillimanite
3.77	3.80
—	3.351
2.683	2.667
1.888	1.870
1.692	1.678
1.463	—
—	1.453
1.406	—
—	1.395

These lines, owing to their different positions, are suitable for identification (according to examinations made by Navias and Davey 1925, Norton 1925, Hyslop and Rooksby 1926, Nahmias 1933 *a*, *b*). Not only the different positions but also the different intensities of the reflections may serve as a basis for the qualitative differentiation of the two minerals (Keyser 1951). Whereas the mullite reflections with spacings $d_{hkl} = 1.266$ and 1.280 kX are of the same intensity, the corresponding sillimanite reflections with spacings $d_{hkl} = 1.258$ and 1.276 kX are not equally strong; the intensity of the former being somewhat higher. As well shown by the examinations just mentioned, characteristic X-ray differences between the two minerals are very fine and difficult to observe.

Wiegmann, Horte and Sücker (1958) consider the X-ray *counter patterns* to be more suitable for the differentiation of the two minerals.

The comparison of the *infrared absorption spectra* of the two minerals has given much better results. Infrared spectra are direct consequences of the molecular structure and yield thus a more distinct picture of the Si → Al substitution than X-ray patterns bound indirectly (through the electron density of the molecule) to the structure.

The infrared spectrum of mullite was investigated by Letort (1952), Roy and Francis (1953) and more recently by Tarte (1959) who made detailed and valuable observations. Infrared absorption spectra of sillimanite and mullite with two different sample widths are given in Fig. 1, according to Tarte's (1959) data. A rough survey of the outline of the two spectra will reveal many differences: it can be seen distinctly that the spectrum of sillimanite is formed by numerous sharp absorption bands, while the spectrum of mullite is characterized, because of the Si → Al substitution, by wide bands few in number.

The following differences are most characteristic and well suitable for identification: mullite shows only an insignificant absorption in the interval of 670—700 cm^{-1}, whereas we see a very distinct, strong absorption with sillimanite at $\nu = 691\ cm^{-1}$. This section of the spectrum is very suitable for detecting the presence of even a small quantity of sillimanite in mullite. Theoretically, the best section to detect a slight quantity of mullite in sillimanite would be the neigbourhood of the absorption band at 860 cm^{-1} which is characterized by a strong absorption of mullite and a low absorption of sillimanite. Bands, however, not being sharp enough in this section make an exact evaluation difficult. The examination of the interval between

1100—1200 cm^{-1} gives better results: both minerals show a characteristic double absorption band in this interval, though in different positions. The positions of the peaks are 1180 and 1200 cm^{-1} for sillimanite, and 1145 and 1178 cm^{-1} for mullite.

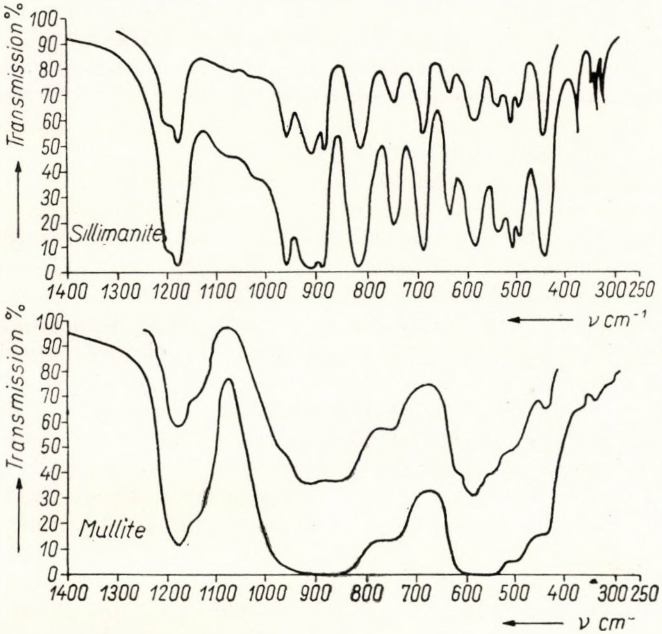

Figure 1

Infrared absorption spectra of mullite and of sillimanite according to Tarte (1959). Curves of two types refer to samples of different layer widths

B) QUANTITATIVE DETERMINATION OF MULLITE

For the quantitative determination of mullite the literature gives several methods. Having investigated these methods most scrupulously, we have found the X-ray internal standard technique (adopted first by Grofcsik and Vágó [1952] and used by several authors independently of them) most suitable for the practical determination of mullite-content.

A *combination* of the methods mentioned above will give even better results.

Optical Methods

Mullite is relatively well recognizable microscopically if we do not have very small crystals. It is usually met with in the form of pin-shaped crystals, interwoven in a felt-like arrangement, but it may occur also in other forms: e. g. Halm (1948) described globular mullite, Karyakin and Margulis (1956), isometrically grained mullite crystals of short prismatic form.

The microscopic method is well suitable for the detection of large mullite crystals, even in low quantities, but it fails if the crystals are tiny or beyond the limit of the resolving power of the microscope.

The crystals being needle-shaped and interwoven, the integrating methods of volume measurement will necessarily be incorrect to a higher or lower extent. Another practical disadvantage of the method is that the preparation of the specimen takes a long time. By using polished thick sections instead of thin ones and by observing the light reflected from the specimen (as in the technique of ore- or metallographic microscopy), the grinding, resp. polishing time can be reduced.

Curtis (1925) has investigated the formation of synthetic "sillimanite" by a microscopic technique and has illustrated his studies with numerous photomicrographs (some of them coloured). The material, described by him as *sillimanite*, is, naturally, mullite. A later study of Curtis (1928) shows that he endeavoured to identify mullite and (partly) to determine it quantitatively in refractories. Here again he used the method of photomicrography. His results are in good agreement with other experiences especially in the case of furnace blocks with high mullite content (Corhart blocks).

Budnikov and Khizh (1930) investigated a refractory lining by microscopic methods. They observed that a high content of mullite crystals, partly with inclusions of *wüstite*, could be seen microscopically in the thin sections cut from the lining after a use of six months. From this the authors concluded that in some cases iron compounds might contribute to mullite formation.

Photo-micrographs (and X-ray investigations) made by Meldau and Stach (1930) have confirmed that a high content of mullite is formed in vitreous silicate phases produced by industrial fly-ash. The original photomicrographs show sferolite-like crystals which the author had taken for mullite, their high reflectivity, however, refers rather to magnetite, while mullite is a constituent of grog.

Krause and Keetman (1935, 1936, 1937) determined mullite content by planimetering thin sections, but even the authors themselves found the measurement of small mullite crystals to be tedious and inaccurate. The growth of mullite is characterized by the following equation

$$L = B \log Z$$

where L — length of the crystal,
Z — time,
B — constant.

Mullite crystals grow at the expense of small crystals.

Harvey and Birch (1936) examined the mullite content of superduty firebrick by microscopic methods. According to them, mullite can be detected microscopically only after a firing at P. C. E. 18, while by X-ray methods, already after a firing at P. C. E. 11, i.e. at a much lower temperature; the amount of mullite, as determined by X-ray methods, was approximately equal in both cases.

Tavasci (1937), a pioneer in the use of reflection microscopy of portland cement clinker, tried this method also for quantitative mullite determination. His results have proved once more that the sure detection and accurate determination of mullite is possible only after a firing at high temperatures; the method of microscopic illumination and the preparation technique of the sections do not affect this criterion.

Massazza (1951), using Tavasci's method of reflection microscopy for the investigation of the texture of porcelain, added an etching technique with 1 + 20 HF. Unfortunately, the paper gives only qualitative and no quantitative data. Porcelains, made by various manufacturers of the world, have almost the same mineralogical composition: quartz, mullite and vitreous phase. Only two exceptions are mentioned: leucite occurs in American china, and quartz partly transforms into cristobalite in German *Hartporzellan*. Budnikov and Fadeeva (1952) used *electron-optical* methods for the determination of mullite by the indirect way of *replicas* (made of several sorts of plastics).

Filonenko and Lavrov (1952) used microscopic methods for studying the rules governing the melting of mullite.

An indirect method of microscopic examination was used by Nazarenko and Sviridenko (1954) for determining the effectiveness of mineralizers: not the growth of mullite crystals, but the decrease of quartz-content was measured and used as a basis of calculations. (The latter process can be observed more easily than the former.)

However, the disadvantage of the indirect measurement is that the results may be affected by extraneous factors.

The mullite content of the transition layer between electro-porcelain and its felspar-bearing glaze was determined by Inzigneri and Peco (1955) who applied the method of reflection microscopy. The hydrogen fluoride etching technique has confirmed its superiority in this case too. Several rules of influence on the formation of mullite were determined microscopically by Hamano (1957). He investigated the products of china clay—felspar mixes after firing in the range between 1270—1450 °C.

X-Ray Methods

The most reliable way to identify mineral mixtures is the X-ray method of powder patterns. It goes without saying that this method has also been tried as a basis for quantitative measurements. Owing to the rapid progress of X-ray methods in the last decades, at present X-ray patterns yield the most suitable method for the quantitative determination of mullite.

The X-ray spectrometric method suggested by Tuttle and Cook (1949) uses an X-ray spectrometer with GM-counter. Their method is reliable only when using a GM-counter X-ray spectrometer, because in case of photographic evaluation many external sources of error may hamper the exact quantitative evaluation of results. Comparative examinations, however, may be performed by means of a photographic X-ray unit too, because similar factors influence the line intensities upon both photographic films. Tuttle and Cook have made the interesting observation that nepheline-sienite, a frequent constituent of American china, does not give mullite while being fired.

Gad and Barrett (1950) studied the mullite formation of clay and clay-bearing bodies during firing. They adopted an X-ray method suitable only for qualitative work.

Mikheev and Stulov (1955) studied the mineralogical constitution products of fired layer silicates by an X-ray method.

The use of single-crystal rotation X-ray photographs gives better results which are also suitable for structure determination. This method was applied by Brindley and Hunter (1955) to identify the firing products of nacrite. The method, naturally, can be used only if single crystals of relatively large sizes are available.

Similar investigations were made by Beznosikova and Poluboyarinov (1955) in order to determine the mullitization temperature of several mixes of alumina and silica content.

Richardson and Wilde (1952) used an X-ray method for the phase identification of fired clays. In their opinion X-ray methods are sensitive enough for the purpose of determining the firing temperature by the mere evaluation of X-ray patterns. It is not probable, however, that this statement could be applied to all sorts of clays; it may stand only for the clay or clay-mineral mix used by the authors.

As mentioned already, X-ray methods may be used for the *quantitative determination of minerals* by measuring the intensity of reflections since this is proportional to the amount of the mineral in the sample. Line intensity, however, is determined by several additional factors, e.g. by the preparation technique of the sample, the quality and amount of bond material (a sample in a plastic tube gives reflections of quite another intensity than do others with Canada balsam bond). Line intensities are affected also by factors depending on photographic evaluation, e. g. the developing process and the quality of the photographic film.

All these difficulties can be avoided by using the method of *internal standards*. Essentially, this method consists of admixing a *reference material* to the sample in a definite quantity and of making an X-ray pattern from the mix. The reflections of the investigated material and of the reference material will appear on the pattern. The intensity of a suitably chosen line of the investigated mineral related to that of a similar line of the reference material will give the amount of the investigated material by a calibration table or by a plot.

A new method of mullite determination was proposed by Grofcsik and Vágó (1952) following the principle of the "internal standard technique". This technique, though used in spectrometry, is new among X-ray methods. *Ammonium chloride* was chosen as a material of an internal standard, because this compound — crystallizing in the cubic system — gives few but sharp, well-defined lines of completely identical positions. These lines do not coincide with the lines of mullite and of the more common accessory minerals. Ammonium chloride is easily accessible and is of a standard quality. It is even better to use NH_4Cl instead of NaCl or MgO since the lines of the two latter coincide with characteristic mullite lines. Grofcsik and Vágó have compared the intensity of the 1.444 kX line of mullite with that of the 1.035 kX line of NH_4Cl. Both lines are medium strong, they do not coincide with the lines of the more common contaminating minerals, occur even in a low concentration and, finally, are close to one another, thus reducing the so-called "macro errors" due to the uneven founding of the photographic film.

Twelve mixes of glass-powder and mullite, each containing 15 per cent reagent-grade ammonium chloride, were prepared for the calibration experiments. The X-ray line couple (mentioned in the foregoing) was photometered by a spectrum line photometer in every pattern. The logarithmic scale of the photometer shows the ratio of

$$\log \frac{I_2}{I_1} .$$

These values plotted as a function of mullite concentration yield an almost linear plot (with only a small and uniform curvature).

The essence of this type of mullite determination is to add 15 per cent of reagent grade, finely ground and desiccator-dried NH_4Cl to the material to be analyzed. By photometering the described line couple of the X-ray pattern the $\log I_2/I_2$ ratio is obtained. The mullite content of the mix can be determined by a calibration table (Table III) or by a calibration plot. The method just described can be used even better with an X-ray unit of GM-counter recording. In this case, of course, the photometering step is replaced by a direct measurement of the intensity ratio.

TABLE III

Calibration table of X-ray determination of mullite

No.	Mullite percentage	Glass powder percentage	$\log \frac{I_2}{I_1}$
1	10	90	4.0
2	14	86	7.0
3	20	80	8.5
4	25	75	9.5
5	30	70	10.0
6	40	60	10.8
7	50	50	11.5
8	60	40	12.1
9	70	30	12.6
10	75	25	12.8
11	80	20	13.1
12	90	10	13.5

Even a small amount of mullite can be exactly determined by this technique. The particle size of mullite crystals does not affect the results.

The application of this method is, however, limited since in case of a high number of different phases (e.g. in stoneware, earthenware, faience, etc.) the lines of the other, non-mullite, non-aluminosilicate phases may interfere with one or the other line of the line couple. The method, on the other hand, is applicable to all materials containing a predominant quantity of alumino-silicates, e.g. fireclay refractories and especially synthetic mixes. The error limit of the method is in these cases within ±5 per cent, as shown by the data of Grofcsik and Vágó.

Independently of these authors a similar method was proposed by Ziołowski (1954, 1955). He relied on the "internal standard principle", but used a focussed camera and a preparation with eccentric rotation. (Owing to eccentricity, the area of the preparation reflecting X-rays becomes larger and the errors due to sample unequalities and partial absorption diminish.) The reference material was reagent-grade *NaCl in a proportion of 10 per cent*. The 2.20 kX line of mullite and 1.99 kX line of NaCl were used as a line couple. The evaluation was made planimetrically (i. e. by measuring the weight of the maximum and of the examined blackening curves).

The mineralogical constitution of kaolin-alumina mixes, fired at different temperatures, was investigated by Moore and Prasad (1955). They also used an X-ray technique of measurements, but took *calcium fluoride* as reference material. Beznosikova and Poluboyarinov (1958) added *20 per cent sodium chloride* as an internal standard material to determine the quantity both of corundum and mullite. The line triplet used was mullite 2.20 kX, corundum 2.05 kX, sodium chloride 1.99 kX.

Other Methods of Mullite Determination

Some other, special methods have been used in order to detect or determine mullite. Thompson and Parmelee (1937) examined the thermal *dilatation* of the glasses in the system SiO_2—Al_2O_3. The evaluation of the dilatation curves has shown that mullite formation begins already at 1000 °C if heating lasts very long.

Results of dilatation examinations made by Gworek and Towers (1945) suggest the hypothesis that mullite is the sole crystalline phase of the system SiO_2—Al_2O_3 at 1200 °C. Kaolinite, γ-alumina, amorphous SiO_2 have been investigated dilatometrically as mixes of different ratios and also as pure substances. The investigations, however, have not yielded an appropriate explanation for the dilatation characteristics of clay.

Shorter (1955) studied mullite formation with the aid of *refractoriness-under-load* tests. His results are of importance chiefly for the selection of suitable mineralizers, i. e. technically. An examination technique of such a complex nature as refractoriness-under-load is obviously affected by a number of factors and is characterized by the superposition of several effects during firing (one of the main factors is, of course, the formation of mullite).

The Quantitative Determination of Mullite Content by Calculation

The quantity of mullite can be determined, though with a limited accuracy, also by calculation. The data of the *base* systems necessary for the calculations are in most cases available. Constituents of low concentration must be either neglected or added to one of the chief constituents. This, however, reduces the accuracy of calculations. In practice the calculation can often be performed according to one of the three-component systems the principal data of which are available in most physico-chemical manuals. The phase constitution and the mullite quantity of say, porcelain may be calculated according to the system $K_2O—Al_2O_3—SiO_2$.

In calculating the general rules of phase theory, first of all the phase law and the center-of-gravity principle are observed. An example was given by Shelton (1948) who determined the phase composition of porcelain according to the phase diagram and by the logical use of the graphic lever rule. Changes of phase composition influence several properties of the porcelain ware in a very characteristic way and to a high extent, e.g. its porosity, shrinkage, dielectric constant, density, etc. Calculated and measured phase quantities are generally in very good agreement.

The mullite content of fireclay refractories was determined by Konopiczky (1954*a*, 1955) according to the system $K_2O—Al_2O_3—SiO_2$. In the original paper of the author only fireclay of 20—40 per cent Al_2O_3 content was examined, but his method — being the application of general phase-equilibrium considerations to this special problem — can be well used with refractories considerably higher in alumina.

A common disadvantage of these calculation methods is the premise that from a thermo-dynamical point of view the *equilibrium* of the system is always presupposed. As is well known, the state of equilibrium in practice is very rare, especially in case of silicates. The phase constitution of porcelain is a good example: the locus of porcelain, according to its chemical composition, falls into the primary crystallization area of mullite, i.e. only mullite is expected to form in large (primary) crystals. Microscopically, however, fired porcelain always contains a high amount of quartz in undissolved form from the quartz originally added as a body constituent. This accounts for the non-equilibrium condition of the system.

The quartz content of porcelain, on the other hand, permits a numerical determination of the deviation from the state of equilibrium. This index, termed *equilibrium index* by Grofcsik and Tamás (1958) can be used for computing the mineralogical composition of the body after firing, quite independently of the firing temperature. Not only phase percentages of the fired ware but also the chemical composition of the vitreous phase can be predicted by this method. According to the authors' calculations, the equilibrium index of Pécs china equals 0.559; it contains 15.2 per cent quartz, 36.0 per cent mullite and 48.8 per cent vitreous phase. The calculated chemical composition of the glass is: 77.6 per cent SiO_2, 13.1 per cent Al_2O_3 and 9.3 K_2O. The method can be generalized to an entire group of non-equilibria (to non-equilibria of the $G + 1$ type, i. e. containing *one* supernumerary phase as compared to the phase rule).

Methods Based upon Solubility Differences

The solubility of mullite is low as compared to other silicates. Several authors have used this property of mullite for its detection and quantitative determination. As solubility differences are affected not only by the *material quality* but by *the particle size* as well, none of such methods can be called the real *determination* technique of mullite. They are only more or less accurate *separation* procedures. As the solution of a solid material in a liquid is a surface process, the effect of the particle size cannot be disregarded; not even by the application of methodologic "tricks" which vary the *concentration, temperature* or *quality* of the dissolving acid. The method of solubility differences, on the other hand, is simple. As it does not require any special device or instrument, it is extensively used in spite of its unsatisfactory results.

The "sillimanite" content of porcelain was determined by Zoellner (1908) according to the method of H_2F_2-dissolving. (At that time mullite was still unknown; the author was convinced to have determined the sillimanite content of porcelain.)

Bowmaker suggested a method (1929) for the prediction of the durability of fireclay tank blocks. He used the technique of dissolving in hydrofluoric acid. Later the method was improved by Bowmaker and Partridge (1931). Since this method determines the amount of silicates insoluble in hydrogen fluoride, it cannot be called a mullite determination.

As early as in 1927 (McVay 1927) *mullite of fine particle size* was observed to *dissolve in hydrogen fluoride*. Its solubility properties were determined by Yoshioka and Isomachu (1930) who measured the effect of different solution times at 0 °C. On the basis of their results a new method was adopted with fixed determination conditions.

The most common method of determination, based on the bad solubility of mullite, was proposed by Rieke and Schade (1930). All solution circumstances are exactly fixed; temperature: 18 °C; hydrogen fluoride concentration: 20 per cent; solution time: 18 hours; particle size: 0.120—0.149 mm. The dissolution should be carried out in a thermostat vessel. Adherence to these prescriptions gives well-reproducible results.

Mullite determination following the principle of solubility differences has found a widespread use. A number of authors have modified some parameters of the determination, e.g. temperature or time of dissolution, the concentration of the dissolving acid, or have prescribed some other circumstances, e.g. the constant stirring of the solution. Practically, every research worker interested in the mullite problem has proposed some major or minor alterations.

The method was investigated by Rieke (1940) once more. He found it satisfactory in its principles, although several authors had pointed out the unavoidable effect of the original particle size (Kraft and Gurvich 1935, Freberg 1939, Filonenko 1948, etc.). The mullite amount, as obtained by the solution method, is, as a rule, smaller than its actual quantity. Goncharov and Kleinberg (1938), on the other hand, are of the opinion that the particle size of the raw materials and the effect of mineralizers affect the results obtained by the solution method to such an extent that this method should be considered *unsuitable*.

Although these drawbacks of the solution methods are well known, some authors have lately suggested several techniques, sometimes combined with others, with the aim of obtaining satisfactory results by the principle of solubility differences.

The mullite content of a ground fireclay refractory was determined by Konopicky's (1954*b*) hydrogen fluoride solution method and completed by the *chemical analysis* of the solution residue. The Al_2O_3 content of the residue has been found as high as 78 per cent. This indicates the presence of either β-mullite (Rooksby and Partridge 1939) or a mixture of mullite and corundum. After 3 hours the solution time does not affect the amount of mullite determined this way.

A modified H_2F_2 solution method of mullite determination was recommended by Konopiczky, Hopmann and Kampa (1956), but it is not suitable for determining the total mullite content of the material, only the fraction of coarse particles, called *Grob-mullite*. Their detailed and systematic studies for clearing up the solution mechanism, have led to the following method of determination: grind the material to a particle size finer than 0.06 mm and weigh samples of 0.5 g each into wide platinum crucibles. Dissolve the samples in 40 per cent hydrogen fluoride solution of 0 °C temperature for 1 and 7 hours. In order to keep temperature constant, cool the crucibles with ice-cold water. Filter and wash the samples after the time fixed and determine the alumina content of the solution residue. Calculate the amount of mullite according to the equation

$$M = W_1 \cdot \frac{\dfrac{A_1}{S_1}}{\dfrac{A_7}{S_7}}$$

where M — percentage of mullite,
W — weight of solution residue,
A — alumina content of the solution residue. (All data are given in weight percentages; indices refer to the solution time in hours.)

In a later contribution Konopiczky and Köhler (1958) slightly modified this method. The new method is, according to the authors' data, suitable for the determination of the vitreous phase too.

In order to determine the joint quantity of mullite and corundum, Demidova and Goncharov (1955) specified a solution method. The steps of their method are: wash the sample of particle size fractions between 0.20—0.15 mm in water and alcohol, dry to constant weight, dissolve in 40 ml hydrogen fluoride for 30 minutes, stir every 5 minutes and repeat the dissolving process after decantation. No dissolving temperature is prescribed, neither is the effect due to particle size mentioned. The solution residue contains the total mullite and corundum content of the material.

Hansson (1952) described a new technique of the dissolving method, comprising a specific gravity separation. Though the author says that the dissolving methods of mullite determination give but relative values, he suggests the modification to separate the solution residue from contaminations by *centrifuging it in a suitable heavy liquid.* Thirty per cent hydrogen fluoride and 0 °C temperature are recommended for the procedure.

From a more detailed investigation Hansson (1955) has concluded that the dissolving characteristics of mullite, corundum, kyanite and sillimanite are almost the same; by centrifuging the solution residue in a heavy liquid of specific gravity 2.95 g/ml, mullite goes quantitatively into the fraction of high specific gravity. Thus mullite *completely separates* from the other, poorly-soluble constituents. Errors due to particle size effects, are obviously not avoided by this modified method.

On the strength of his X-ray results, Maennel (1958) who studied the effect of H_2F_2 dissolving upon the mullite content of porcelain samples, stated that the mullite quantity, determined by the H_2F_2 method, is always less than its real amount. This phenomenon is due to particle size and specific surface effects.

The method of mullite determination by dissolving the material in hydrogen fluoride has been used in several varieties by a number of other authors as well: by Miehr, Immke and Kratzert (1928), Freberg (1939*b*), Avgustinik and Ushakova (1945), Bartuška (1957) and by Nandi (1950). The latter, being aware of the afore-said difficulties, says that the method of solubility differences can give only the so-called "technical mullite content". The real mullite content can be obtained from this by multiplying it by an empiric factor which has the average value of $\frac{100}{83}$.

Combined Methods

According to the considerations described in the foregoing, no variant of the method based upon the solubility differences between mullite and other minerals is suitable for the exact determination of mullite. The errors of this method, being inherent in its principle, cannot be avoided either by modifying or by completing it. The various methods of mullite detection and determination, however, can be successfully *combined* with each other. Some examples: Budnikov, Tresvyatski and Kushakovski (1953) and McVay and Thompson (1928) combined *X-ray methods* with *optical* (microscopic) investigation; Comeforo, Fisher and Bradley (1948) and Lundin (1955) used *X-ray methods* with *optical, electronoptical and electron diffraction* investigation; Letort (1952) examined mullite formation of natural substances and artificial mixes by combining *X-ray methods* with *infrared spectroscopy.*

The hydrogen fluoride technique can be combined with other detection or determination methods too: Yoshioka, Horie and Karashima (1934) combined it with *microscopic* examinations, Parmelee and Rodriquez (1942) and Budnikov and Shmukler (1946), with *X-ray* methods.

Such combined methods of investigation are not free of misconsiderations. As an example "*keramite*" or "*porcite*", described by Bradley and Roussin (1932) as an individual phase, should be mentioned. This mineral, separated by the hydrogen fluoride technique from porcelain, has given an X-ray diffraction pattern slightly different from that of pure mullite: the differences of some intensities were well marked. But these differences, as proved by the investigations of Wyckoff (1933) and Posnjak and Greig (1933), were not due to the crystal structure but to the orientation of mullite particles during the filtering step of the process.

The number of methods combined may be increased: Palmeri (1951) and Krushel (1952) e.g. examined the hydrogen fluoride solution residue both by X-ray diffraction and by microscope as well as by electron microscope. One of the difficulties involved in optical methods is the interesting fact that (though its most common crystal form is a needle-shaped habit) under the electron microscope and even under high-magnification optical microscope mullite may sometimes occur in a globular form. A previous separation by hydrogen fluoride is very advantageous in such cases.

Summing up what has been said about methods in this chapter, we may say that under given circumstances any one of them, alone or combined, may be suitable for detecting mullite or determining its quantity.

If the absolute quantity of mullite is *low* (and mullite crystals are big enough), optical determination under microscope will prove the most suitable; if the quantity is *high*, X-ray techniques are recommended. A most exact *quantitative determination* can be made by the X-ray method with the application of an internal standard, which gives the actual mullite content of the material, irrespective of its particle size distribution. This method, however, cannot be applied in case of a high quantity of non-aluminosilicate disturbing minerals. A very high quantity of mullite makes the microscopic planimetering difficult, as the interlaced network of needle-shaped crystals hampers exact planimetering.

The quantity of mullite cannot be determined by a solution method; dissolving technique, however, may serve as a very useful aid in determining the quantity of coarse mullite (the so-called *technical mullite content),* very important in quality specifications, e.g. of refractories. Fine mullite crystals being overwhelming in the vitreous grog of fireclay refractories, the melting of the vitreous phase involves the fine mullite crystals and is therefore inefficient for determining refractoriness-under-load properties. From this point of view the determination of "mullite" content by a dissolving method may be very important; but this amount necessarily differs from the actual mullite content of the material. A further advantage of the solution method is that it separates mullite from contaminating minerals and makes it possible to investigate the properties of pure mullite.

Mullite-detecting, resp. determining methods, based upon dilatation, infrared spectrography, electron microscopy, etc. may be used only for special purposes.

PART TWO

THE SYSTEM $Al_2O_3-SiO_2$

CHAPTER 3

INVESTIGATIONS INTO THE SYSTEM Al_2O_3—SiO_2

A) THE TWO-COMPONENT SYSTEM

The first investigators of the physico-chemical properties of the system Al_2O_3—SiO_2, Shepherd, Rankin and Wright (1909) described *sillimanite* as the sole crystalline compound of the system, that has a *congruent* melting point at 1811 ± 10°C. The eutectic composition between cristobalite and sillimanite contains 10 per cent alumina; its melting point is at 1600 °C.

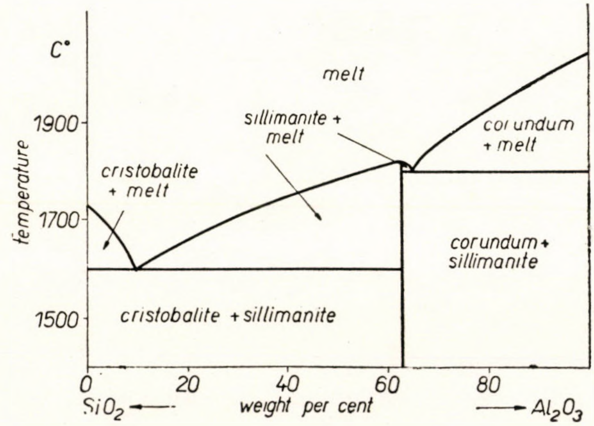

Figure 2

The system Al_2O_3—SiO_2 according to Rankin and co-workers (1909)

Although, according to the earlier data of Beekman (1902), the refractive indices of artificial sillimanite are lower than those of the natural mineral, the study of Shepherd and co-workers does not explain this phenomenon; on the other hand, later investigations by Shepherd and Rankin (1911, 1915) again determine similar positions of the eutectic points, modifying only some temperature data (Fig. 2).

According to an interesting statement made by Shepherd, Rankin and Wright (1909), the inclusions, well visible in sillimanite aggregates, contain a vitreous phase (called "sillimanite-glass" by the authors), and have a refractive index $n_D = 1.530$.

The existence of this sillimanite-glass was very soon discredited. According to former investigations by Rankin, sillimanite has such a high crystallization ability that it does not remain in a vitreous form even if the melt is most rapidly quenched; consequently, this glass can be no sillimanite-glass.

The investigations by Bowen and Greig (1924) and the phase diagram published by them have changed all theories concerning this question. They used a static method of investigation with raw materials of natural sillimanite, pure synthetic alumina and silica. Mixes of different compositions were made of these materials, fused in high-temperature furnaces in pure air-atmosphere and quenched in a suitable cooling agent. The phase diagram according to Bowen and Greig is reproduced in Fig. 3.

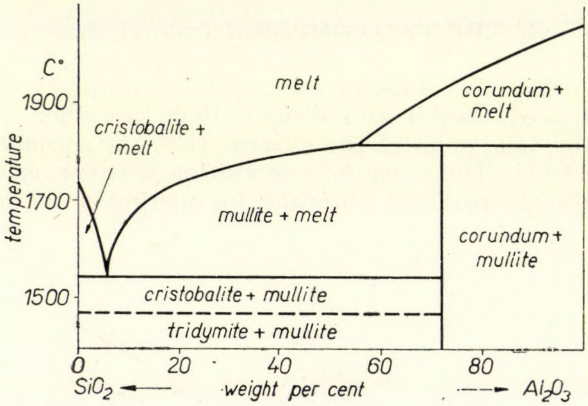

Figure 3
The system Al_2O_3—SiO_2 according to Bowen and Greig (1924)

The binary compound of silica and alumina has a composition of $3Al_2O_3 \cdot 2SiO_2$ and melts *incongruently* at 1810 °C. This crystalline solid is identical with natural mineral *mullite*.

Although the phase diagram, published by Bowen and Greig, has been subjected to criticism for a long time, its main statement: *mullite* is the only stable compound of the system, is thought correct even today. Though Scholze and Wondratschek (1956) have proved by precision X-ray methods that sillimanite inclusions of basalts transform into mullite above 1400 °C, some authors, e.g. Budnikow and Mtschedlov—Petrossian (1958) have but recently assumed sillimanite as the stable alumino-silicate and considered mullite a defect-lattice variation of the former.

The *eutectic* invariant point between silica and mullite contains, according to Bowen and Greig, 5.5 per cent alumina and lies at 1545 °C. Between mullite and alumina there is no eutectic invariant point but a reaction *(peritectic)* invariant point. System Al_2O_3—SiO_2 contains only one liquid phase; the phenomenon of liquid segregation is absent.

Some characteristic temperatures of the system were modified by Morris (1935). According to him, the temperature of the eutectic between silica and mullite is 1551°C, the melting points of mullite, cristobalite and corundum are 1827, 1729 and 2083 °C, respectively.

Mixes of molar composition yield 50 per cent fine separate corundum crystals and a vitreous substance if quenched from a temperature above the incongruent melting point of mullite. This composition falls already into the primary field of corundum. The simultaneously formed vitreous phase, rich in silica, has a refractive index of 1.530, i.e. identical with the refractivity of "sillimanite-glass" described by Rankin and co-workers.

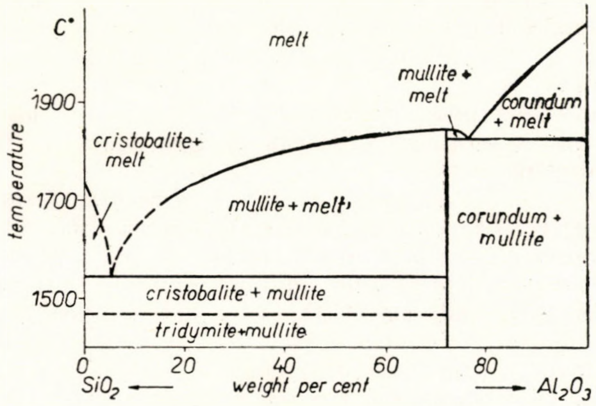

Figure 4

The system Al_2O_3—SiO_2 according to Toropov and Galakhov (1953)

By heating the melts of sillimanite or of the artificial mixes of similar composition, SiO_2 vapour volatilizes from the melt. With constant evaporation the residue will be soon enriched with Al_2O_3 and finally reaches the composition of mullite. The striking flattening of the liquidus curve of the phase diagram from the eutectic in the direction of the alumina side and its steepness in the direction of the silica side can be well explained by this phenomenon of evaporation.

According to Eitel (1941) there is a vapour pressure maximum as well as a boiling point minimum near the composition of the sillimanite melt. Mullite is the product of the solidification of a liquid phase of constant composition in equlibrium co-existing with a silica-rich vapour phase.

The importance of SiO_2 evaporation was emphasized by Toropov and Galakhov (1951, 1953). Mullite melts, according to them, without decomposition *(congruently)* at 1810 °C. Fig. 4 gives the phase diagram as determined by them. A tungsten-wound microfurnace operating *in vacuo* was used; the samples could be covered by a thin tungsten-film in this furnace during heating and prevent possible evaporation. According to the authors, if the evaporation of the silica is not prevented by a tungsten coating, corundum is due to form during the melting process, as the partial leave of SiO_2 enriches the residue in alumina. The use of samples coated by a tungsten-film has not led, however, to any corundum in the quenched melt, which showed a decomposition-free (i.e. congruent) melting of mullite. The presence of a second eutectic between corundum and mullite with an alumina percentage of 77.5 and at a temperature of 1845 °C is clearly visible in the phase diagram published by Toropov and Galakhov.

According to the aforesaid considerations, two important questions arise: (i) the melting character of mullite, i.e. its congruent or incongruent nature; (ii) the composition stability of mullite, i. e. whether it has a constant composition or if it forms solid solutions. Should the latter statement prove to be correct, the direction and extension of the solid-solution field must be determined too.

Being points of primary importance, both questions have been carefully investigated. A thorough criticism of data found in the literature suggests the following answers:

To question (i): *The melting of mullite is of congruent nature.*

To question (ii): *The composition of mullite is not stable.* This instability is due to the formation of *solid solutions* (mixed crystals) and not to possible mechanical effects. The field of solid solutions extends in both directions, i.e. towards the SiO_2 and the Al_2O_3 side, but studies concerning the limits of solid solution are contradictory to such an extent that it would be premature to make a definite statement.

Bowen and Greig's opinion (the incongruent melting of mullite) was not disputed for about a quarter of a century. In 1951, however, Soviet scientists observed the primary crystallization of mullite in an area of a three-component system, in the immediate vicinity of the figurative mullite point. This is impossible in case of incongruent melting.

As a final result of a number of detailed experiments, Toropov and Galakhov (1952, 1953) stated that the characteristic melting process of mullite was *congruent.* In the first form of their phase diagram (Fig. 4) they determined the maximum of the liquidus curve, which represents the melting point of mullite, and established the eutectic between mullite and corundum.

Further examinations were made by Budnikov, Tresvyatski and Kushakovski (1953) in order to determine the melting characteristics of mullite. The high-alumina part of the system was investigated by differential thermal analysis, by means of a tungsten-molybdenum thermocouple. The thermocouple had previously been calibrated by silicates, aluminates, etc. of definitely known melting points. Compositions of 100, 85, 77 and 72 per cent alumina were investigated. According to these experiments, the melting point of mullite lies at 1900° ± 20 °C. A careful X-ray study of the 77 per cent alumina mix undoubtedly showed the *congruent* character of mullite melting.

Experiments made by Bauer, Gordon and Moore (1950) and aimed at the production of single-crystal mullite from Al_2O_3—SiO_2 mixes by oxy-hydrogen flame fusion at appr. 1945 °C and by a slow cooling seem to confirm congruent melting.

The second question, the occurrence of solid solutions between mullite and silica on the one hand and of alumina on the other, has also been a subject of thorough investigations.

The formation of solid solutions between sillimanite and mullite (i.e. between silica and mullite) were considered impossible by Bowen and Greig, because the refractory indices of several types of mullite (isolated from porcelain, or from those synthesized from pure components of the system, etc.) were completely identical, independently of the original composition (i.e. high-alumina or high-silica nature) of the mix. Some analytical data showed a lower alumina content than thought of in theory; this, however, was explained by the unavoidable presence of substances rich in silica.

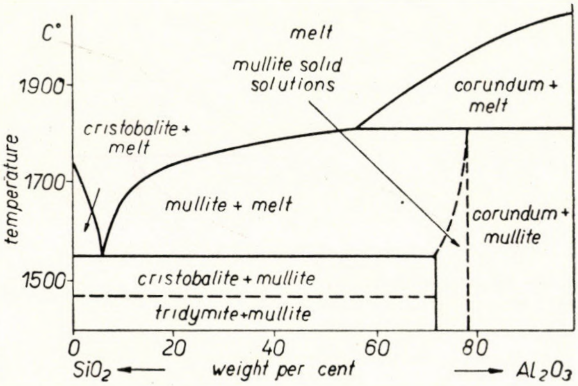

Figure 5

The system Al_2O_3—SiO_2 according to Shears and Archibald (1954)

Nahmias (1933) shared this opinion. If analytical data show that a sample of mullite has a higher silica or alumina content than presumed theoretically, it can never be a solid solution, only a mechanical mixture. The presence of solid solutions was disclaimed also by McAtee and Milligan (1950).

The absorption of alumina by the mullite lattice in form of solid solution was first presumed by Posnjak and Greig (1933), and corroborated experimentally by Sosman's (1933) investigations. According to the most cautious statement of the former, the lattice of mullite can take alumina in the form of a solid solution to a limit of approximately 75 per cent of alumina content (i.e. a quantity 3 per cent higher than the theoretical formula $3Al_2O_3 \cdot 2SiO_2$). This formation of solid solution causes an expansion in the lattice of mullite and is shown by minute differences between the refractory indices of natural and artificial mullite; the refractivity of natural mullite is, as a rule, higher, more similar to sillimanite than the artificial mineral and is frequently slightly coloured. All these characteristics are due to the usual iron and titanium contaminations of natural mullite.

Following Posnjak and Greig's (1933) investigations many scientists, e.g. Rooksby and Partridge (1939), Barta and Barta (1956) and others, have confirmed that solid solutions can form between mullite and corundum. Several authors have even proposed a new silica-alumina phase diagram.

The correction proposed by Shears and Archibald (1954), is represented in Fig. 5. The corrected diagram differs from the original by the marking of the solid solution area. The boundary curve is drawn as a dashed line, to show its uncertainty. The phase diagram modified by Konopiczky (Fig. 6) is similar.

All these corrections and modifications, however, result either from speculation or from experiments regarding minutiae only. A final solution of the problem can only be hoped from a detailed and careful study which would comprise not only the examination of solid solution formation or of some other selections but would give a wide synthesis of all the problems in this criticized area of the system.

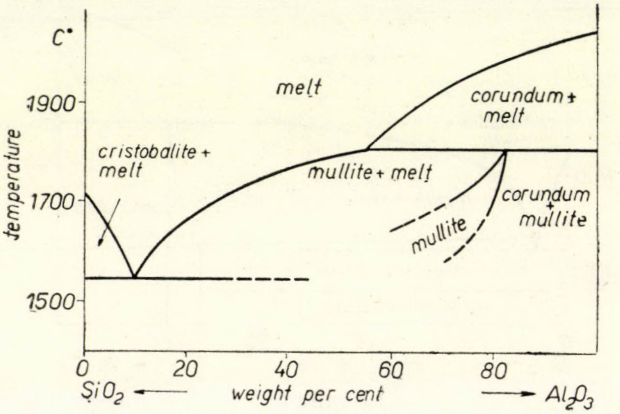

Figure 6

The system Al_2O_3—SiO_2 according to Konopiczky (1956)

Toropov and Galakhov's study (1958) elucidates the entire problem in all its complexity by using a precise experimental technique. The only insufficiency of the study is that no more than ten samples of different composition are analyzed. This is perhaps too small a number to represent a collection of quantitative data yet the authors give an excellent qualitative account of the process taking place in the vicinity of the mullite melting point.

In order to put an end to the phase equilibria of the Al_2O_3—SiO_2 system, Toropov and Galakhov investigated artificial mullite, synthesized in Galakhov's tungsten-furnace (Galakhov 1951) from chemically pure raw materials: alumina gel made of ammonium alum, and ground rock crystal. All raw materials were chemically pure and contained only spectrographic traces of contaminations. Investigations were made by the usual quenching method; quenched samples were analyzed by microscope, using either thin sections with immersion objectives or polished sections with an illumination of reflected light, and also by X-rays.

The phase diagram, determined by them and considered the most correct at present, is reproduced in Fig. 7. According to this diagram, mullite melts congruently and solid solutions occur between mullite and corundum. The position of the liquidus curve of solid solutions, as represented in Fig. 7, is probably correct. As a consequence of rapid crystallization, no glass or only a small quantity was found but the tiny secondary crystals, formed during the cooling of the melt, were excellently distinguishable from the big primary crystals formed during the thermal exposition slightly below the liquidus. Since the rapid crystallization of the residuary melt is in equilibrium with the solid phase, the determination of the position of the solidus boundary line of mullite is not very exact. In this case, crystal size is no longer a governing principle, as in the determination of the liquidus. The solidus is represented by a dotted line in Fig. 7. The characteristic points of the phase diagram are as follows: the composition and temperature of the eutectic between mullite solid solution and corundum are 79 per cent alumina, 21 per cent silica and 1850 °C, respectively. The limit composition of mullite solutions lies at about 78 per cent alumina, roughly corresponding to the composition of $2Al_2O_3 \cdot SiO_2$, given by Trömel and co-workers (1957).*

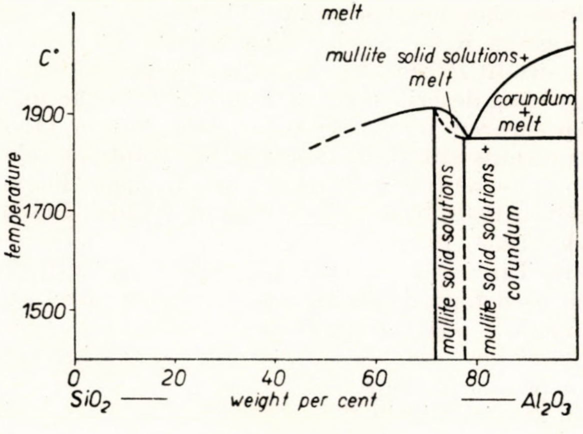

Figure 7

Part of the system Al_2O_3—SiO_2 according to Toropov and Galakhov (1958)

When the manuscript was ready we found a paper of high importance published in 1960: J. H. Welch *A new interpretation of the mullite problem*, in *Nature* **186,** 545. Mullite is, according to Welch, just one member of an extensive solid-solution series; the optical data given by most of the authors correspond better to a material of composition $2Al_2O_3 \cdot SiO_2$ than to one of composition $3Al_2O_3 \cdot 2SiO_2$. By determining the liquidus boundary lines of the Al_2O_3—SiO_2 phase diagram in a direct way (high-temperature microscopy), he has found that though the primary area of mullite contains the composition of $3Al_2O_3 \cdot 2SiO_2$, this compound has no special significance. The area of solid solutions extends to an alumina percentage of 75 per cent. Mullite melts at 1880 °C incongruently into corundum and a melt-phase.

B) THREE-COMPONENT ALUMINO-SILICATE SYSTEMS

Mullite is a natural constituent of three-component alumino-silicate systems too. Since the evaporation of SiO_2 during most experiments has been neglected (and owing to the high reputation of Bowens and Greig's phase diagram) the mullite area in these three-component systems has been represented without containing the mullite composition itself. In other words mullite is described as an incongruently melting compound even in three-component systems.

Among three-component alumino-silicate systems most studies have dealt with the system K_2O—Al_2O_3—SiO_2 because the composition of porcelain is most easily fitted into this system. The phase diagram of the complete system has been described by Bowen (1943); some unanswered questions have been cleared up by Schairer and Bowen (1947, 1954, 1955), whose phase diagram is still used as a starting point for calculations; most of them presuppose — as is general in the use of phase diagrams — a phase equilibrium (Shelton 1948, Kempcke and Treufels 1950, Brisbane and Segnit 1953, Konopiczky 1954, 1955).

Grofcsik and Tamás (1958) have suggested a method with which phase diagrams can be used for calculation also *in certain cases of* non-equilibria (if *one* supernumerary phase is present in addition to those required by Gibbs' phase rule). They used the method for calculating the mineralogical composition of a porcelain body.

The area of mullite within the system Na_2O—Al_2O_3—SiO_2 determined by Schairer and Bowen (1947, 1956) does not contain the figuratvie composition point of mullite, which indicates its incongruent melting.

Although the dhase diagram of the system MgO—Al_2O_3—SiO_2 has been known for long (Rankin and Merwin 1918), the exact position of the boundary curves became more reliable only after Foster's exact re-examination (Foster 1950). The melting of mullite is incongruent also according to this phase diagram. If the mix of oxides, with a gross composition of cordierite, is fired for half an hour at 1620 °C, homogeneous glass is obtained by quenching (Sugiura 1951); but if this glass is annealed for a longer time at 900 °C a devitrification process takes place, yielding mullite crystals. At higher temperatures these crystals react with the glass, and cordierite is formed again. This "inverse" incongruency is difficult to imagine; Sugiura ascribes to this phenomenon the failure of Rankin and Merwin (1918) to have determined crystalline substance as μ-cordierite which, in fact, is mullite formed in the vicinity of the cordierite-mullite boundary curve.

The position of the corundum-mullite boundary curve in this ternary system and in the system CaO—Al_2O_3—SiO_2 was more exactly determined by Aramaki and Roy (1959). The latter system was first investigated by Greig (1927).

Dietzel and Scholze (1955), investigating the system B_2O_3—Al_2O_3—SiO_2 have described that the liquidus temperatures of the mixes lying upon the primary field of mullite are but slightly lowered by the addition of B_2O_3. The d_{hkl} spacings of the mullite X-ray pattern are decreased by adding boron trioxide because mullite forms solid solutions with the borate of composition $9Al_2O_3 \cdot 2B_2O_3$; B-ions replace Si ions in the tetrahedral positions. This is why the mullite tank blocks corrode to a great extent with the borosilicate glasses.

The system $FeO—Al_2O_3—SiO_2$, investigated thoroughly by Schairer (1942) and later by Schairer and Yagi (1952) shows the melting character of mullite to be incongruent. It is very interesting, however, that the iron-bearing compound, corresponding to cordierite, $2FeO \cdot 2Al_2O_3 \cdot 5SiO_2$ melts at 1210 °C, forming mullite, tridymite and a melt. Although from the point of view of phase theory nothing prevents the formation of an incongruently melting compound during the decomposition of a compound melting incongruently itself, it is worth while to consider whether the melting character of mullite is really incongruent.

This question arose during the investigation of the system $TiO_2—Al_2O_3—SiO_2$ by Agamavi and White (1952), and also in the mullite field of the system $BaO—Al_2O_3—SiO_2$, investigated by Thomas (1950). Although Thomas ascribes the observed irregularities to the formation of solid solutions, the imperfect knowledge of the mullite-field and especially of the boundary curve may also yield some discrepancies among experimental data. No experiments were made by Thomas in the neigbourhood of the point representing the composition of mullite. According to Toropov and Galakhov's contribution, the system $BaO—Al_2O_3—SiO_2$ was the first to call in question the melting character of mullite.

Subsolidus equilibria in the system $Al_2O_3—SiO_2—H_2O$

All systems discussed in the foregoing are of the dry type; they do not contain any volatile materials. Owing to the extreme experimental difficulties, the phase equilibria in the system $Al_2O_3—SiO_2—H_2O$ have been determined but recently and even these concern only the subsolidus equilibria of the system. The present experimental equipment does not yet allow to investigate areas above the solidus; the possibilities for a super-liquidus investigation are even less promising.

The complete $Al_2O_3—SiO_2—H_2O$ system was examined by Roy and Osborn (1954). Results of their investigations are given in Fig. 8, which shows the compatibility triangles (in a slightly modified form) at an approximate pressure of 700 atm, as a function of temperature. It is interesting that these triangles show also *andalusite* as a stable phase (among anhydrous aluminosilicates), though this is most probably a metastable phase.

Triangles Nos I and II show phase distributions below 130 °C and between 130—175 °C, respectively. The difference between the two distributions is that two alumina hydrates *(gibbsite* and *boehmite)* are stable below 130 °C and only one (boehmite) is stable at a higher temperature; in addition to this, there is a possibility of a new co-existence between boehmite and *endellite*. Above 175 °C endellite (halloysite) is no longer stable. At 280°C a new phase appears: pyrophyllite, which is maintained up to 575 °C. Above 405 °C *kaolinite* becomes unstable, and a new phase, *hydralsite* is formed. Hydralsite is very similar to pyrophyllite; it has not yet been reported as a natural mineral though it may be also present in rocks. At this interval also anhydrous phases become stable: *mullite* and possibly *andalusite* may be present. Above 420 °C, *montmorillonite*, being no longer stable, disappears. A number of transformations take place above 450 °C: hydralsite decomposes, and a pyrophyllite-mullite co-existency is formed at about the same temperature. The last water-bearing phase, pyrophyllite

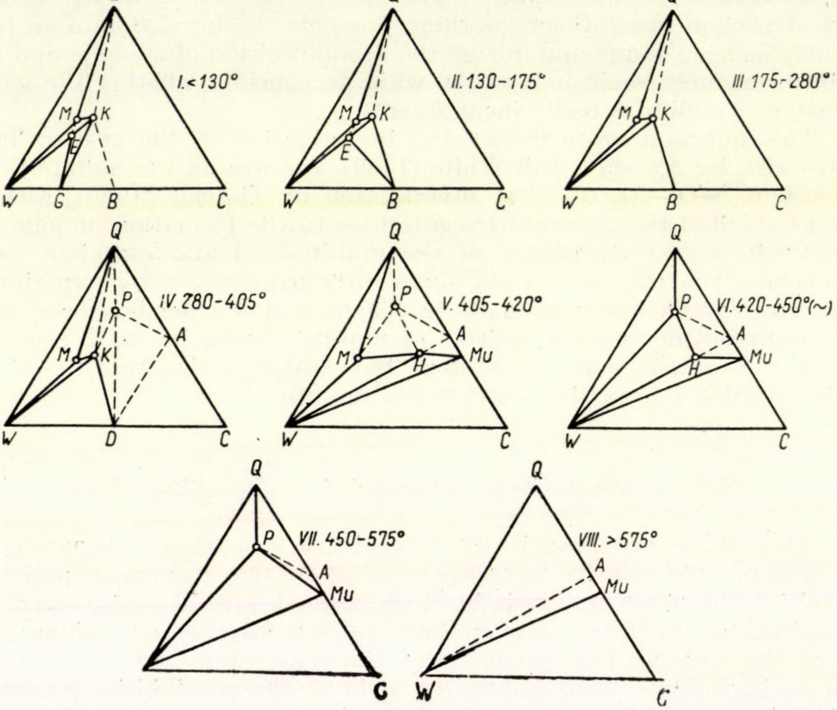

Figure 8

Subsolidus compatibility triangles of the system Al_2O_3—SiO_2—H_2O according to Roy and Osborn (1954) *A* andalusite, *B* boehmite, *C* corundum, *D* diaspore, *E* endellite (halloysite), *G* gibbsite, *H* hydralsite, *K* kaolinite, *M* montmorillonite, *Mu* mullite *Q* Quartz, *W* water

decomposes at 575 °C; at higher temperatures there are no water-bearing compounds in the system.

A number of interesting conclusions may be drawn from these triangles, e.g. all *dioctahedral* layer-lattice silicates have a lower decomposition temperature than the corresponding *trioctahedral* ones. Hydralsite which is very similar to pyrophyllite, has not yet been described as a natural mineral. It is possible, however, that some minerals described as pyrophyllite, are after all hydralsite or contain some of it.

As can be seen from the diagram, only mullite and the three apex-constituents are present in the system above 575 °C (the uncertain possibility of andalusite omitted). This feature of the system suggests a very important conclusion: all ceramic materials of a composition, falling within the system (and, in fact, many of them do), can be fired to mullite slightly above 575 °C. Present firing technologies, however, are higher by several hundred degrees centigrade. The phase distribution diagrams calculated and plotted according to exact measurements show the physico-chemical reality of the system under curing conditions described. With due regard to the above, a new technology, putting firing temperatures considerably lower, may be expected to develop. The firing of water-bearing alumino-silicates to mullite at a temperature slightly above 575 °C has no essential obstacles from a *theoretical* point of view.

PART THREE

THE STRUCTURE OF ANHYDROUS ALUMINO-SILICATES

CHAPTER 4

THE STRUCTURE OF $Al_2O_3 \cdot SiO_2$ ALUMINO-SILICATES

There are four types of anhydrous alumino-silicates to be found in nature: *kyanite* (named also *cyanite* or *disthen)*, a component of rocks formed under high pressure of crystalline shales and an accessory mineral in mica-shale; *andalusite*, a product of the contact metamorphosis of argillaceous rocks, to be found in crystalline shales and gneiss; and *sillimanite*, a characteristic component of gneissic rocks, of granulites and their pegmatites. The chemical composition of all these minerals corresponds to the formula $Al_2O_3 \cdot SiO_2$; all of them transform upon the action of heat into *mullite* (having the approximate formula $3Al_2O_3 \cdot 2SiO_2$) and SiO_2.

Mullite sometimes occurs in nature as a mineral of argillaceous contacts (cf. p. 11) but is very common in ceramic products. As seen from the genetic conditions, alumino-silicate minerals of the formula $Al_2O_3 \cdot SiO_2$ are products of high pressure, while mullite is formed under low pressure but at high temperatures. That is why kyanite, andalusite and sillimanite are, according to Miyashiro (1949), rock-forming minerals, whereas mullite seldom occurs in rocks but is common in industrial ceramic products.

(Dumortierite, of formula $8Al_2O_3 \cdot 6SiO_2 \cdot B_2O_3 \cdot H_2O$ also belongs to this group of minerals [Jeffery 1943] but since it contains not only Al_2O_3 and SiO_2, it has been excluded from the scope of this book.)

The crystal structures of the four alumino-silicates are closely related. In order to get a better understanding of the structure of mullite, a thorough study of the other three minerals is indispensable.

A) THE STRUCTURE OF KYANITE

According to crystallographic data, kyanite crystallizes in the *pinacoidal* class of the *triclinic* system. The measured characteristics of the kyanite unit cell are: axial lengths a — 7.09, b — 7.72, c — 5.56 Å; axial angles α — 90°, β — 101°02′, γ — $105°44\frac{1'}{2}$.

The structure of kyanite has been completely determined by Náray-Szabó, Taylor and Jackson (1929). According to their data the unit cell of the mineral contains 4 molecules of Al_2SiO_5.

The relatively high (1.75) refractive index and, the relatively low (15.05 $Å^3$) volume occupied per oxygen ion indicate that the structure of kyanite may be based on a *close-packed* arrangement of oxygen ions. This close packing belongs to the cubic system. Considering the base of the structure as described, we obtain the pattern shown in Fig. 9. The axial ratio of this pattern is: $OA : OB : OC$ — 0.935 : 1 : 0.707, the axial angles are α — 90°, β — 100°53′, γ — 105°38′. These figures are almost completely identical with the measured axial ratios and angles.

Considering the diameter of the oxygen ion as 2.70 Å, the axes of the close-packed structure unit cell are: OA — 7.14; OB — 7.64; OC — 5.40 Å.

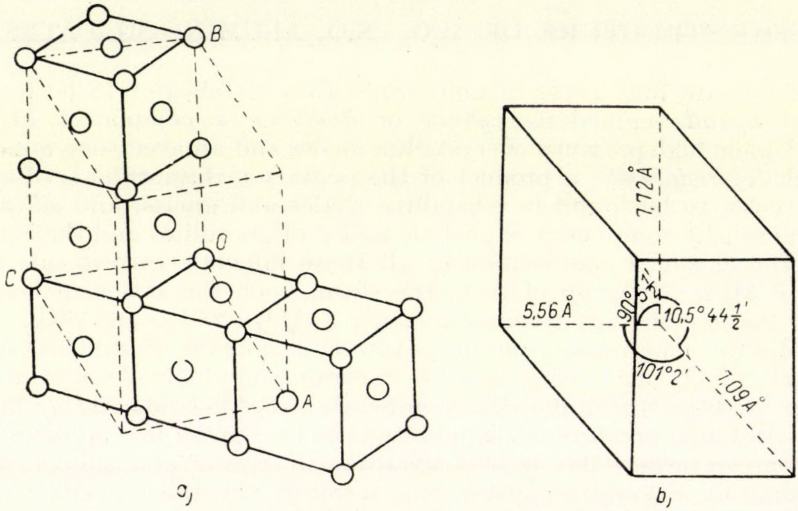

Figure 9

Connexion between triclinic unit cell derived from the cubic lattice (*a*) and the real unit cell of kyanite (*b*) according to Náray-Szabó, Taylor and Jackson (1929)

The unit cell as determined by these axes contains 20 lattice points, i.e. 20 oxygen ions. Thus the presupposed cubic close-packed grouping of oxygen ions has been determined. The theoretical arrangement of the kyanite structure in this first approximation is obtained by assuming the *silicon* and *aluminium* ions to be placed into the middle of the *tetrahedra*, respectively *octahedra* of oxygen ions. The comparison between the measured X-ray data and those calculated according to this presupposed structure shows a remarkably good correlation compared to the first approach. More exact data, however, cannot be obtained this way; for this purpose a well known structure may serve as a basis.

Regular intergrowth of kyanite and *staurolite*, a phenomenon known for a long time, frequently occurs in nature. The two minerals intergrow in such a way that the common face is parallel to the (100) plane and to the (010) plane of staurolite. The *c* axes of both minerals are common in this case, consequently the two structures must show a close similarity. The structure of staurolite, which had earlier been completely determined by

Náray-Szabó (1929), could be used for the determination of the kyanite structure. (Though the structure of staurolite was slightly modified by Náray-Szabó and Sasvári in 1958, the close structural similarity between kyanite and staurolite still prevails since the latter has repeatedly been shown to be formed by the regular repetition of $Fe(OH)_2$ and Al_2SiO_5 layers, and kyanite to contain only Al_2SiO_5 layers.)

The structure of staurolite is shown in Fig. 10, viewed parallel to the c axis. Iron ions are represented by large open circles, aluminium ions by smaller open circles, silicon ions by small black circles. The figures inside and beside the circles give the heights as fractions of the c axis of the ions above the base-plane. The oxygen ions are hatched differently; hatching slanting to the left shows the position of oxygen ions of heights 0.00 and 0.50; hatching slanting to the right means oxygen ions of heights 0.25 and 0.75.

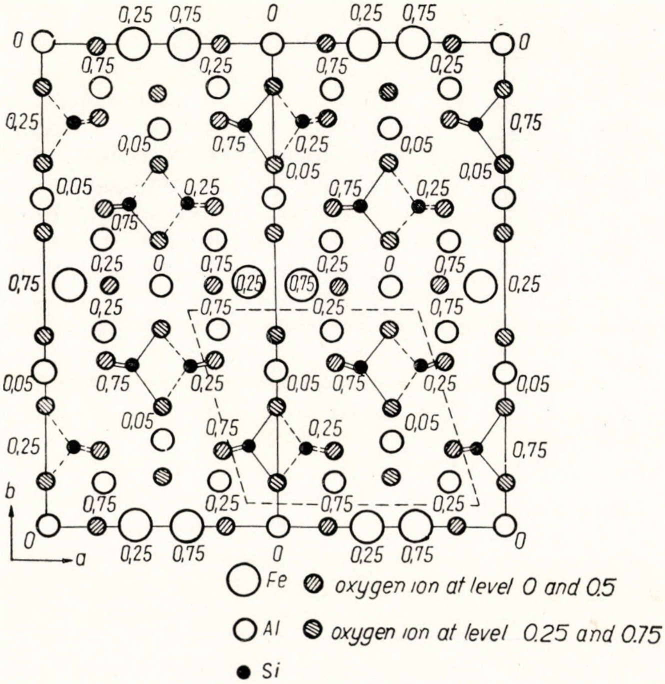

Figure 10

Two unit cells of staurolite viewed from the direction of the c axis. Directions of axes a and b and the unit cell of kyanite (dashed lines) are drawn. (According to Náray-Szabó and Sasvári 1958)

The most characteristic feature of the structure is that iron ions and OH groups are arranged along the (010) reflection plane in heights of 0.0 and 0.5. The space between these planes is filled up by a group of $Al_8Si_4O_{20}$

composition. The composition of this group, being exactly four times the kyanite formula of Al_2SiO_5, is the same as that of kyanite. Consequently, as to chemical composition, some parts of the staurolite structure are identical with those of kyanite; the unit cell of kyanite, with its dimensions and elements of symmetry can be easily arranged into the relevant part of the staurolite structure. Such an arrangement is shown in Fig. 10, where the unit cell is given in dashed lines. The X-ray intensity data, calculated according to this arrangement, have led to a better correlation with the measured data than those of the first approximation.

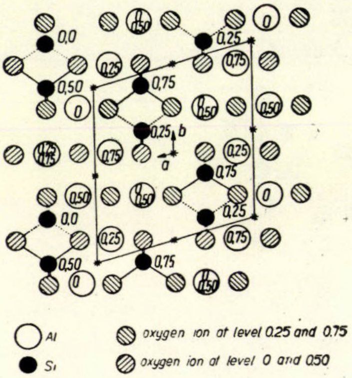

Figure 11

The structure of kyanite viewed from the direction of the *c* axis. (According to Náray-Szabó, Taylor and Jackson 1929)

A slight difference in the oxygen arrangement of kyanite and that of ideal staurolite may be presumed since the cubic close-packed arrangement is slightly distorted in the former. These distortions could be determined by the try-and-see method but, as there are 16 ions in the halved unit cell of kyanite (10 oxygen, 2 silicon and 4 aluminium ions), and as the position of each of them must be fixed in 3 crystallographic directions, it would be cumbersome to find the 48 parameters influencing the X-ray intensities and determining the structure, and the results may also be misleading.

Náray-Szabó and co-workers have therefore determined the differences between the ideal and the actual kyanite structure according to some other characteristics of the staurolite structure and according to data obtained from the *chondrodite* minerals, also of similar structure. X-ray intensity data, calculated from these slightly changed ion parameters, are in agreement with the measured data.

The final structure of kyanite is represented in Fig. 11. Large open circles indicate aluminium ions and small full circles, silicon-ions. Circles indicating oxygen are hatched. The hatching slanting to the left indicates heights of 0.25 and 0.75, the hatching slanting to the right, heights of 0.0 and 0.5, measured as fractions of the *c* axis. The figures inside the circles representing aluminium ions and beside the circles representing silicon ions give the height of the ion above the base plane as fractions of the *c* axis. The base plane is the (001) plane of the unit cell; the symmetry centre is thus at the centre of the unit cell at level 0.50. The directions of the *a* and *b* axes are marked; the direction of the *c* axis is perpendicular to the plane of drawing.

The structure of kyanite is interesting from several points of view. Fig. 11 shows that *half* of the aluminium ions are arranged into columns parallel to the direction of the crystallographic *c* axis. Each of such aluminium ion is surrounded by oxygen ions forming an *octahedron.* The octahedra following each other share edges (i. e. two adjacent octahedra have two common oxygen ions). This arrangement, parallel to the *c* axis, is very interesting because a similar arrangement of oxygen ions was found in sillimanite (Taylor 1928) and andalusite (Taylor 1929). (Cf. Fig. 17*d*)

The *other half* of the aluminium in the lattice of kyanite is also surrounded by oxygen octahedra; these, together with the SiO_4 tetrahedra, give the framework of the structure. The SiO_4 tetrahedra are isolated from one another, i. e. there is no common oxygen ion between two adjacent tetrahedra.

The two distinct cleavage directions of kyanite, the directions parallel to the (100) and (010) planes are well explained by this structure. A further interesting feature, the high degree of hardness parallel to the *b* axis (6—7 Mohs degrees), and a much lesser hardness parallel to the *c* axis (4—5 Mohs degrees), is quite obvious from the structure just described: since the (100) plane contains only oxygen ions, it is moderately charged and can be easily scratched.

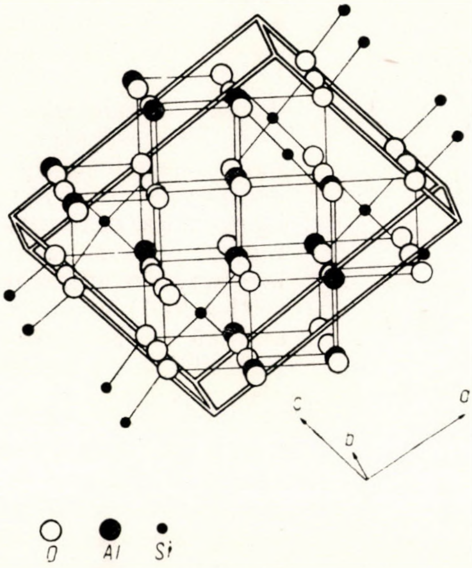

Figure 12

The structure of kyanite in perspective, according to Náray-Szabó, Taylor and Jackson (1929). Directions of the cell edges are shown by arrows at the bottom of the Figure

Co-ordination conditions are well discernible in Fig. 12 showing the perspective view of the structure. The octahedral co-ordination of oxygen ions around the aluminium and the tetrahedral co-ordination around the silicon ions is clearly shown. The silicon ion and the oxygen ions belonging to it are connected with full lines. The unit cell is marked by a double line.

The electrostatic valence rule is strictly complied with in the structure of kyanite. Any arbitrary oxygen ion of the structure is bound either to one cation of the SiO_4 tetrahedron and simultaneously to two cations of the AlO_6 octahedron, or to four cations of the AlO_6 octahedron. The bivalent bond is thus realized in any case.

B) THE STRUCTURE OF ANDALUSITE

According to crystallographic data, andalusite crystallizes in the holohedral class of the orthorhombic system (space group V_h^{12}); unit cell dimensions according to Mark and Rosbaud (1926) are $a - 7.90$, $b - 7.90$, $c - 5.55$ Å; according to measurements made by Taylor (1929) the more exact cell parameters are $a - 7.77$, $b - 7.90$, $c - 5.56$ Å. The unit cell of these dimensions contains four molecules of Al_2SiO_5 as calculated by the 3.18 g/ml density of andalusite.

These cell dimensions and the symmetry elements of the orthorhombic holohedral class confirm the following preliminary rules of the structure: the grouping of oxygen ions will be very simple because there are reflection planes parallel to the (001) plane in the height of 0.0 and 0.5 (heights are considered as fractions of the crystallographic c axis). The distances between these reflection planes are $5.56/2 = 2.78$ Å. Oxygen ions, however, have a diameter only slightly shorter than this distance (2.70 Å) so that there are only two possibilities left for oxygen ions to arrange: to lie either *exactly in the reflection plane* or *almost exactly at mid-distance* between two reflection planes.

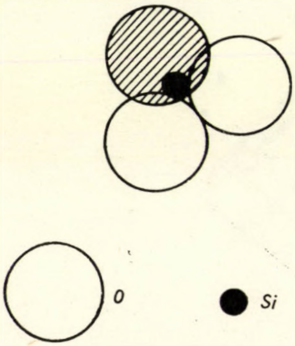

Figure 13

Arrangement of the SiO_4 group in andalusite. Silicon ion and unhatched oxygen ions lie in the plane of the drawing, hatched oxygen ions above, and below the plane with 1,35 Å. Oxygen ions touch one another. The plane of the drawing is a reflection plane (According to Taylor 1929)

There are four silicon ions in the unit cell. According to the symmetry elements, they may lie either in *symmetry centres,* on *digirs* or in *reflection planes*. Oxygen ions surrounding the silicon ions have a tetrahedral coordination. The silicon ion cannot lie in a symmetry centre, as this would not allow a tetrahedral arrangement. From this single point of view silicons may lie on digirs. Should this be the case, the oxygen ions of the SiO_4 group would not find any place between the mirror planes. Consequently, silicon ions lie in a *reflection plane*, surrounded by a tetrahedral group of oxygen ions, two of which lie in the mirror plane, the two others above and below the reflection plane with the outer electron shells just touching the mirror plane.

The group formed by silicon and oxygen ions is drawn in Fig. 13. The silicon, the central ion of the group, is situated in the reflection plane (in our case the plane of drawing). Also two of the four oxygen ions lie in the reflection plane (unshaded circles) while the two others are situated above and below the mirror plane, with their centres at a distance of 1.35 Å from it. One of the latter oxygen ions is represented by hatching in Fig. 13; the other, being covered by the first, is invisible.

The arrangement of oxygen ions surrounding the silicon, has thus been determined with approximate accuracy. But the sharing of these SiO_4 tetrahedra has been left uncleared. As is generally known, there are three possibilities: the tetrahedra may be separated from one another, they may share corners or edges. In the case of andalusite, however, the SiO_4 tetrahedra are *separated*, for the two other forms are inconsistent with the symmetry elements of the cell.

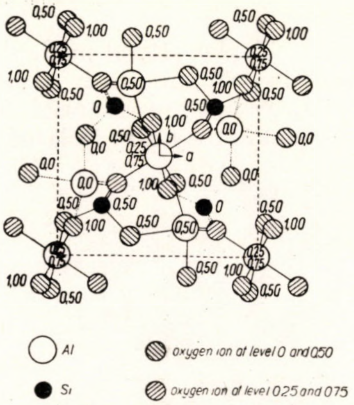

Figure 14

The structure of andalusite as viewed from a direction parallel to the *c* axis. Numbers beside the circles indicate heights of ions as fractions of the cell height. (According to Taylor 1929)

So far we have fixed the approximate position of the four silicon ions and the sixteen oxygen ions belonging to them. Four oxygen and eight aluminium ions are left to be arranged along the crystallographic *c* axis. There is only one possibility of arrangement, as verified by a trial-and-error method; half of the aluminium ions form AlO_6 octahedra, sharing edges and forming chains. The other half of aluminium ions has an AlO_5 type co-ordination, with the Al ion in the centre and O ions in the corners of a trigonal bipyramid (three in the plane of the aluminium, one above, one below it). Every second AlO_5 group has two common oxygen ions (i. e. shares edges) forming Al_2O_8 complexes.

In Fig. 14 the structure is given from a direction parallel to the *c* axis. Large circles represent aluminium ions, small full ones silicon ions. Circles indicating oxygen are shaded. The right-side hatching indicates heights of 0.25 and 0.75, left-side hatching, heights of 0.0 and 0.5, measured as fractions of the *c* axis. This view of the unit cell shows the four SiO_4 tetrahedra particularly well; also five AlO_6 octahedra are visible (in the centre and at the corners of the cell). A closer inspection reveals four other aluminium ions. These are characterized by the strange fivefold (AlO_5) co-ordination mentioned. An aluminium ion of this kind can be studied in the left side of Fig. 14, between the centre and the upper left corner at a height of 0.5. All such ions lie at heights of 0.0 and 0.5 (measured as fractions of the axial length *c*). There are three oxygen ions in the same plane and one above and one below the plane, at heights of 0.25 and 0.75 resp. covering each other. These cannot be represented separately in the Figure. They are demonstrated by one single circle, which, to express the two-directional co-ordination, is connected to the aluminium ion by a double line.

The correctness of the structure may best be proved by the comparison of X-ray data observed and of those calculated according to the presupposed structure. The comparison shows that calculated data and those observed by X-ray agree very well. The electrostatic valence rule, however, cannot be completely fulfilled. The manifold and complex bond mechanism permits only average valences between 1.6 and 2.2 to be calculated for oxygen ions of different crystallographic positions.

The unusual five-fold co-ordination of some aluminium ions in the lattice of andalusite has been confirmed again by Hey and Taylor (1931).

C) THE STRUCTURE OF SILLIMANITE

Taylor (1928) made detailed investigations into the structure of sillimanite. Sillimanite is orthorhombic; its cell belongs to space group V_4^{16}. SiO_4 groups are essential elements of the sillimanite structure; as they do not share they give isolated SiO_4 tetrahedra. A further characteristic feature of sillimanite is the almost complete repetition of the oxygen ion arrangement after a distance of $c/2$; i. e. a reflection plane lies in the middle of the c axis, perpendicular to it. (This is, however, only a pseudo-reflection plane, as the arrangement of oxygen and silicon ions is not exactly the same on the two sides of the plane).

The arrangement of the silicon ions and of the oxygen ions surrounding them, is as follows: the co-ordination of oxygen ions is tetrahedral; two oxygen ions are in a reflection plane, the two others above and below it, touching the plane and one another by their outer electron shell. Oxygen ions lying in the reflection plane are in an independent position, the position of the two others is determined by the reflection plane. These two latter oxygen ions are almost exactly at mid-distance between the reflection planes, since the diameter of oxygen ions is 2.75 Å and the reflection planes follow one another at distances of 2.85 Å. So far the arrangement of four SiO_4 groups (i. e. of four silicon and sixteen oxygen ions) has been determined; the places of the eight aluminium and four oxygen ions left are still to be fixed.

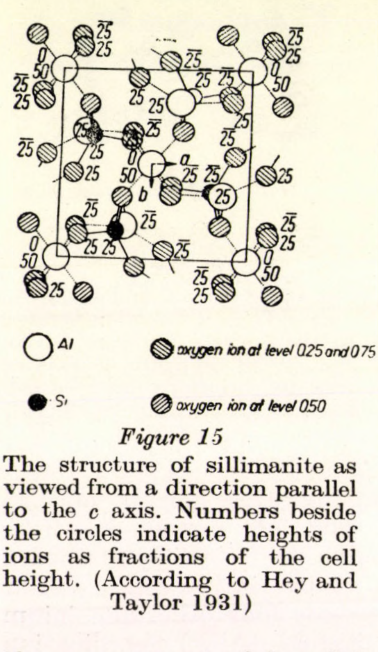

Figure 15

The structure of sillimanite as viewed from a direction parallel to the c axis. Numbers beside the circles indicate heights of ions as fractions of the cell height. (According to Hey and Taylor 1931)

As is mentioned in the foregoing, the unit cell is divided into two halves by the pseudo-reflection plane at the height of $c/2$. Accordingly, the four silicon ions, already fixed, must be compensated by four aluminium ions on the other side of the "mirror plane". This compensation arranges the position of half of the aluminium ions leaving four aluminium and four oxygen ions to be fixed. The laws of crystal symmetry permit only four possibilities of different arrangement for the positions of the eight outstanding ions; by measuring (001) reflections of the X-ray patterns the correct arrangement type can be chosen.

The ultimate conception of the structure is proved by calculating the *structure factors* of the different ion positions, and by comparing them with measured X-ray intensities. Those agreeing best will give the closest approximation to the actual structure.

Presupposing the real structure to be only slightly distorted as compared to the ideal one (Fig. 15), the final ion co-ordinatas are determined by a similar method. By this method Taylor has found that chains of edge-sharing AlO_6 tetrahedra are formed parallel to the crystallographic c axis also in sillimanite; the other half of aluminium ions form AlO_4 tetrahedra, while silicon has the usual fourfold co-ordination. SiO_4 and AlO_4 tetrahedra share corners, i. e. have one common oxygen ion. Thus complex double chains of formula $(SiAlO_5)_n$ are formed and are characterized also by the fact that two silicon or two aluminium tetrahedra can never be in immidiate neighbourhood. From this point of view sillimanite is very similar to amphiboles.

The correctness of the structure, determined by this method, has been controlled by Taylor on 90 planes of different indices; there was an excellent correlation between the measured intensities of the X-ray pattern and the calculated structure factors. The modification introduced by Hey and Taylor (1931) concerned only a few ion parameters, with no change in the essence of the structure.

CHAPTER 5

COMPARISON BETWEEN THE STRUCTURES OF THE THREE Al_2SiO_5 ALUMINO-SILICATES

The structure of andalusite, sillimanite and kyanite, described in the previous chapter, allows an interesting comparison (Taylor 1932). In Fig. 16 the three structures are viewed from the direction of the crystallographic *c* axis. The length of this axis is almost identical in the three structures (5.56 Å in case of kyanite and andalusite, 5.74 Å in case of sillimanite). The directions of the *a* and *b* axes and the boundaries of the unit cell are also given in Fig. 16. The heights of oxygen ions are marked by various types of hatching.

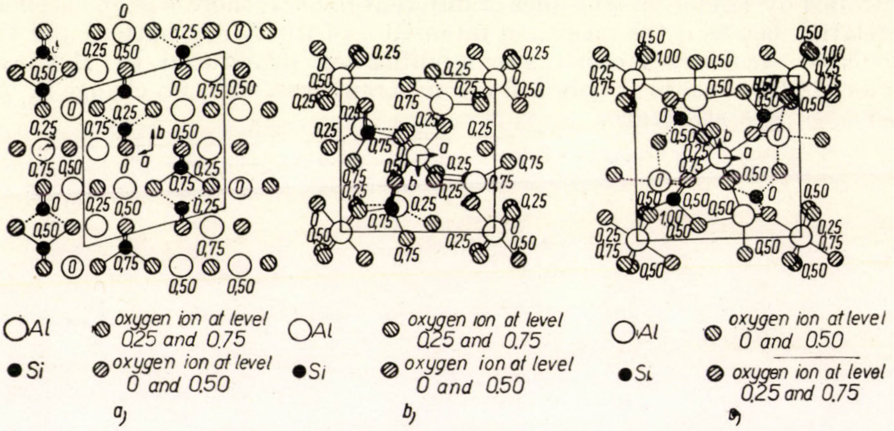

Figure 16

Comparison of structures of kyanite (*a*), sillimanite (*b*) and andalusite (*c*) viewed from the direction of *c* axes. Outlines of unit cell and directions of *a* and *b* axes are shown. (According to Taylor 1932)

Symmetry conditions of the unit cells: the only symmetry element of the kyanite cell is the symmetry centre in the middle of the cell at a height of 0.50. The sillimanite cell is divided by two reflection planes, both parallel to the (001) (basal) plane, at heights of 0.25 and 0.75. Andalusite contains three reflection planes of this kind at heights of 0.0, 0.5 and 1.0.

The best way to understand the structures is to observe the octahedral bundles, built up by AlO_6 groups, which form continuous chains parallel to the c axis by sharing edges (cf. Fig. 17*d*), and have two common oxygen ions each. These chains which contain half of oxygen ions are linked by the remaining positive ions, i. e. by silicon ions co-ordinated tetrahedrally by oxygen ions, on the one hand, and by the rest of aluminium ions on the other.

Sillimanite is also characterized by the formation of these continuous AlO_6 chains which contain half of aluminium ions. The tetrahedral co-ordination of silicon ions is also realized in sillimanite; the characteristic feature of the structure, as in the other two Al_2SiO_5 alumino-silicates, consists in the other half of aluminium ions which have an AlO_4-grouping best interpreted as a slightly distorted tetrahedron.

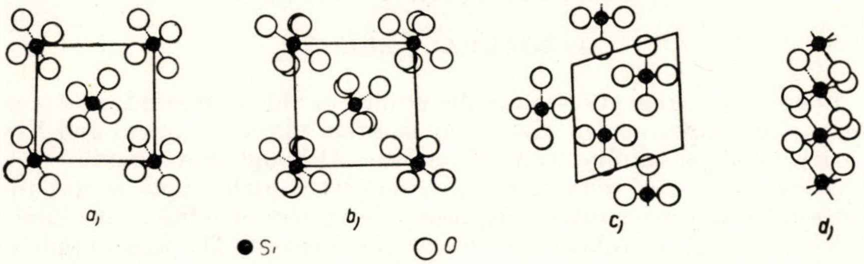

Figure 17

Octahedral bundles in Al_2SiO_5 modifications; *a* sillimanite, *b* andalusite, *c* kyanite, *d* the arrangement of the octahedral chain. (According to Hey and Taylor 1931)

In case of *andalusite* the conditions are similar: Si ions are of tetrahedral co-ordination, half of the Al ions form octahedral chains of nearly identical crystallographic positions (Fig. 17). The second half of the aluminium ions, however, are in the middle of a symmetric group formed by five oxygen ions. These oxygen ions form a trigonal bipyramid; three oxygens lie equatorially in the plane of the aluminium ion, the two others above resp. below this plane in polar positions.

The characteristic feature of the *kyanite* structure is the cubic close-packed arrangement of oxygen ions; the AlO_6 chain, built up parallel to the c axis is easy to distinguish. Here again the silicons are tetrahedrally surrounded by oxygens. The rest of the aluminium ions have an octahedral oxygen co-ordination in kyanite.

Connexions between the three members of the series may be summarized in the following: in all the three structures half of the aluminium ions are in the centre of an octahedral group of oxygens. These octahedra with sharing edges form continuous chains parallel to the c axis. Silicon ions are surrounded by a tetrahedron of oxygens; these tetrahedra, however, are isolated, i. e. have no common oxygen ions. The other half of the aluminium ions show characteristic differences in the three structures: they are surrounded by symmetric oxygen groups, built of *six*, *five* and *four* oxygen ions in the structures of *kyanite*, *andalusite* and *sillimanite*, respectively.

CHAPTER 6

THE STRUCTURE OF MULLITE

A) NATURAL MULLITE

Bowen and Greig (1924) describe mullite as the most stable compound of the system Al_2O_3—SiO_2. They also mention the close optical and X-ray similarity between mullite and sillimanite. Although pure mullite has a slightly lower index of refraction and a somewhat higher optic angle, these insignificant differences often disappear when traces of refractivity-increasing cations, e. g. titanium and iron, are present. The same applies to the slight difference in specific gravity; this approaches also that of sillimanite by the admixture of heavy metal ions. The X-ray data of mullite and sillimanite are almost completely identical; it is therefore rather difficult and cumbersome to distinguish them by X-rays (cf. Chap. 2).

From a chemical point of view, however, there is a significant difference between mullite and sillimanite. The great difference in chemical composition between the two minerals and their almost identical X-ray patterns evidently shows the *substitution* of Si by Al in mullite. The structures of the two mineral phases must be very similar. It is well known, however, that silicon and aluminium are of *diadoch* character and so the SiO_4 tetrahedra of the sillimanite lattice may partly be substituted by AlO_4 tetrahedra in the lattice of mullite.

The unit cell dimensions of the two phases present another subject for many-sided dispute. According to Greig (1926), the mullite cell must be considerably larger than that of sillimanite. Wyckoff, Greig and Bowen (1926) say that one cell unit of mullite contains three molecules of mullite, i. e. eight molecules of sillimanite.

Taylor (1928) thinks that the unit cell of mullite is four times larger than that of sillimanite, because X-ray patterns, taken from rotating single crystals of mullite with a very long exposure, show some weak spots in levels corresponding to indices 1 or 3. These reflections, weak but distinct, can be detected even on patterns taken from different crystals with different axes of rotation. In spite of this evidence, the dimensions of the unit cell have not yet been determined for sure as aluminium and silicon ions have almost the same diffraction power. Hence the mullite cell may be the double of sillimanite. Taylor says, however, that the essential problem is not the *almost* complete identity of the *number* and of the *diffraction power* of the ions of the unit cell in both minerals, but the *exact* identity of the *number* of ions, having almost the same diffractivity *(aluminium and silicon ions)*, and the *almost* complete identity of the *number of oxygen* ions in the two structures.

The unit cell of sillimanite, as described, contains eight aluminium and four silicon ions (i. e. twelve cations) and twenty oxygen ions; if the mullite unit cell is assumed to be of equal size, it will contain nine aluminium and three silicon ions (i. e. twelve cations) and 19 1/2 oxygen ions.

The essential feature of the mullite structure is, that part of the SiO_4 tetrahedra are substituted by AlO_4 tetrahedra. The character of substitution is shown in Fig. 18. The circles represent ions; unhatched circles lie in the symmetry plane, the hatched ones above and below it. Circles of continuous line give the oxygen grouping around silicon; circles of dashed line show the slight changes in position due to the substitution of the silicon ion by the somewhat larger aluminium ion. The two position types, being almost identical, will hardly influence X-ray patterns.

This partial substitution of silicon ions by aluminium ions is the main difference between the structures of sillimanite and mullite. According to valence rules, however, one oxygen ion must *leave* the structure whenever two silicon ions are substituted by two aluminium ions. In case of stoichiometric mullite this means the release of one oxygen per unit cell. Beside fulfilling valence rules, this brings into agreement the measured and calculated densities.

It is generally supposed that the oxygen, leaving while sillimanite transforms into mullite, will form tiny bubbles; the surroundings of mullite crystals, indeed, often show bubble-like inclusions. If we accept Taylor's (1928) assumption that the mullite unit cell is the quadruple of the sillimanite cell, then four silicon ions will be replaced by four aluminium ions in one cell unit; this will release two oxygen ions, and four of the remaining ones will assume (insignificantly) modified positions due to the slightly larger diameter of aluminium ions.

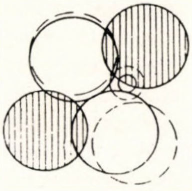

Figure 18

Comparison of SiO_4 and AlO_4 groups. Unhatched oxygen ions lie in the plane of the Figure, hatched ones, above and below it with 1,35 Å. Small circle represents the silicon ion. Circles in dashed lines show the change of the arrangement due to the Si → Al substitution. (According to Hey and Taylor 1931)

This assembly, made up of 12 silicon, 36 aluminium and 78 oxygen ions, forms the unit cell of mullite; the supposed cell is indeed of orthorhombic symmetry.

These slight changes will influence the X-ray patterns only to a small extent, but the optical characteristics of mullite and sillimanite will be different — in spite of the small changes in oxygen positions — because aluminium has a considerably lower charge than silicon. Even greater differences are awaited in the infrared absorption spectra of the two minerals. Tarte (1959) considers infrared spectrography the most suitable method for distinguishing mullite from sillimanite.

Taylor thought the substitution of silicon ions by aluminium ions to be regular; in the light of recent studies it seems to be rather of a random nature. Mullite has a defective structure; that of sillimanite is (under ideal circumstances) complete. The correctness of this statement was confirmed by Posnjak and Greig's (1933) careful X-ray investigations.

The mullite structure, as supposed by Taylor, does not completely fulfill the condition of electroneutrality. The four joining AlO_4 tetrahedra have one common oxygen ion, resulting in a valence of $4 \cdot 3/4 = 3$ (instead of the bivalence of oxygen). This contradiction can be explained, according to Warren (1933), by assuming that one oxygen anion joins three AlO_4 tetrahedra (and not four as thought by Taylor) and gives a resultant valence of $3 \cdot 3/4 = 2 \cdot 1/4$. Being much closer to the real bivalence of oxygen, this is more probable than Taylor's original conception.

Scholze (1955) made thorough X-ray investigations in order to determine the defective lattice structure of mullite. X-ray patterns, obtained from oscillating single crystals of mullite, have shown besides the regular reflections three other levels of reflection, indicated by diffuse spots. This is a sign of lattice imperfections caused by the unit cell not containing integer "molecules" of mullite. Scholze regards this method as suitable for distinguishing mullite from sillimanite if a Guinier pattern is used. (This method is seldom practicable for single crystals of the required size are often not available.)

B) ARTIFICIAL MULLITE

Before the study of Bowen and Greig (1924) sillimanite was considered the most stable anhydrous alumino-silicate and artificial anhydrous alumino-silicate was also called sillimanite.

Deville and Caron (1865) were the first to report on an artificial silicate, synthesized from silicon tetrafluoride and calcined alumina at high temperatures (in a Deville kiln). The Al_2O_3 content of this product varied between 71.2 and 70.9. The authors did not realize that they had synthesized mullite.

Vernadsky (1890) isolated some crystals by the hydrofluoric-acid treatment of Sèvres china. Zoellner (1908) repeated the experiment; both of them described the isolated acicular crystals as sillimanite. The hydrofluoric-acid treatment of fired clays had also given a certain amount of residue; this residue of crystals difficult to solve was analysed by Cox (1918); the reported Al_2O_3 content of these crystals was between 69.3 and 71.1 per cent.

Bowen and Greig (1924) but especially Taylor (1928) have convinced the experts that mullite is the only stable composition of the Al_2O_3—SiO_2 system.

Thanks to Taylor's pioneering work, the structure of mullite has been completely determined leaving only some details to be solved. The nature of the mineral of acicular characteristics in fired clays, porcelains, etc. was the subject of discussions for a long time: some authors considered them sillimanite in spite of the investigations and structure determinations, already described. Later they were thought to be *mullite* crystals, although recently Horte and Wiegmann (1956) took up the sillimanite hypothesis again.

Some authors were of the opinion that the insoluble acicular aluminosilicate of fired ceramic products is neither sillimanite nor mullite, but a third mineral, differing in structure from both.

Bradley and Roussin (1932) proposed the name "*keramite*" or "*porcite*" for the denomination of this phase. The evidence was drawn from the X-ray pattern of the material being separated from fired ceramic products by hydrofluoric-acid treatment, which showed differences in intensity as compared with natural mullite or with mullite obtained by the crystallization of melts. This was disproved by Wyckoff (1933) who interpreted the intensity differences observed by Bradley and Roussin as due to *orientation* effects: during the process of hydrofluoric-acid treatment and the following filtration the particles got oriented and gave an X-ray pattern of different intensities as compared with the sample of random orientation.

These orientation effects were investigated also by Posnjak and Greig (1933): the mineral obtained by sintering does not differ from the one obtained by the crystallization of melts: both of them are mullite.

The chemical analysis of mullite crystals, separated from porcelain, fireclay products, etc. showed a surplus of alumina as compared with the formula $3Al_2O_3 \cdot 2SiO_2$. This alumina surplus can be considered either as an isomorphous substitution (formation of solid solutions) or as a simple mechanical admixture.

Eitel (1937) shared the latter opinion; he thought mullite was *not an individual phase*, just a mechanical mixture of sillimanite and alumina. The alumina, however, being ill-crystallized or amorphous, only sillimanite reflections can be detected on X-ray patterns. The X-ray differences between mullite and sillimanite are, according to Eitel, merely orientation effects. This can hardly be accepted since the alumina excess is not due to mechanical effects but to the fact that mullite differs from sillimanite and has a probable formula of $Al_{18}Si_6O_{39}$ (Kurylenko 1952).

The formation of solid solutions may render the alumina content of mullite even higher than expressed by this formula. The recent literature confirms Rooksby and Partridge's (1939) opinion that there are three different types of mullite: α-mullite containing the theoretical amount (71.8 per cent) of alumina; β-mullite with an excess of alumina in the form of solid solution. The type containing even iron and titanium as solid solutions, as was presumed by Posnjak and Greig (1939) is termed γ-mullite by Rooksby and Partridge. All three types can be synthesized but only β- and γ-modifications are found in nature. The maximum Al_2O_3 quantity of β-mullite may reach 78 per cent, corresponding to a formula of $2Al_2O_3 \cdot SiO_2$. The lattice of mullite, however, is slightly distorted even above 72 per cent of alumina content.

According to the foregoing and in compliance with the investigations of Toropov and Galakhov (1958), the isomorphic replacement of alumina may be considered as a proved fact. There arises, however, the question whether the *silica* content of mullite, present as an excess as compared with the theoretical formula, is a mere mechanical admixture or a solid solution. According to Nahmias (1933), the excess of SiO_2 is *never* present as a solid solution but always as a mechanical admixture, i. e. there is no stable crystal phase between sillimanite and mullite.

Careful investigations were made by Zimmermann and Favejee (1941) in order to determine the isomorphous replacement possibilities of aluminium by iron in the lattice of mullite. According to their measurements, this substitution is possible, but only to a Fe_2O_3/Al_2O_3 ratio of 0.12. Should there be a higher quantity of iron present, it could only be a mechanical admixture and, being loosely held by the lattice, very easily reducible. The product of reduction is α-iron, which becomes further oxidized to hematite.

The problem of replacement was extended also to other substances by Gelsdorf and Schwiete (1956) who synthesized pure mullite of theoretical composition from reagent-grade raw materials and investigated the extent to which the mullite lattice can take foreign oxides in the form of solid solutions as well as the amount that will either form a mechanical admixture or distort resp. destruct the lattice. From their experiments they have come to the conclusion that the isomorphous replacement limit of alumina is at 6 weight per cent; a higher amount of alumina gives not a solid solution but is a mechanical admixture. This limit is at 5 and 1.5 weight per cent in case of iron oxide and titania, respectively. Both of these admixtures slightly expand the lattice of mullite. Calcium oxide and magnesia, on the other hand, destruct the mullite lattice, for the action of CaO and MgO, causes the forming of corundum + anorthite and sapphirine, respectively. By the action of alkali oxides α-carnegieite resp. α-kaliophylite are formed at a temperature as low as 1000 °C ; both of these secondary products melt incongruently at 1300 °C to corundum and to glass of a high silica and alkali content.

Although the substitution between sillimanite and the $2Al_2O_3 \cdot SiO_2$ compound of mullite structure is very probably continuous, a number of authors suggested individual names for the members of this series. Thus Barta and Barta (1956) produced a compound of the formula $5Al_2O_3 \cdot 4SiO_2$ by firing a mixture of finely powdered silica and alumina in oxidizing and reducing circumstances. This compound, and a single crystal of 77.3 per cent alumina content gave X-ray patterns slightly differing from β-mullite described by Rooksby and Partridge (1939). This mineral was named "*praguite*".

Bartuška (1957a) investigated several sorts of mullite in detail: there were sintered, flame- and electro-fused substances as well as others separated from porcelain and fireclay among the samples. Pure oxides, andalusite, kyanite, sillimanite and dumortierite served as raw materials. Mullite, synthesized from reagent-grade oxides is the purest from a chemical point of view; the most impure substance among these samples is the one separated from fireclay brick (containing about 4.25 per cent iron- and titanium-oxides). The R_2O_3/SiO_2 ratio varies from 3.05 to 2.12. The densities of the samples are slightly increased by Al_2O_3 excess and, more considerably by Fe_2O_3 and TiO_2 excess; SiO_2, on the other hand decreases specific gravity. Refractivity is influenced in a similar way. The X-ray patterns of these types of mullite slightly differ in position, intensity and sharpness of lines.

PART FOUR

THE FORMATION OF MULLITE

CHAPTER 7

THE FORMATION OF MULLITE FROM Al_2SiO_5 ALUMINO-SILICATES

All aluminium silicates, aluminium hydrosilicates, artificial mixtures or mixed gels of $Al_2O_3+SiO_2$, etc. transform into mullite at a high temperature. Be the reaction slow or rapid, be it built up of one or more steps, the final product is always mullite. Although the investigation of these reaction steps has attracted the attention of many research workers, a number of questions have remained unsolved.

It is very important both in theory and in practice to be acquainted with these thermal reactions, especially with those of *clay minerals* and above all of kaolinite. Kaolin or kaolin-bearing substances are the most important raw materials of all traditional and many new ceramic products. Naturally, pottery products of highest quality may be manufactured even without the slightest theoretical knowledge (the unrivalled quality of ancient Chinese and old European china is well known), the high requirements of growing industry, however, can be met only by the constant development of manufacture. It is this conscious development that needs a theoretical foundation and the knowledge of the processes taking place during the firing of ceramic raw materials.

Considering their theoretical and practical importance, the thermal processes of kaolin and kaolinitic clays will be dealt with in separate chapter.

*

Norton (1925) and Greig (1925) were the first to study the transformation of the three Al_2SiO_5 alumino-silicates into mullite. Their method consisted of a firing process at systematically chosen temperatures, followed by microscopic examinations and by volume measurements. They have found that *kyanite* transforms the most easily: traces of mullite can be detected even after a firing at 1200 °C. Mullite formation is accelerated at higher temperatures and, besides mullite, a siliceous glass is formed. When heating kyanite a characteristic exothermic effect may be observed at 1400 °C. The reasons of this reaction are not reported either by Norton or by Greig. It is most probably due to recrystallization and not to mullite formation.

Fired *andalusite* also transforms into mullite, but only above 1400 °C. An exothermic effect, similar to that of kyanite, can be observed during this process.

Sillimanite transforms into mullite after a firing above 1550 °C (a temperature roughly equal to the eutectic temperature of the Al_2O_3—SiO_2 system). No thermal effect has been detected during this transformation.

All these data were summarized once more by Greig (1926).

According to the phase theory, only one compound (in this case, mullite) can be stable at ordinary pressure; all other compounds are metastable and transform into mullite. The transformation in all three cases is *monotropic*, i. e. mullite is at every temperature more stable than the other alumino-silicates; metastable phases, however, may remain in this state for an unlimited time if the temperature does not reach the characteristic transformation temperature. This transformation temperature may not be higher than the eutectic temperature of the system, i. e. 1545 °C between SiO_2 and mullite (Bowen and Greig 1924) and 1850 °C between Al_2O_3 and mullite (Toropov and Galakhov 1958).

Several factors may affect the transformation temperatures given by Greig. The most important of them are the effect of *heating velocity* and that of *time*.

Heating circumstances used by Greig result in a characteristic sequence of transformation: crystals of andalusite and kyanite begin to transform at the edges of the crystals and the transformation proceeds towards the centre; sillimanite transforms in all its bulk at the same time.

Peck (1925) studied the transformation of the three minerals from a crystallographic point of view. Though transformation temperatures described by him differ from those of Greig (1925) because of the effects mentioned, the sequence of transformation of the three minerals remains unchanged. Also Peck has confirmed that the transformation of kyanite and andalusite into mullite is a gradual process; pure and homogeneous crystals of andalusite and kyanite slowly change into an aggregate of mullite and vitreous material. In the case of kyanite the process takes place at a lower temperature and yields a more irregular and finer aggregate than with andalusite. The two compounds also differ in colour since the vitreous phase, produced during the mullitisation process of kyanite, has a green shade, while that of andalusite is colourless. The third difference is of utmost importance: in the thermal mullitization process of kyanite the volume undergoes a considerable change causing a characteristic crumbling whereas andalusite is not subject to such extensive volume changes. These phenomena are very significant from the point of manufacturing mullite refractories (cf. Chap. 12).

The early literature on the transformation process of natural alumino-silicates was summarized by Wherry (1925). At a later stage, it was the thermal processes of clays and clay minerals that attracted attention.

Miyashiro (1949) investigated the crystallization conditions of the three natural anhydrous alumino-silicates only qualitatively, with due regard to the effect of pressure. He found mullite to be the only stable mineral at ordinary pressure, and the three others to become stable under higher pressures. He has not published the pressure intervals of stability but it is known that at pressures of 700 kg/sq. cm mullite is the only stable phase, though the stability of andalusite cannot be excluded either (Roy and Osborn 1954). The stability range of the other alumino-silicates must lie at even higher pressures (cf. Chap. 2).

Keyser (1957), describing the results of his investigations into the thermal changes of kaolin, sillimanite and kyanite, examined the products by electron microscopy and X-rays. He found these transformation processes to be influenced even by traces of contaminating substances.

According to the phase diagram, at ordinary pressures the compound at the final equilibrium of all mixes or minerals of the system SiO_2—Al_2O_3 is *mullite*. The equilibrium of the pure system is, however, influenced by foreign substances, especially by alkalies and other fluxes through the formation of glass. Although glass is not a stable phase but a metastable state as compared to crystals, it cannot be eliminated since the complete crystallization of glasses would usually take a very long time. The cristobalite quantity formed during the firing of alumino-silicates is — according to Keyser — inversely proportional to the amount of fluxes and to the amount of the vitreous phase produced by them. In large quantities of glass the silica formed during firing completely dissolves, i. e. no cristobalite forms. High glass content, on the other hand, enhances the formation of large mullite crystals.

CHAPTER 8

THE FORMATION OF MULLITE FROM KAOLIN-TYPE MINERALS

It has been known for long, in fact since the ancient art of pottery, that kaolinite and clays containing kaolinite undergo certain characteristic transformations when fired.

The first investigator to approach the problem scientifically was Le Chatelier (1887) who used thermal analysis to establish the most important laws of these transformations. The second "classical" study is that of Mellor and Holdcroft (1911) who used the full scientific arsenal of their time (thermal analysis, dissolving methods with acid and alkaline dissolving agents, precision density-determinations, rehydration, etc.) in order to determine the chemical constitution of the "kaolinite molecule" and, indeed established many new data of basic importance.

Although the two initial "classics" were followed by a number of studies, no reliable and unambiguous theoretical explanation of the thermal effects on kaolin has so far been advanced. The main difficulties rest with the fact that after a heating between 500 and 950 °C kaolin becomes almost completely *amorphous* for X-rays, and this adequate method of solid-state investigation becomes unapplicable in research.

Some well-defined reactions take place when kaolin or kaolin-bearing substances are heated. These reactions can be investigated most comfortably by differential thermal analysis. DTA, however, is a non-equilibrium research technique giving no direct evidence by the comparison of its results to those of other methods. (Structure-determining methods, obviously, must be used under similar circumstances.)

The characteristics of the enthalpy-change vs. temperature plots (DTA curves) of kaolinite, halloysite and generally of kaolinite-type clay minerals are as follows:

1. A characteristic heat-absorbing *endothermic* reaction due to the release of hydroxyl ions takes place between 500 and 600 °C. (According to the early literature, this reaction is due to "water loss" or "dehydration". This terminology, though widely used, is not correct, for the kaolinite lattice does not contain any water, but OH groups.)

2. A characteristic and sharp exothermic reaction takes place between 900° and 1000 °C *("first" exothermic effect)*, which can be utilized also for the quantitative determination of kaolinite (Pospišil 1959).

3. Kaolinite-bearing clays show another exothermic effect between 1200 and 1300 °C *("second" exothermic effect)*.

4. Some clays show an exothermic effect above 1300 °C ; to a high extent the temperature of this reaction depends on the material used (*"third" exothermic effect*).

Between the endothermic reaction and the first exothermic one, clay is almost completely amorphous for X-rays. The state between the endothermic reaction and the beginning of crystallization is called *metastate*, thus kaolinite in this state may be called meta-kaolinite. The real nature of the metaphases, as of meta-kaolinite has not been completely explained yet; there are various theories. It is most probable that meta-kaolinite is not completely amorphous, some structural elements of the original kaolinite lattice survive also in meta-kaolinite.

The name "*promullite*" is used by some authors instead of meta-kaolinite.

Kaolin, heated above the temperature of the first exothermic peak, already contains crystals. In spite of this, we still have no clear and exact idea of the processes taking place during the first exothermic peak. There are two hypotheses to explain the first exothermic reaction. One of them, propounded by Insley and Ewell (1935), ascribes the first exotherm to the formation of *γ-alumina* which, according to them, is an intimate mixture of amorphous alumina and amorphous silica, containing some ordered elements necessary for the formation of mullite. This phase, called "γ-alumina" is supposed to have a spinel-type structure (Brindley and Nakahira 1959).

The second theory was elaborated in detail by Comeforo, Fisher and Bradley (1948), although several authors had suggested this possibility earlier. According to this hypothesis, *mullite* nuclei are formed from meta-kaolinite when fired at the temperature of the first exotherm and later these nuclei begin to grow. The formation of γ-alumina is considered by this theory only an occasional occurrence.

As can be seen from the foregoing, we have no exact knowledge of this process. The contradictions are chiefly due to the fact that the firing products of kaolinite and, generally speaking, of clay minerals are greatly influenced by the presence of foreign materials and a very low quantity as a few per cent of contaminations, e. g. mica completely changes the mineral composition of the product. These intermediary products, on the other hand, are hardly suitable to be analyzed by X-ray methods.

The processes responsible for the thermic effects have been investigated for a long time. Among the earliest methods of investigation was the *chemical* method, since the silica and alumina content of heated kaolinite (with heating temperature in the metaphase interval) is easily dissolved in diluted solutions of alkalies and acids, respectively. Dissolving methods, however, being influenced by particle size and other effects, do not give clear results.

Several authors have used *thermal* methods under either static or dynamic circumstances. Also the thermochemistry of the processes has been measured. Thermochemical data are most useful for drawing thermodynamical conclusions.

X-ray methods, as already mentioned, are not to be used in the interval between the endothermic and the first exothermic reactions because heated kaolinite behaves like an amorphous substance. Although some precision techniques, e. g. X-ray oscillation examinations of monocrystals, may be applied, X-ray methods in general are suitable only above the temperature of the first exothermic peak.

Optical methods, similarly to X-ray technique, have not proved useful in case of these products of very small particle size and hardly recognizable crystal form. The determination of the refractive index and similar methods may, nevertheless, be used for clearing up some details.

Besides these most widely used methods a number of others, as e. g. *dilatometry*, *infrared spectrography* and *electron diffraction* have also been used.

Before going into details, the *temperature* of the reactions is to be seen clearly. These temperatures largely depend on the heating rate and, to a smaller extent, also on the atmospheric pressure. The temperature of the endothermic reaction is between 550 and 600 °C, that of the first exothermic one, at about 950 °C, provided the heating rate is 10 °C/min. The *slower* the heating, the *lower* the temperature of the reactions. Extrapolated to a zero heating rate, the temperature of the endothermic peak at 760 torr pressure is $583° \pm 3$ °C, $550° \pm 8$ °C and 550—565 °C for pure kaolinite, pure halloysite and various fireclay-types, respectively (Grimshaw and co-workers 1945). The decrease of pressure results in the lowering of the temperature of the endothermic reaction, as already determined by Mellor and Holdcroft (1911). Exothermic effects are influenced by the heating rate to a smaller extent and not influenced by the pressure at all.

The temperature of the second exothermic effect is 1200—1250 °C, of the third (if detected at all), 1300—1400 °C.

A) INVESTIGATION METHODS

Chemical Methods

Chemical methods were mainly used at a time when endeavours were made to give a chemical foundation to the purely empiric ceramic knowledge. As determined already by Le Chatelier (1887), almost the total alumina content of heated kaolin can be extracted with diluted hydrochloric acid; when, however, kaolin is fired to white heat, the alumina becomes insoluble again. This reaction was later investigated by Sokoloff (1912) in detail; he found the solubility of alumina to begin, after a sufficiently long heating time, above 450 °C, but after a high heating rate, only above 550 °C. The upper limit of solubility lies at 850 °C, a temperature not influenced by the heating rate.

According to Neumann and Kober (1926), the alumina content of clays and kaolins becomes soluble after a moderate heating (between 550 and 850 °C). The degree of solubility does not depend on the heating temperature. Neumann and Kober were of the opinion that heated kaolin disintegrates into a mixture of free alumina and free silica.

Keppeler's (1925) observations have showed that the Fe_2O_3 content of kaolin, insoluble under normal conditions, also becomes soluble after heating.

Tammann and Pape (1923) investigated this phenomenon by chemical model experiments. They prepared intimate artificial mixes of silica and alumina and compared their dissolving rates to that of heated kaolin. They found that at 940 °C very carefully ground and intimately mixed alumina and silica powders may give an exothermic reaction of the same nature as the first exotherm of kaolinite. In both cases, alumina becomes insoluble again above the temperature of this exothermic process. Pure alumina lowers the dissociation temperature of alkaline earth carbonates; kaolin, heated at 550 °C, is very similar in this respect to alumina. The exothermic effect, according to Tammann and Pape, is due to the recrystallization of the oxides.

Agafonoff and Vernadský (1924) suggested another theory. Heated kaolin adsorbs dyes in a completely homogeneous way, while a silica-alumina mix behaves against dye-absorption heterogeneously even in case of most careful mixing. From this phenomenon Agafonoff and Vernadský derived that kaolinite-anhydride, of a composition of $Al_2O_3 \cdot 2SiO_2$, is not completely disintegrated into a mixture of free oxides.

Krause and Wöhner (1932) investigated the solubility of silica and alumina simultaneously; the former was leached by a sodium carbonate solution, the latter by a hydrochloric acid solution. The maximum solubilities of alumina were obtained at 400 °C and 800 °C, of silica at 400 °C and 600 °C. Contrary to these results, Hyslop (1944) found an insolubility of the silica content of heated kaolin in a sodium carbonate solution and confirmed Budnikoff's (1935) similar result.

Thermal Methods

Le Chatelier (1882) used a thermal method to investigate the reactions occurring during the heating of kaolinite. He made a simple thermal analysis, determining the relationship between the temperature of the furnace and that of the heated sample. If endothermic or exothermic reactions take place within the investigated substance, sample temperature will be below or above furnace temperature. There are several possibilities to plot the process. Le Chatelier marked the sample temperature by lines, drawn at equal intervals (e. g. in every minute); the heating program of the furnace was regulated so as to give an exactly uniform heating rate. Using this plotting method, endothermic and exothermic reactions are shown by a drop of line frequency, followed by an increase and vica versa.

Wohlin (1913) refined the method of thermal analysis and developed a new plotting method. In this method furnace temperature was the abscissa and sample temperature the ordinate. A straight line shows that no thermal effects occur in the sample, breaks indicate thermal changes. If the slope tangent, tang α' is decreased, as compared to the original tang α, an endothermic, if it is increased, an exothermic process takes place in the sample.

The heat of reaction was first measured by Cohn (1924) and by McGee (1926). Both authors agree that the endothermic reaction is accompanied by a heat absorption of 95—100 kcal/g; the first exothermic reaction, by a heat evolution of 16.5 kcal/g.

The nature of meta-kaolinite was investigated thermochemically by Klever and Kordes (1929), by measuring the heat of solution at higher temperatures. They found a characteristic increase of the heat of solution of kaolin samples heated previously between 420 and 550 °C. The heat of solution of an artificial mixture of 1 mol. γ-alumina and 2 mol. quartz, on the other hand, is 18 calories lower than the heat of solution of the dehydroxylation products of kaolin. This figure shows, at the same time, the difference between the heats of formation of pure oxides and of dehydroxylation products *(Hess' law)*. If this difference is a real one and not due to scattered measurement results, the dehydroxylation product of kaolin is a separate compound and not a simple mix of oxides.

This method gives an answer to the question: mix or compound; and this is what Klever and Kordes aimed at. The difference of 18 calories, however, lies very close to the error limit of measurements, so this experiment alone cannot be accepted as proving the existence of meta-kaolinite.

Belyankin (1932) has showed that thermal methods are not always suitable for revealing the reactions of kaolin during firing. As mentioned before, one of the most characteristic thermal reactions of kaolinite is the 950 °C exothermic effect. This effect can be screened by the presence of alumina-containing substances, e. g. boehmite or hydrargillite. Chasov-Yarsk (USSR) kaolin e. g. does not show any exothermic reactions, in spite of the presence of the endothermic reaction. All the same, the rock gives a perfect X-ray pattern; every line corresponds to those of kaolinite. The main difference between Chasov-Yarsk clay mineral and kaolinite is only (besides a slight excess of alumina) the absence of the first exotherm. The mineral must not be given a special name as it is not more than a screening effect; nevertheless Belyankin called this mineral "*monothermite*". The structure of monothermite was determined by Sedletski (1949), and was found almost completely identical with that of kaolinite. Some small differences are probably due to the admixture of illite and mica.

According to Gruver, Henry and Heysteck (1949), some materials, in the first place fluxes, may decrease or eliminate the thermal effects of kaolinite. The 950 °C exothermic peak is screened by the admixture of e. g. iron oxide and sodium oxide.

Thermal analysis may be made more accurate and definite by plotting the difference between the temperatures of the sample and of the furnace as a function of temperature, and not the sample temperature as a function of furnace temperature. A simple electric wiring will suffice to achieve a difference. This method gives the derivate of the simple thermal analysis curve. The method, called *differential thermal analysis* (DTA), has been used by a number of authors both for diagnoses and for explaining the mechanisms of thermal reactions. The theoretical and practical aspects of the DTA method were summarized by Földváriné-Vogl (1958).

Yamauchi and Kato (1943) have e. g. used differential thermal analysis for the investigation of raw clays. Exothermal peaks were found between 150 and 300 °C and between 900 and 1000 °C, endothermal ones at about 100 °C and 450—600 °C. Exothermal effects between 150 and 300 °C are probably due to the burning out of organic substances, the 100 °C endotherm to the release of mechanically bound water. If the SiO_2/Al_2O_3 ratio is above 7, the 575 °C effect of quartz can be detected too.

Differential thermal analysis can be used for measuring the heats of reaction. According to Segawa (1949), an artificial mix of the ratio $3Al_2O_3/2SiO_2$ gives the maximum exothermic heat of reaction (7.6 cal/mol). The reaction velocity changes with the temperature; a maximum reaction velocity between Al_2O_3 and SiO_2 powders was found at 950 °C.

The reliability of these thermal data, however, is very questionable. Shorter (1948) states that all calorimetric data, obtained either by differential thermal analysis or by heating curves, are usually inaccurate. This is due primarily to the low thermal conductivity of the substance around the thermocouples. An error of even 30—50 per cent may be due to this effect. The accuracy of calorimetric data is influenced also by the amount of the sample. By using a large sample, the apparent development resp. absorption of heat will be less. Data obtained by these methods give but a rough estimate. The 137 cal/g endothermic heat of reaction of dickite, derived from DTA curves by Stone (1952), is therefore disputable.

The effect of foreign materials is also significant: according to Nakamura and Noguchi (1957), the interval between the endotherm and the first exothermic peak of kaolin is increased by the effect of a γ-alumina admixture.

Thermal weight losses and also the rehydration of clay mineral are, according to Radczewski and Rath (1952), easily followed by a simple thermobalance.

Optical Methods

Optical methods are, as mentioned previously, not very suitable for investigating the thermal reactions of clay minerals, although a number of authors have used the optical microscope as an auxiliary means. An electron microscope, however, holds out as a more promising method. Eitel, Müller and Radczewsky (1939) were the first to follow the dehydration (dehydroxylation) of clay minerals (kaolinite and dickite) by electron microscope investigation. Original hexagonal crystals of kaolinite are well discernible under the electron microscope. During dehydroxylation these crystals break, become smaller, but their hexagonal habit is well recognizable even after firing. These results were confirmed later by Comer, Koenig and Lyons (1956).

According to the theory of Comeforo, Fischer and Bradley (1948), based on X-ray and electron microscope evidences, meta-kaolinite contains long AlO_4-chains parallel to the crystallographic a axis; this structure, however, collapses at higher temperatures and mullite nuclei form directly, without any intermediate phase, e. g. γ-alumina. Dietzel and Dhekne (1957) used an electron microscope to study the rehydration of meta-kaolinite. They state that the amount of fine particles is increased by autoclave treatment.

X-ray and Electron Diffraction Investigations

The first X-ray investigation of the thermal reactions of kaolinite is connected to the name of Rinne (1924). According to the theory of the free oxides, lines due to some silica and to some alumina-modifications will be seen on the X-ray pattern of kaolinite heated above the temperature of the endothermic reaction. In spite of this presupposition, Rinne did not find any distinct lines, only some wide bands at places corresponding to kaolin lines. A new theory has been evolved upon this experimental base: a compound of distorted structure, though slightly similar to kaolinite, is formed during the endothermic process of kaolinite; this new compound is called "meta-kaolinite". This result was confirmed by Hyslop and Rooksby (1928).

Krause and Wöhner (1932) criticized Rinne's hypothesis. According to their theory, what is formed during the endothermic reaction, is a mixture of amorphous SiO_2 and Al_2O_3 and not meta-kaolinite. The first exotherm is due, according to the X-ray results obtained by Krause and Wöhner, to the formation of sillimanite which transforms later into mullite.

After these pioneering investigations, a very careful and thorough study was made by Insley and Ewell (1935) in order to determine the real nature of the thermal changes of kaolinite. They described the endothermic reaction as a formation of an amorphous substance which later turns into a crystalline one; at 950 °C γ-alumina is formed which finally recrystallizes into mullite. The final product then is — in accordance with the Al_2O_3—SiO_2 phase diagram — a mixture of mullite and cristobalite. The characteristic, sharp exothermic effect of kaolinite, dickite and co-precipitated alumina-silica gels is at 980 °C.

Tscheischvili, Buessem and Weyl (1939), on the other hand, think that some elements of the original kaolinite lattice are preserved in the transition phase of meta-kaolinite, even after dehydroxylation. There are also some X-ray lines of kaolinite to be seen after a 800 °C heating if the X-ray radiation is carefully monochromatized, and lines due to γ-alumina begin to develop after a firing at higher temperatures. The distribution of meta-kaolinite was studied by the adsorption of different fluorescent substances; according to this measurement, meta-kaolinite is most finely dispersed after a heating of approximately 800 °C.

Toropov and co-workers (1954) determined a slow mullite formation at 900—1000 °C; the velocity of this reaction, however, is increased above 1200 °C. This result was obtained by a high-temperature X-ray technique, using an ionization chamber as radiation detector, an electronic amplifier and an electronic recorder.

Electron diffraction, on the other hand, seems to be a more promising method. Eitel and Kedesdy (1943) used this method to investigate the dehydroxylation process of kaolinite. They state that after a firing of 700 °C kaolinite consists of the mixture of very finely dispersed silica and γ-alumina. Mullite formation begins only above 950 °C. These results were confirmed by Radczewsky (1953), with the addition that diffraction spots due to γ-alumina disappear only after a heating above 1100° C, and cristobalite forms only above 1200 °C.

The most detailed electron diffraction study has been made by Roy, Roy and Francis (1955). The most important result of their single-crystal electron diffraction study is that kaolinite, dried at 110 °C, gives a two-dimensional, pseudo-hexagonal pattern of diffraction spots, corresponding to projection *hk*0. It is very interesting to note, however, that even 300 °C above the dehydroxylation reaction, shown by DTA, electron diffraction patterns remained almost unchanged as compared to those of unheated kaolinite: they were accompanied only by a slight change in some of the intensities. Samples heated above 855 °C showed the formation of a new compound, but there remained some characteristic kaolinite reflections even above this temperature. The new compound, as determined from this electron diffraction study, was identified as γ-alumina (of various orientation). Between 855 and 1000 °C, this was the only compound found by electron diffraction. According to Roy, Roy and Francis, in this temperature interval, the presence of γ-alumina is beyond question.

Some X-ray investigations were made simultaneously with this study; the patterns, however, showed no reflections at all. The structure of heated kaolin is, as can be seen from this example, not to be investigated by X-ray, but only by electron diffraction. The structural residues of kaolinite disappear only after a heating of 820 °C.

The data obtained by Roy and co-workers are, no doubt, exact and reliable. Although they support the interpretation of thermal reactions of kaolinite, the final solution of this problem has not yet been reached. Data published, including temperature data, correspond only to the particle size fraction between 1 and 4 microns of *Langley* kaolin, used by the authors. The temperature data, however, presumably vary with the different kaolin occurrences and even with the particle sizes of the same occurrence.

Other Investigation Techniques

The characteristic dilatation of the heating products of kaolinite has been investigated by several authors. Salmang and Rittgen (1931) e. g. using differential dilatometry have determined the following characteristics of the dilatation curve of kaolinite: between 80 and 160 °C there is a slight shrinkage due to the loss of moisture, a second shrinkage step, between 200 and 300 °C, is of a colloid character; meta-kaolinite is formed, by further shrinkage steps, between appr. 450 and 650 °C; the width and limits of this interval vary for every sort of clay. Above 600 °C the shrinkage is followed by a dilatation which may last to 850 °C. The meta-kaolinite phase is destroyed at 800—1100 °C while silica and γ-alumina and perhaps sillimanite are formed. These phases transform into mullite above 1200 °C. The shrinkage effects are constant concomitants of clay-heating; the dilatation between 600 and 850 °C is, however, an anomalous phenomenon due to vitreous substances.

Schwarz and Klös (1931), studying the break points of dilatometric curves, published the following results as averages of the investigation of several kaolinite samples: 100 °C and 582 °C breakage points are due to the release of adhesion water (moisture) and structural water, respectively. The release of structural water is completed at 845 °C; at the same temperature the formation of amorphous oxides begins. Mullite and tridymite formation starts at 938 °C. Meta-kaolin is present between 582 and 845 °C.

Schwarz and Trageser (1932) combined dilatometry with weight loss determinations. In this study Schwarz slightly modified the data of his 1931 paper, and distinguished two steps in the dehydration of kaolinite; in the first step *anhydro-kaolinite* is formed, maintaining some residues of the original structure. This step is followed by *meta-kaolinite* which is no longer a compound but a mixture of free oxides.

Geller and Bunting (1940) investigated dilatation characteristics of several sorts of china clays and ball clays using different heating rates strictly controlled and adhered to. Admixtures and other contaminations affect the dilatation of kaolins to a great extent. *Kaolins of mica content*, for instance, show a very characteristic thermal dilatation between 500 and 900 °C. There is a proportionality between mica content and dilatation. If mica were not present, a shrinkage would occur in this interval. Above 900 °C, however, a shrinkage occurs independently of the presence or absence of mica. The authors ascribe this effect to the recrystallization of γ-alumina into corundum and support their hypothesis by referring to the fact that this shrinkage is proportional to the alumina content.

Hyslop and Gworek (1950) observed two characteristic contraction effects during the heating of kaolin: at 850 and 1000 °C. The first effect is due to the formation of γ-alumina, the second to that of mullite.

For the investigation of the dehydroxylation characteristics of kaolinite some additional methods have been introduced.

Keyser (1940, 1959) studied the dehydroxylation process of Zettlitz kaolinite by measuring dielectric constants. The dielectric constant of kaolinite, plotted as a function of temperature, shows an abrupt change at 400° C, a temperature corresponding to a water content of 14.4 per cent, i. e. 1.75 mol H_2O per Al_2O_3. The dielectric constant shows irregular changes at about 820 and 950 °C. The former temperature changes can be associated with meta-kaolinite collapse and with the simultaneous formation of sillimanite, whereas the latter are due to the sillimanite→mullite transformation.

Also Avgustinik and Kozlovski (1952) have investigated the dielectric constant of fired kaolinite. Although confirming anomalies at 950 °C, they have explained this phenomenon by the formation of γ-alumina, which causes a weakening in interionic bonds. The firing of talc shows a similar phenomenon, while thermal effects of pyrophyllite find a better explanation in direct mullite formation.

Zimens and Hedvall (1943) have investigated the thermal transformations of dickite by magnetochemical methods. The magnetic susceptibility of original dickite does not change with field strength; prefired dickite, however, shows changes in susceptibility as a function of field strength, a phenomenon attributed by the authors to the crystallization of some ferromagnetic material. It should be noted that Zimens and Hedvall used dickite in their experiments, but it is most probable that kaolinite behaves in a similar way under given conditions. The final conclusion as to the formation of a ferromagnetic material can, however, be accepted only with restrictions as it may rightly be supposed that contaminations in dickite are responsible for the effect to a considerable extent.

The thermal reactions of kaolinite were followed by Nikitin (1955) who used the method of water sorption. By expelling the structural water of kaolinite at 250 °C *in vacuo,* he found the sorption capacity to increase but slightly and the specific surface to remain about 50 sq. m/gas before. Under the same circumstances, the sorption capacity of aluminium hydroxide considerably increases, whereas that of silicon hydroxide shows a somewhat weaker increment. Consequently, fired kaolinite cannot be a mixture of heated $Al(OH)_3$ and $Si(OH)_4$. It is an individual phase which may be called "meta-kaolinite".

Also Brown and Gregg (1952) used adsorption measurements when investigating the thermal processes of kaolinite, but they substituted water vapour by carbon tetrachloride. Measured by this method, the specific surface of kaolins heated to 400—500 °C showed an increase by about 50 per cent. At the same time, specific gravity decreased (from 2.59 to 2.44 g/ml). These results have been confirmed by Gregg and Stephens (1953) who applied nitrogen as adsorbate.

Concluding from results obtained by the infrared spectroscopy of dehydrated kaolin and artificial materials, Fisher, Rabovski and Finkelshstein (1958) consider kaolinite anhydride as a molecular compound of *allophanoid* structure.

Roy, Roy and Francis (1955), when publishing the characteristics of the infrared absorption spectra of kaolinite, halloysite and firing products, refrain from evaluating their experiments as the dehydroxylated samples had not given spectra of any diagnostic value.

B) CHARACTERISTICS AND PRODUCTS OF THERMAL REACTIONS

Endothermic Process of Kaolinite

Hypotheses elaborated in search for a final explanation of the endothermic process of kaolinite, may be divided into three groups characterized by the following statements: (i) during the endothermic process, kaolinite transforms into a mixture of amorphous silica and amorphous alumina with the simultaneous destruction of the original lattice; (ii) during the endothermic process a new compound, "*meta-kaolin*" or "*meta-kaolinite*" is formed. This compound is ill-crystallized and preserves some structural elements of the original lattice; (iii) some authors have proposed various other mechanisms for the explanation of the endothermic process of kaolinite.

The theory of the thermal decomposition of kaolin into free oxides was proposed by Mellor and Holdcroft (1911). Tammann and Pape (1923) and also Keppeler (1925) were of the same opinion (cf. page 69).

Neumann and Kober (1926) were of a similar conviction saying that during the endothermic process of kaolins and clays, free silica and free alumina are formed. Their iron oxide content, even if originally present as an insoluble substance, becomes acid-soluble after the endothermic process. Early investigations were followed by the detailed elaboration of the theory, substantiated also by Insley and Ewell's (1935) careful X-ray examinations. They consider the reaction product an intimate mix of amorphous silica and alumina with the total water content of alumina leaving during the process. Heated kaolinite does not give any distinct X-ray lines, only a few uncertain bands which show the amorphous nature of the product. The exact and careful investigations of Insley and Ewell are of decisive importance in the examination of this problem. Meier (1940) also agrees with the above theory concerning the origin of endothermic peaks.

Richardson (1951) supports the view that decomposition into free oxides must yield individual oxide particles of extremely fine distribution, adding, however, that the distribution of alumina-silica mixture particles, being of molecular fineness, may be considered a solid solution and not a common mix of the two components. Colegrave and Rigby (1952) say that the characteristics of dehydroxylated kaolinite are completely amorphous; during the exothermic reaction, the simple mixture of components turns into a compound.

The hypotheses of the second group consider that the endothermic effect of kaolinite is due to the dehydration (dehydroxylation) of the mineral and to the simultaneous formation of a new *compound*. This compound, although of an amorphous character, is no simple mechanical mixture of amorphous oxides. Agafonoff and Vernadský (1924) were the first to advance the above theory. They designated the new compound as *kaolin-anhydride* of composition $Al_2O_3 \cdot 2SiO_2$, possibly a separate crystal phase. They had been led to this conclusion by their adsorption examinations: kaolinite heated above the temperature of endothermic reaction, adsorbs organic dyes in a completely homogeneous way while their adsorption by an artificial mix of oxides is heterogeneous, where only alumina-particles adsorb dyes. Budnikov and Khish (1929) explain the endothermic effect of kaolinite by the same process; they call the compound formed during dehydration *meta-kaolinite*. Saldau and co-workers (1940) give the same compound the name *anhydro-kaolinite*.

One phase diagram of the system Al_2O_3—Si_2O, as determined by Bowen and Greig (1924), was already known at the time of these early works. Sosman (1933) concluded from phase equilibrium data that meta-kaolinite must be formed during the dehydration of kaolinite as an individual phase, effecting an endothermic peak at about 600 °C. It is somewhat far-fetched, however, to draw conclusions of this type, merely on phase equilibrium data, as these show only the final, stable distribution of phases but not the unstable intermediate circumstances. In order to investigate the latter, some other methods are to be chosen. Such method is e. g. the technique of *isobar decomposition,* used by Endell, Hofmann and Wilm (1933). Kaolins and clays lose little water up to 450 °C, but above 450 °C they suddenly lose all of their water content. Endell and his co-workers conclude from these data the existence of meta-kaolinite. Bentonite e. g. which is a clay sort, made up chiefly of montmorillonite and not of kaolinite, behaves quite differently during heating: it loses the bulk of water between 100 and 200 °C, while the rest leaves only at high temperatures. In this case it is more probable that an oxide mixture is formed.

The composition of meta-kaolinite is not necessarily constant. According to Belyankin and Fedot'ev (1949), this structure is very similar to that of allophanoid clays.

External mechanical tension makes the bond between hydroxyl ions and SiO_2 skeleton less dense. Compressed with a load of 20 to/sq. cm, a kaolin sample will show a higher loss of water between 400 and 500 °C. (Trifonov and Spasov 1950.)

As a result of very careful X-ray and DTA examination Belyankin (1951) and later Glass (1954) look upon meta-kaolinite as a real compound. Several sorts of kaolin and halloysite give the same thermal decomposition product.

According to Budnikov and Gevorkyan (1951), meta-kaolinite is formed during the decomposition of kaolinite between 500 and 550 °C. During subsequent heat treatment some structural elements of meta-kaolinite give mullite as a product of solid-state reaction. Budnikov and Gevorkyan describe meta-kaolinite as an indispensable intermediate product of mullite formation. This opinion, however, has been disproved by Grofcsik (1957) on the basis of results obtained when investigating co-precipitated gels.

By the close similarity of the DTA curves of natural meta-kaolinite and artificial allophanoid Keler and Leonov (1955) proved the presence of meta-kaolinite to be an independent and allophanoid-type phase.

Meta-kaolinite was rehydrated at high pressure and high temperature by Saalfeld (1955). The rehydrated product, however, was not identical with the natural mineral, since instead of regular kaolinite-reflections, a disturbed, fireclay-type X-ray pattern was obtained. The higher the temperature of meta-kaolinite production, the higher the disorder of the X-ray pattern as compared to regular kaolinite reflections. These observations conform to Nikitin's opinion (1955) who, by comparing the water sorption of meta-kaolin, alumina and silica gel, determined meta-kaolinite as an individual phase.

As seen from the above, the data in the literature reveal a number of contradictions and discrepancies due, according to Lebedev (1953), to the assumption that the bond of alumino-silicates is purely ionic. They are not, as for instance, SiO_4 groups of kaolinite are to a high degree (almost 5/8) of a covalent-type bond. In kaolin heated above the temperature of the endothermic process, octahedral layers completely decompose, and tetrahedral layers are distorted. Half of the aluminium ions migrate during heating into the empty positions of the tetrahedral layer (i. e. into the positions formerly occupied by the OH ions). In this way a highly disordered "amorphous pseudomorph" is formed called meta-kaolinite by most authors. Meta-kaolinite contains some structural elements, but in a disordered state; the higher the heating temperature, the higher the degree of disorder (Saalfeld 1954).

The intensity of the endothermic process as well as the degree of disorder in meta-kaolinite greatly depends on the degree of the crystallization of the original kaolinite. The temperature of the endothermic peak and its width will be higher in case of well-crystallized sorts than in ill-crystallized kaolin. Also the reaction is more intensive in the latter case. Meta-kaolinite formed from well-crystallized kaolin has a much higher degree of structural order than that of poorly crystallized kaolin.

Careful and thorough X-ray investigations were performed by Comeforo, Fischer and Bradley (1948) in order to determine the existence of a meta-kaolinite phase. By the evaluation of some characteristics of the X-ray pattern and primarily by the investigation of 4.3 kX and related reflection bands, they conclude that the product formed during the endothermic process of kaolinite is not perfectly crystallized, although it has a much more ordered structure than really amorphous solid substances. Comeforo and co-workers consider this structure a "co-ordinated chain of AlO_6 octahedra"; this chain is linked only at a few places with the SiO_4 layer because the OH ions, which have given the bond in the state of (unheated) kaolinite have left during the endothermic process. The order of meta-kaolinite could be restored only in the presence of further oxygen ions.

The existence of meta-kaolinite was confirmed also by Glass (1954); meta-kaolinite decomposes into amorphous silicon dioxide and crystalline γ-Al_2O_3 at the temperature of the exothermic process.

Not only kaolinite yields a metaphase during heating. Lebedev (1958) points out the close similarity of the DTA curves of kaolinite and of serpentine and confirms the distorted nature of metaphases, which are present in both minerals after heating.

The existence of meta-kaolinite has been corroborated also by Stubičan and Günthard's (1957) infrared spectrography; investigating unheated kaolinite they found 4 absorption bands, due to the Si—O bond, in the interval between 8.7 and 10.4 μ. Further bands in the spectrum of unheated kaolin: a wide one at 10.9 μ, due to the octahedral AlO_6 layer and one at 2.7 μ, due to the octahedral lattice of OH ions. After the heating of kaolin, i. e. in the meta-kaolin phase, the 10.9 μ band is not seen any longer and also the 2.7 μ band disappears. The 4 absorption bands between 8.7 μ and 10.4 μ remain and show the presence of Si—O bonds, in spite of the octahedral layer having been completely destroyed in the endothermic process. The remaining bands are, as a rule, shifted towards shorter wavelengths. Meta-kaolin (according to infrared spectroscopy data) is less disordered than mixed alumina-silica gels under similar circumstances.

It was Tscheischvili, Büssem and Weyl (1939) who first gave the probable structure of meta-kaolinite. According to them, meta-kaolin decomposes into free oxides below the temperature of the exothermic peak already. The probable structure as given by Tscheischvili and co-workers, as well as the structure of the original kaolinite, are given in Fig. 19 (the actual structure is much more disordered in reality). Essentially, the structure is characterized by the original Si—O network of kaolinite remaining almost unchanged while the original octahedral Al—O network is transformed into edge-sharing tetrahedral Al—O chains. Three layers of oxygen ions are formed in this way within one unit cell, with a sequence of 6—4—4 oxygen ions; the height of one such layer of tetrahedral co-ordinations is 2.2 Å (measured in the direction of the *c* axis). The total height of

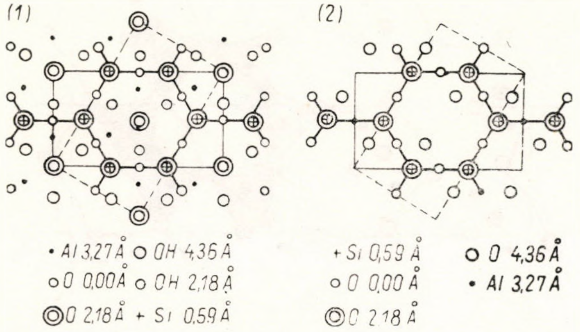

Figure 19

Structure of original and dehydroxylated kaolinite according to Tscheischvili and co-workers (1939)

the unit cell is 6.6 Å as a minimum or probably even higher because, cations being absent in one layer, there is an enhanced repulsion between oxygen ions. Taking also layers between oxygens into consideration the layer sequence is as follows: — $O_6Si_4O_4Al_4O_4$—$O_6Si_4O_4Al_4O_4$ —. This pattern clearly shows that 10 oxygen ions join in the neighbourhood of the cell boundary; the later formation of mullite resp. γ-alumina can hardly be explained by the condensation of these oxygens. The density calculated according to this structure is too high as compared to the density measured. Being formed during the endothermic reaction of kaolinite the phase is considered a *compound* whose structure is also given by Brindley and Nakahira (1958*b*). The structure, as obtained by careful X-ray single crystal examinations, is as outlined in the following:

Three layers of oxygen ions are formed per unit cell; two of them contain six close-packed oxygen ions, each. Both of these layers are of tetrahedral symmetry, i. e. silicon as well as aluminium ions are surrounded by a regular or slightly distorted quadruple group of oxygen ions. The height of this double layer is 4.4 Å, the bulk height of the structure (as determined from density data) parallel to the *c* axis is 6.3 Å. Only a height of 1.9 Å remains for the third layer of oxygen ions; the remainder of oxygen ions is partly sunk into the holes of the Si—O network. The structure is given in Fig. 20; the upper and the lower sketches show the structure as viewed from the direction of axis *c*, resp. of axis *a* (i. e. "from above" and "from the front"). Large full circles respresent Al ions, small full circles Si ions. Hatched circles are oxygen ions. A leaned hatching shows oxygen ions of tetrahedral co-ordination; hatching slanting left indicates oxygen ions belonging to the Si—O network (these oxygen ions obviously belong partly to Al ions too), while hatching slanting right indicates those oxygen ions which belong to Al only. The oxygen ions, hatched vertically are those partly sunk into the holes of the upper Si—O network.

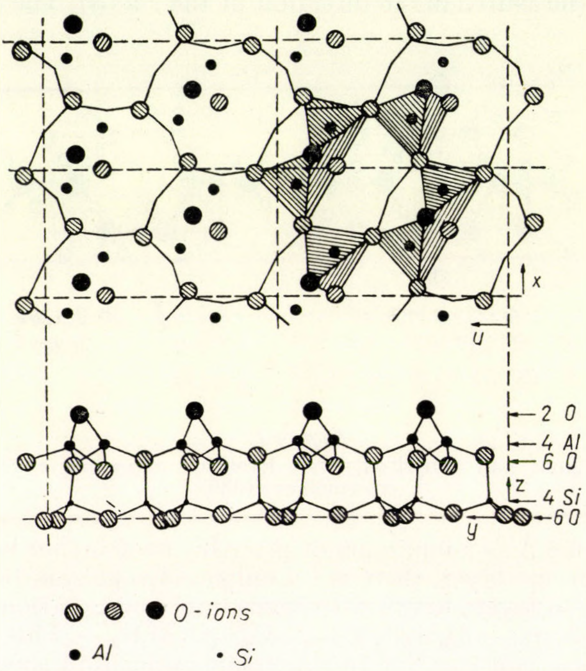

Figure 20

Structure of meta-kaolinite according to Brindley and Nakahira (1959*b*). Upper part of the figure shows the projection of the structure upon the (001) plane, the lower part, the view of the structure from the direction of the *a* axis. The layers are well seen in the lower figure. The unit cell is outlined in dashed lines

The lower part of Fig. 20 clearly shows that the layers of the structure contain in sequence 6—6—2 oxygen ions per unit cell. As a consequence of further heating, i. e. of increased thermal vibration, the two upper oxygen ions of the structure, together with the adjacent 6 lower oxygen ions of the next cell, may easily form a close-packed cubic structure (spinel structure). Theoretically, this transformation takes place in two steps:

The original layer sequence of —$O_6Si_4O_6Al_4O_2$—$O_6Si_4O_6Al_4O_2$— transforms (Step 1) into the —$O_8Si_4O_6Al_4$—$O_8Si_4O_6Al_4$— layer sequence. This structure is unstable and it readily transforms (Step 2) with the release of SiO_2 into sequence —$O_6Si_3O_6Al_4$—$O_6Si_3O_6Al_4$—* which contains only

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* A misprinted item in the original paper of Brindley and Nakahira.

oxygen layers of identical loading. This compound is of a spinel structure. According to Brindley and Nakahira, the formation of this compound causes the first exothermic effect of kaolinite.

On the strength of these considerations the formation of meta-kaolinite during endothermic reaction of kaolinite is more probable than the formation of amorphous free oxides.

The First Exothermic Process during the Heating of Kaolinite

Having recognized the heating characteristics of kaolin, investigations were started to find out the cause of the thermal effects, among them also that of the "first" exothermic peak, but have resulted so far only in some hypotheses.

Spangenberg (1927) investigated the first exothermic reaction by a combined microscopic, X-ray and solution method but admitted that he had been unable to identify the reaction product. Other authors were not so prudent in drawing conclusions. Surveying the literature with a critical eye, it may be stated that the characteristic "first"exothermic process of kaolinite, of kaolinite-containing clays and ceramic bodies, which takes place between 900 and 1000 °C, has not been exactly and positively explained so far. The failure should be ascribed to the different nature of raw materials: since the reaction does not yield the same products with every raw material, the experimental results cannot be generalized without further consideration.

Two contradictory theories prevail among the authors. One of the theories says that the exothermic effect is due to the recrystallization of the amorphous or loosely bound alumina and/or silica formed during the endothermic process and the product of recrystallization is γ-alumina. According to the second theory, it is mullite. The first theory was developed by Zwetsch (1936), the second by a number of authors, with Comeforo, Fischer and Bradley (1948) going into details about it. Stability conditions refer to the formation of mullite at this temperature but the formation of sillimanite from some kaolinite-bearing clays must also be accepted as a possibility. Some authors mention other reaction mechanisms.

Budnikov and Khizh (1929) have given the scheme of kaolin decomposition. This scheme explained the recrystallization of γ-alumina and the formation of amorphous silica (from the meta-phase of composition $Al_2O_3 \cdot 2SiO_2$). These transformations take place at 950 °C with a simultaneous exothermic reaction. γ-alumina reacts at approx. 1000 °C with amorphous silica, and turns into sillimanite. This latter reaction is without any thermal effect.

Tscheischvili, Büssem and Weyl (1939) considered the formation of γ-alumina as the cause of the first exothermic effect of kaolin. Essentially this reaction is the transformation of AlO_4-tetrahedra of meta-kaolin into more stable AlO_6 octahedra. This process may lead to the formation of either γ-alumina or corundum, the former being more probable.

Insley and Ewell's (1935) classical investigations have proved that the amorphous material, formed during the endothermic process of kaolin, recrystallizes at the temperature of the first exothermic peak into *γ-alumina*. Some contaminations and/or admixtures, however, affect this reaction; the exothermic effect of gel mixes e. g. is due to mullite formation. If heated to a temperature high above the first exotherm, kaolin as well as gel mixes yield mullite crystals.

Careful X-ray examinations were made by Richardson and White (1952) in order to determine the reaction products of various kinds of clays. According to the authors, the exothermic reaction is due to the formation of γ-alumina. At a higher temperature this compound reacts with the present amorphous silica and transforms into mullite.

Colegrave and Rigby (1952) try to explain the sudden formation of γ-alumina during the exothermic effect of kaolin. According to their considerations and experiments, at lower temperatures SiO_2 prevents the amorphous oxide from turning into crystallized γ-alumina. γ-alumina later reacts with SiO_2 and yields mullite; Colegrave and Rigby consider the presence of γ-alumina an indispensable precondition for the formation of mullite. Their opinion, however, cannot be accepted, as mullite is formed from some kaolins, from gels as well as from pyrophyllite without any intermediary step of γ-alumina (Bradley and Grim 1951).

Keler and Leonov (1955) tried to reconcile the two hypotheses. DTA investigations made on contaminated mixes of natural kaolinite and artificial allophanoid have led them to the conclusion that the first exothermic reaction of kaolinite yields mostly γ-alumina, with the simultaneous formation of a small quantity of mullite; the total quantity of the substances present transforms into mullite only at the temperature of the second exotherm. MgO, CaO, MgF_2 and CaF_2 increase the amount of mullite, formed during the first exothermic process.

Lundin (1958) made detailed X-ray and dilatometric studies in order to determine the mullite-formation kinetics of kaolin-bearing clays. He has found that during the first exothermic reaction γ-alumina is formed which transforms into mullite between 1100 and 1200 °C.

The results of their infrared spectrography examinations have led Stubičan and Günthard (1957) to a similar conclusion. Somewhat above the temperature of the exothermic reaction, the infrared spectra show the characteristic absorption bands due to bonds of γ-alumina; at the same time Si—O bonds become more distinct. The statement that the first exothermic peak of kaolinite is due to the crystallization of γ-alumina, has been modified recently by a number of authors explaining this exothermic process by the formation of mullite.

Comeforo, Fischer and Bradley (1948) have showed by electron microscope investigation that after a heating above 950 °C, needle-shaped crystals of mullite are found parallel to the "hexagonal" plate contours of well crystallized kaolin.

Belyankin's (1949) similar opinion was based on his X-ray results.

The first exothermic reaction of kaolinite is, according to Hyslop and Gworek (1950), a two-step process. These two steps may be well distinguished by dilatometry: after the 850 °C contraction the formation of mullite causes a second contraction below 1000 °C.

Johns (1953*b*) proved that if the original kaolin is well crystallized, mullite is formed from kaolin at the temperature of the first exothermic peak. A starting material of disordered or ill-crystallized kaolin induces much more complicated phenomena during heating.

According to the X-ray and DTA investigations by Glass (1954), primary mullite is formed from pure kaolin at 950—980 °C. A low quantity of γ-alumina, however, is always produced, even from the best crystallized kaolin sorts. Should the crystallization of original kaolin be imperfect, the amount of γ-alumina will be higher. Halloysite, having a disordered lattice, yields during the first exotherm process γ-alumina only. The contaminations of the starting material influence also the nature of the product obtained by the first exothermic process; a mica-containing kaolin e. g. gives no mullite during this process.

Roy, Roy and Francis (1955), though not sure about the formation of mullite during the first exothermic reaction, consider this possibility closer to real conditions than the theory of γ-alumina formation. The characteristic X-ray reflections of kaolin heated to a temperature just above that of the exothermic reaction, may be missing in some cases. This can be explained by the minuteness of crystals formed primarily by the process and yielding a diffuse, gel-like X-ray diagram.

Gerard-Hirne and Meneret (1956) consider mullite formation the cause of the first exothermic process independently of the crystallization degree of the starting material. Consequently, their opinion is in discordance with that of Glass (1954). In his former theory Grofcsik (1952) judged the formation of mullite the sole cause of the first exothermic peak of kaolin.

Besides the two theories, just dealt with, some other explanations have been given to the first exothermic effect of kaolin. Some authors regard e. g. the formation of *sillimanite* as the cause of this thermal peak.

Budnikov and Khizh (1929) think that this reaction consists of two steps, the first being the formation of an oxide mix from meta-kaolinite, the second, the recrystallization into sillimanite. This second process has a higher temperature, but still below 1000 °C.

Although the phase diagram of the system Al_2O_3—SiO_2, as described by Bowen and Greig (1924), was already known at the time, Budnikov and Khizh thought that the stable mullite phase was reached through a sillimanite step. Keyser (1940) came to the same conclusion through his dielectric measurements. Due to the formation of sillimanite the dielectric constant of kaolinite shows certain irregularities at about 950 °C; this is, however, only an intermediate product and, slightly (10—30 °C) above its formation, it decomposes into mullite and silica.

Wiegmann and Horte (1956*a*, *b*) say that the exothermic process of kaolinite is a reaction of two steps, the first being the formation of γ-alumina, the second, that of sillimanite. Though their investigations concern primarily precipitated gels, the authors extend their results to kaolinite resp. to meta-kaolinite as well.

Lebedev (1958) was of the same opinion with the limitation that only well-crystallized kaolins yield sillimanite during heating.

Some authors regard the formation of *mullite nuclei* as the cause of the first exothermic peak. Comeforo, Fischer and Bradley (1948) are of the opinion that during the first exothermic process the original structure of meta-kaolinite decomposes and mullite nuclei form from the AlO_4 chains present in meta-kaolinite as residues of the AlO_4 chains of original kaolinite parallel to the *a* axis.

Lebedev (1953) relying upon modern physico-chemical and crystallo-chemical theories considers meta-kaolinite a highly disordered, though still crystalline amorphous pseudomorph which transforms, between 880 and 900 °C, into a less disordered phase, γ-alumina, with the electrostatic field in the tetrahedral layer disappearing simultaneously. The unstable oxygen positions have a high electron affinity; new Al—O and Si—O bonds, as crystallization nuclei of sillimanite and mullite, are formed. The first exothermic peak is a consequence of this reaction of double nature.

Brindley and Hunter (1955), using rotation single-crystal X-ray patterns, have found that mullite nuclei form from meta-nacrite, while the excess of SiO_2 is present as cristobalite. Mullite nuclei, oriented according to the position of the original nacrite single crystal, begin to grow above 1100 °C and finally transform into a circular mullite crystals.

Budnikov and Gevorkyan (1951) are of the opinion that, during the first exothermic reaction of kaolinite, silica and alumina of a peculiarly "active form" appear and later transform into mullite.*

Several authors have tried to reconcile the most important theories explaining the first exothermic process of kaolin (γ-alumina and mullite formation, respectively). Keler and Leonov (1955) as well as Mikheev and Stulov (1955) e. g. have described the simultaneous formation of γ-alumina and mullite during the exothermic reaction. There is however, a contradiction between these two descriptions, for Keler and Leonov consider γ-alumina to be the main product whereas Mikheev and Stulov regard it to be mullite. The two antitheses may obviously be explained by the unequal purity of raw materials. As Glass (1954) has proved, it depends on the crystallization degree and on the mica contaminations of the kaolin whether the product of the exothermic reaction will be chiefly mullite, or γ-alumina.

Avgustinik and Kozlovski (1952) have found that during the exothermic reactions the inter-ionic bonds are weakened by the formation of γ-alumina. This result was obtained by measuring the dielectric constant of heated kaolin, i. e. not by a method of structure determination. This mechanism of reaction however holds true only for a starting material of

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* Having finished the manuscript, we read a paper of high importance by F. Freund, *Die Deutung der exothermen Reaktion des Kaolinits als "Reaktion des aktiven Zustandes"* in *Ber. dtsch. keram. Ges.* **37,** 209 (1960). He claims that meta-phases incorporate an "unstable lattice" which is destroyed at a well-defined temperature resulting in strong exothermic reaction. The heat of reaction can also be calculated by this theory. Freund considers the first exothermic process a representative of a reaction type still uninvestigated. This type of reaction may be called the "reaction of the active state".

adequate purity because it is greatly influenced by the contaminations of the raw materials. The effect also depends on the quality of the contaminating mineral; talc e. g. is ineffective from this point of view, while the heating of pyrophyllite gives mullite directly. Hyslop and Gworek (1950) have come to the same conclusion by dilatometry, which is no structure determination method either.

Thermochemical investigations have led Vaughan (1951) to the conclusion that during the first exothermic reaction of kaolinite several products, mullite, γ-alumina and silicon dioxide, are formed (the latter appears in the form of tridymite or cristobalite).

All opinions, described above agree in assuming the formation of either an oxide (γ-alumina, tridymite or cristobalite) or of mullite or sillimanite. West and Gray (1958) are of quite a different opinion. On the basis of investigations performed by thermochemical, X-ray and other methods they say that the exothermic peak observed at about 980 °C upon the DTA curve of kaolinite is due to three simultaneous reactions. The first is the recrystallization of alumina from its γ- to its α-modification, the second the crystallization of a hydrogen aluminium spinel of composition HAl_5O_8 and the third the reaction of this spinel with silica, yielding mullite. West and Gray, though experimenting with synthetic silica-alumina mixes, extend this theory also to kaolins.

Brindley and Nakahira (1958, 1959) made careful X-ray oscillation investigations of kaolinite single crystals and came to a new theory, much more suggestive than old ones. They suppose that the phase which other authors call γ-alumina is, after all, no individual phase but a solid solution which contains a considerable quantity of silica. This phase of solid-solution character has a cubic spinel-type lattice.

This theory gives a better explanation of the thermal process than the old ones speaking about the formation of γ-alumina and hardly giving any reliable reason for the presence of silica, formed in a considerable extent according to the reaction equation but detected only in traces, if at all, by X-ray patterns. Authors generally thought this silica to be amorphous, and that it cannot be shown by X-ray patterns.

Brindley and Nakahira give a clear and comprehensible explanation of all thermal effects of kaolinite by attributing them to the diffusion of silica from the crystal lattice of kaolin.

The gross process of the dehydroxylation of kaolinite is the following:

$$\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} \rightarrow \underset{\text{meta-kaolinite}}{Al_2Si_2O_7} + 2H_2O$$

The first step of diffusion may be represented by the equation:

$$2Al_2Si_2O_7 \rightarrow \underset{\text{spinel-phase}}{Al_4Si_3O_{12}} + SiO_2$$

i. e. an aluminium-silicon spinel is formed and this causes the 950 °C exotherm. In a further exothermic process (2^nd exothermic effect) the spinel transforms into a mullite-type phase of the (probable) composition: $Al_2O_3 \cdot SiO_2$,

$$Al_4Si_3O_{12} \rightarrow \underset{\text{mullite-type phase}}{2Al_2SiO_5} + SiO_2$$

causing the second step of SiO_2 diffusion. The stable mullite phase is formed between 1200 and 1400 °C with a further diffusion step of silica:

$$3Al_2SiO_5 \rightarrow \underset{\text{mullite}}{Al_6Si_2O_{13}} + SiO_2$$

Owing to contaminations, lattice defects, etc. one or another of these reactions may be missing.

The reaction sequence described by Brindley and Nakahira shows a uniform approach to the problem. The presupposition of an aluminium silicon spinel is more probable than that of a pure aluminium spinel (γ-Al_2O_3). The two phases are related, but in consequence of the changed chemical composition, the number of lattice defects will be higher in aluminium silicon spinel than in pure aluminium spinel ($5\frac{1}{3}$ and $2\frac{2}{3}$ per unit cell, respectively, as calculated with the formulae given above). The important role of lattice defects has been emphasized also by Mitra (1958) and Budnikow and Mtschedlow-Petrossian (1958).

Though very important, the theory of Brindley and Nakahira does not put an end to the discussion of the problem. Only a careful quantitative determination of the products formed during the reaction, could lead to a final conclusion. Grofcsik (1957) made experiments with co-precipitated gels and has come to the conclusion that mullite is formed in the stoichiometrical maximum during the exothermic reaction at about 950°; this statement, however, needs verification by examinations of several sorts of natural kaolinite.

The Second Exothermic Effect

Differential thermal analysis has been used up to 1000—1100 °C only, because above this temperature the design of a suitable high-temperature kiln and the exact measurement of temperature involved difficulties. There appeared an additional problem when examining clay or clay-containing bodies, namely, that the shrinkage of the material is rather considerable at this temperature and changes the heat conductivity within the sample to such an extent that thermal effects can hardly be recognized. In the course of development difficulties have been overcome and a number of furnaces designed for differential thermal analysis up to 1400—1500 °C (e. g. Székely and Vajdáné 1955).

During these investigations it was soon recognized that between 1200—1300 °C kaolinite showed a *second* exothermic process, less distinct and less intensive than the first. The peak of this second process is frequently of a double nature. Research into the causes of the second exothermic effect began in the early fifties of this century. In 1949 Belyankin still declared that the cause of the second exothermic effect was unknown. In the very same year, however, in a paper written together with Fedot'ev (Belyankin and Fedot'ev 1949) he attributed it to the *recrystallization of amorphous* silica into cristobalite. The formation of cristobalite was confirmed later by Radczewski's (1953) investigations with electron diffraction.

The majority of authors, however, were of the opinion that the second exothermic peak of kaolinite was due to the *formation of mullite*. Authors, who considered the first exothermic effect as being due to some other non-mullite formation, attached the mullite-forming process to this reaction. Others who considered the first exothermic process as mullite formation, explained the second effect by the formation of "secondary" mullite.

Budnikov and Gevorkyan (1951*a*) presume that meta-kaolinite, disintegrated into component oxides between 900 and 1000 °C, rearranges into mullite in a second exothermic process. Relying on this hypothesis they propose a practical method for the production of large mullite crystals: a lasting heat treatment of kaolinite between 1200 and 1300 °C. In the interval of the two exothermic peaks, the components (silica and alumina) are according to them, in an "active" form of free oxides and these active free oxides transform into mullite during the second exothermic process.

Richardson and Wilde (1952) conclude from their thorough X-ray investigations that during the second exothermic process γ-alumina and amorphous silica transform into mullite. This conclusion, however, has been drawn from experiments made with kaolin-bearing clays and not with pure kaolinite.

Lebedev (1953) considers the second exothermic reaction as the formation of sillimanite or (more probably) mullite from the nuclei formed during the first exothermic process. (Led by crystallochemical considerations Lebedev ascribes to the first exothermic effect the formation of nuclei.)

Attention was drawn by Glass (1954) to the interesting phenomenon that the *temperature* of the second exothermic peak greatly depends on the crystallization degree of the starting material, on the one hand, and its contaminations, on the other, although these factors do not affect the *presence* of this exothermic reaction which is, according to Glass, due to the formation of secondary mullite. If a kaolin sample is heated above the temperature of the *second* exothermic peak, X-rays will always detect mullite in it, while above the *first* exothermic process, even mullite nuclei are sometimes absent. The SiO_2 released during the process of mullite formation is amorphous, but later recrystallizes into cristobalite and causes another exothermic effect. The temperature of the second exothermic peak is 1250 and 1200 °C in case of well- and ill-crystallized kaolinite, respectively. It is worth mentioning that halloysite, this most disordered mineral of the kaolin group, gives this effect also at 1250 °C.

From the investigation of a Japanese kaolin, Sudo, Takahashi and Matsui (1954) conclude that the first X-ray lines attributable to mullite are seen at 1100—1200 °C. This process is accompanied by heat evolution.

Keler and Leonov (1955) investigated the effect of contaminations upon this reaction and observed that the temperature of the second exothermic process was lowered by additives. Also Keler and Leonov regard mullite formation as the cause of the second exothermic peak but say that part of the mullite may have been formed during the first exothermic process already.

Gérard-Hirne and Meneret (1958) emphasize that the second exothermic peak (not to be mistaken for the third exothermic process, observed in some clays) is a result of the formation of secondary mullite.

Having investigated thermal processes of Al_2O_3—SiO_2 gels Bidet and Jouenne (1958) say that the second exothermic effect is caused by the secondary mullite formation from silica and from γ-alumina still present. Insufficient mixing and alkali contaminations will prevent this reaction. Although the reaction conditions of kaolinite are not completely identical with that of gels, also kaolinite yields secondary mullite during its second exothermic process. Similar results were published by Wahl (1959).

In their paper already discussed Brindley and Nakahira (1958, 1959*c*) described that the silicon aluminium spinel of formula $2Al_2O_3 \cdot 3SiO_2$, formed during the first exothermic effect, rearranges at approximately 1100 °C into a mullite-type phase of formula $Al_2O_3 \cdot SiO_2$. The authors consider the presumption of this mullite-type 1 : 1 phase, as one requiring further confirmation.

The "Third" Exothermic Peak

A number of clays (though not all of them) show a third exothermic effect, i. e. an exothermic peak on their DTA curve between 1300 and 1400 °C. The majority of authors, e. g. Glass (1954) or Gérard-Hirne and Meneret (1956), attribute the presence of the peak to the crystallization of cristobalite from the silica earlier present as an amorphous substance.

Having investigated the high temperature reactions of kaolins and kaolin-type clays, West (1957) gives no explanation to the third exothermic peak, but describes that in case of several clays, owing to the formation of silicon *monoxide*, an irregular *endothermic* peak may be seen on the DTA curves. This compound later evaporates and oxidizes. His opinion is based upon X-ray and other data.

Brindley and Nakahira (1958, 1959*c*) explain the third exothermic peak by the final formation of mullite and by a simultaneous crystallization of cristobalite.

C) THE REASON OF THERMAL PROCESSES OF KAOLINITE

Factors Affecting Kaolinite Thermal Reactions

The literature dealing with the thermal processes of kaolin abounds in contradictory data. First of all, the causes of the contradictions must be revealed. A critical survey of the literature and Grofcsik's investigations

(1957) show that most of the authors failed to consider the following possibilities:

(i) *Rehydration.* Heated kaolin, as proved by many authors, easily becomes rehydrated (cf. Chapter 8, par. D). As a consequence of rehydration (reconstitution), minute particles of heated kaolin, rehydrating during the examination even by air moisture, may cause weak kaolinite reflections in X-ray patterns. The possibility of reconstitution is the least when investigating by electron diffraction or electron microscope because high vacuum and high temperature during electron bombardment will cause all water to leave (except structural water).

Grofcsik and Tamás (1959) tried to clear up the quantity of water bound by rehydration. After heating between 600 and 700 °C, followed by shaking in room-temperature water and drying at 105 °C, a sample of Zettlitz kaolin, when heated to 600 °C again, shows a loss of weight of a few tenths of one per cent. In order to prevent rehydration the fired kaolin should be put into absolute alcohol or benzene when still hot.

(ii) *The effect of particle size.* Particle size, as is well known, influences X-ray results to a certain extent; very small particles give diffuse bands instead of distinct lines, while X-ray patterns of materials of coarse particle size show individual dots. It may be supposed that the change of the original particle size of the investigated material is responsible for most of the contradictions. It has been proved by Grofcsik (1957) and Grofcsik and Tamás (1959) that among the particle size fractions obtained by sedimentation in alcohol, the coarsest fraction (i. e. the fraction sedimenting in the shortest time) gives *ceteris paribus* distinct, sharp kaolinite reflexions in the X-ray pattern; a middle fraction was less distinct while the finest fraction did not show any pattern due to crystalline materials. As the surface layers of a crystal are always more disordered than the inner ones, this may cause also a change in heating products.

Particle size, obviously, influences also the temperature of thermal changes. Hence, an approximately homodisperse fraction of carefully sedimented material with a fixed upper and lower particle size limit is required for all such investigations.

(iii) *Foreign materials,* being either natural or artificial admixtures, affect results to a great extent. Johns (1953) e. g. proposes different reaction sequences in case of mica-free and mica-bearing kaolinite sorts, Slaughter and Keller (1959) in case of illite-free and illite-containing ones.

Mullite formation is generally enhanced by contaminations (Visconti and Nicot 1957).

Reaction Products

The final products of the thermal reactions of kaolinite are, no doubt, mullite and cristobalite. Any other products above 575 °C, i. e. above the temperature which gives the final phases in the system Al_2O_3—SiO_2—H_2O are obviously metastable phases. The structure of kaolinite greatly differs from that of mullite; a considerable rearrangement of the ions and a change of bond character take place during transformation. Consequently, transition phases are of great significance.

The heating of kaolinite to a temperature above the endothermic process does not disturb all the characteristics of the original kaolinite structure (as seen by the presence of some *hk0* X-ray reflections, Brindley and Hunter 1955). It may be supposed that the structure of the dehydroxylated phase is, at least in two directions of space, similar to that of kaolin. The structure of meta-kaolinite must be close to an arrangement described by Tscheischvili, Büssem and Weyl (1939), but with a changed sequence of layers, since the sequence, suggested originally by the above authors, would give a mineral of too high stability; neither would measured and calculated values of density correspond.

The existence of *meta-kaolin* may be considered to have been proved. The fact that the alumina and silica content can be easily extracted from heated kaolin, does not contradict this supposition; it only means that this metastable phase is not stable from a chemical point of view either.

Crystals of meta-kaolinite can be examined also visually with an electron microscope. Such an examination shows the hexagonal outline of crystals or crystal fragments; 120° edges can be seen at least at some corners of the crystal outline. Crystals of meta-kaolinite, however, are by no means made of individual crystals of the type seen in the electron microscope. The hexagonal symmetry of electron microscope photographs covers some possible discontinuities not seen in the electron microscope but acting in X-ray investigations as crystal boundaries; the crystal size, effective in X-ray investigations, is thus greatly reduced.

In the third direction of space (the direction of the crystallographic c axis), the changes are much more intensive than in the two other directions. The superposition of these effects causes a lack of distinct X-ray diagrams.

This state called "meta-kaolinite" decomposes at a higher temperature. Some authors consider the formation of γ-alumina an inevitable consequence, others an occasional or incidental phenomenon of heating.

A careful and critical evaluation of the relevant data shows that the formation of γ-alumina cannot be regarded as a merely occasional phase, nor can it be accepted as a phase present only in some special cases. γ-alumina is not completely free of silica; probably the quantity it contains contributes to the forming of a spinel-structure phase, similar to the one described by Brindley and Nakahira. γ-alumina is formed from the hydrargillite layer of kaolinite. It is very probable that hydrargillite and tridymite layers of kaolinite separate during heating and these, resp. their fragments, being electrostatically compensated, maintain as individual phases for some time. γ-alumina, though unstable itself, is a survival of one of these individual phases. In any case the final phase is mullite.

The presence or absence of these transient phases cannot be detected in every case; their quantitative determination is even less possible. Interconnected and stubborn *non-equilibria* may be present, complicating the processes and causing a number of intermediate compounds before the final phase. γ-alumina is one of the most important of these phases.

Considering the foregoing, the existence of γ-alumina as an intermediate phase may be accepted as proved. This does not mean, however, that the first exothermic peak of kaolinite is caused by the formation of γ-alumina ! Halloysite e. g. shows, after a heating of 700 °C, distinct X-ray lines undoubtedly due to γ-alumina; the exothermic reaction has a temperature of 950 °C in spite of the former presence of γ-alumina. The 950 °C exothermic effect ("first" exothermic peak) means, on the strength of the above theoretic considerations and in the author's own experiments, the *formation of mullite*.

Some authors mention the presence of mullite at a temperature below the first exothermic peak; this phase, however, can be accepted only as a mass of nuclei with some structural elements of the mullite lattice. There are other authors who, when applying X-ray methods, have not found any mullite in kaolinite samples heated just above the temperature of the first exothermic peak. This is possibly due to the remaining structural elements of the kaolinite lattice which enhance the formation of elongated mullite crystals; a crystal habit, not favourable for X-ray diffraction. It may also happen that, as a further prove of non-equilibrium, γ-alumina is present besides mullite. But the final equilibrium is not reached even above 950 °C. (Mullite, one of the components of the stable phase assembly is present but the other stable phase, cristobalite (of tridymite, if Fenner's diagram is considered correct is absent.)

All that has been said above is insufficient to explain which product is formed during the exothermic peak, and no adequate explanation can be given as long as the question is inaccurately put without considering that the exothermic reaction is, correctly spoken, due to the *decomposition* of a phase at the given temperature and not to the production of a new phase. The substance, being decomposed at the temperature of the exothermic peak, is of the same type both in case of kaolinite, halloysite, and also in fireclay type clay mineral (of a structure between the two minerals mentioned). As soon as the energy of thermal motion becomes high enough to surpass the energy barrier needed to destroy the continuous two-dimensional Si—O network, the two-dimension structure decomposes and transforms into a more stable structure while the difference in energy between the old and the new (stable) structure is released in the form of heat. Although the compounds produced during this process may not be identical in all cases, the phase which decomposes is always the same: a layer structure that may be called a meta-phase.

D) THE RECONSTITUTION OF HEATED KAOLIN MINERALS

Schachtschnabel (1930) has observed that saturated water vapour often causes heated (and dehydroxylated) kaolin to *rehydrate*. Kaolin heated to 700 °C has an extremely high reaction capacity; in general, however, the lower the temperature of calcination, the higher the reaction capacity. In the course of rehydration the fired product reverts into a kaolin-type mineral. Rehydrated mineral, however, has its endothermic reaction at a lower temperature than the original mineral. This is probably due to the fact that not the original structure is reconstituted, but structures of disordered lattice are produced. The line series of the X-ray pattern though similar to that of the original untreated sample, gives widened and more diffuse lines, showing the formation of lattice defects. The rehydrated material differs from the original also, by its low acid resistance; expecially alumina can be easily extracted.

Salmang, Körner and Pukall (1935) investigated the rehydration of kaolin by the method of *isothermic* decomposition. According to their observations, kaolinite becomes almost completely rehydrated by a treatment at 450 °C; pressure: 15 torr.; time: 7 to 18 months. Under such conditions a hydrate of 1.5 mol. water content is formed as contrasted to the original water content of 2 mol. At a lower pressure a hydrate of 1 mol., at a higher (e. g. 490 °C) temperature, a hydrate of 0.5 mol. water content is obtained. These data of exactly 0.5; 1.0 etc. mol. water content are hard to accept although the existence of kaolin hemihydrate has been confirmed by Rieke and Mauve (1942). It may be supposed that the investigated kaolin was not a pure phase and had a slight mica content. Mica, as known by the investigations of Schwarz (1926), is easily transformed into kaolin in a hydrothermal way.

Rehydration may be used also for the qualitative detection of clay minerals. According to Berkelhammer (1943), montmorillonite, kaolinite and illite heated to 300 °C are rehydrated in entirely different ways. Rehydration can be achieved best at 30 °C in an atmosphere of saturated water vapour. The process takes 29—80 days. Differences in rehydration characteristics are observed best after a rehydration time of 80 days; this period is also suitable for the identification of the original mineral. Rehydrated kaolin is not quite the same as the original one, as also confirmed by Berkelhammer.

According to Saalfeld's (1954) opinion, meta-kaolin preserves some structural elements from which the lattice of kaolin can be rehydrated under hydrothermal conditions. This reconstitution (rehydration), however, is not perfect; there is a disorder in the direction of the *c* axis. Reconstituted kaolin is, from this point of view, no kaolin. It is rather a fireclay-type mineral. The higher the original heating temperature, the higher the degree of disorder. Saalfeld (1954) says that the best conditions of rehydration are: temperature 300 °C, pressure 85—100 atm. Rehydration properties are influenced by many a factor, the effect of contaminations being most important. The easiest method of decontaminating is that of ion exchange.

Bertetti (1956) produced hydrogen clay minerals by acids after the destruction of organic materials with a hydrogen peroxide treatment. These hydrogen clays were then heated to 600—700 °C for four hours and rehydrated after heating in an autoclave at 250 °C (and a corresponding pressure of 40 atm.). Rehydration time was 32 hours. After rehydration the substance was dried and the water content of the dry material determined. This determination has shown that the total water content of the substance had been restored; the DTA curves of the untreated and treated materials were, however, not the same and the base exchange capacity had increased by the treatment. This phenomenon can be explained by the disintegration of crystals during the rehydration process. A future technical evaluation of this phenomenon was suggested by Hill (1956) who observed an increase in the compressive strength of kaolin with material first heated to 600 °C and rehydrated at 200 °C for 24 hours. This is probably due to an increase in the active surface of meta-kaolin particles.

Roy and Brindley (1956) state that not only kaolinite but all kaolin minerals decompose by heat treatment, the process being accompanied by the formation of metaphases. All metaphases yield kaolinite if reconstituted; the velocity of the reconstitution process, however, greatly depends on the quality of the original mineral. As directly confirmed by the microscopic investigations of Dietzel and Dhekne (1957), the size of kaolinite particles decreases during rehydration. Under the electron microscope, rehydrated kaolin shows particles similar to the shape of the original particles, but with quantity of fines increased. The specific surface of the material, naturally, also increases, in spite of the particle size having remained unchanged, as determined by sedimentation. This phenomenon is due to the adhesion of the fine particles. Rehydration does not affect plasticity.

Besides rehydration under hydrothermal curing conditions, fired clay minerals (especially fired kaolin) are at least partly able to rehydrate also at room temperature and at atmospheric pressure. This type of rehydration, though never complete, may disturb the X-ray patterns. Rehydration disturbs infrared spectra to an even greater extent. Stubičan and Günthard (1957) described fired halloysite as very hygroscopic and said that also the fired minerals of the kaolin group could adsorb water. Because of this, infrared spectra containing no bands due to OH groups can be obtained only by the careful exclusion of air moisture.

CHAPTER 9

THE FORMATION OF MULLITE FROM ARTIFICIAL RAW MATERIALS

Since the earliest times research workers have tried to copy the characteristic thermal effects of kaolin by model substances: by artificial mixtures of Al_2O_3—SiO_2 powders of an arbitrary composition. These types of research have used a great variety of methods and are still going on; they have resulted in producing mullite from artificial raw materials and in detecting a number of characteristic kaolin thermal effects.

It must be kept in mind that mixtures, produced even by the most scrupulous methods with a special view to perfect homogeneity, are not identical with kaolin or its fired products. Kaolinite has a layer lattice structure; a layer containing aluminium is followed by another, containing silicon. The same layers are present in meta-kaolinite and transform only above the temperature of the first exothermic peak. Artificial mixes or gels have *no* similar layer structure. Consequently, even if the same reactions are supposed to take place during the heating of kaolinite resp. the mixture or the gel, the heat of reaction will, no doubt, be higher in case of an artificial mix than with kaolinite. This is quite obvious if we consider that the layers of kaolinite follow in a distribution of molecular fineness whereas in case of gels or mixes, all that can be stated is that the particles are situated next to each other without any trace of the arrangement in space mentioned above. In short: while meta-kaolinite contains alumina and silica in *layers* of alternating molecular fineness, gels or mixes contain more or less coarse *linear series of particles* in the three directions of space. The single elements of the *linear series of particles* are obviously microscopic or sub-microscopic aggregates of silica resp. alumina.

Investigations in Artificial Mixes

Tammann and Pape (1923) tried to imitate the characteristic endothermic reaction of kaolin on artificial mixes. The trial was successful: intimate mechanical mixes of SiO_2 and Al_2O_3 gave an exothermic reaction at 940 °C with similar characteristics to that of kaolin. The two authors did not identify the nature of the mineral produced; it was Insley and Ewell (1935) who stated that mixtures and gels give mullite at such low temperature already.

Also Thompson and Parmelee (1937) investigated artificial mixes, but they produced glasses from the raw mix and examined their dilatation. They have found that dilatation curves have a slope tangent similar to that of mullite at 1000 °C already or slightly above. Characteristic mullite-like curves were obtained by a long-lasting heat treatment. Gworek and Towers (1945) identified mullite as the sole crystalline phase of silica-alumina mixes at temperature above 1200 °C; this conclusion was confirmed also by dilatometric investigations. The dilatometric curves of kaolinite, clay, γ-alumina and amorphous silica, examined simultaneously, were not comparable, so the authors could not reach their aim: the explanation of the dilatation properties of clay.

A number of experiments have been made in order to determine the most favourable Al_2O_3/SiO_2 ratio of the synthesis. In the experiments with the sintering and fusing methods of sample preparations, artificial mixes and co-precipitated gels were used as raw materials. The results obtained are contradictory: Al_2O_3/SiO_2 ratios of 1 : 1, 2 : 1 and 3 : 2 were described as the most advantageous by Horte and Wiegmann (1950), by West and Gray (1958) and by Demediuk and Cole (1958) and Goncharov (1955), respectively. The differences can be explained (according to Neuhaus 1957) by the fact that sintering and fusion do not give the same product even if they start from the same material. A starting material of composition $3Al_2O_3 + 2SiO_2$ yields e. g. mullite if sintered, and a compound of composition $2Al_2O_3 \cdot SiO_2$ if fused. The melting point of the latter is 100 °C higher than that of mullite. It differs from mullite also in its *a* and *b* cell dimensions. A mix of equimolar composition gives the same product; the excess of silica is present unbound (no solid solutions are formed). The observation that mullite and 2 : 1 alumino-silicate cannot be stable simultaneously has confirmed the necessity to supervise Bowen and Greig's phase diagram.

It is difficult to produce single crystals of mullite by fusion because under ordinary circumstances (the volatilization of SiO_2 not being prevented) mullite melts *incongruently*. Consequently, for a long time the preparation of single crystals of fusion-synthesized mullite could not be realized. At last Bauer, Gordon and Moore (1950) succeeded in producing single crystals of mullite in a *Verneuil* kiln by using oxyhydrogen flame. Bauer and Gordon (1951) adjusted the flame to a very steep temperature gradient; in this way the length of the corundum—melt equilibrium is low in the flame and mullite is formed as a primary crystal and not by resorption. Correctly adjusted flames leave no corundum crystals in the product.

A number of minerals and mineral mixtures were synthesized by Barta and Barta (1956) who used finely dispersed and thoroughly mixed powders as starting materials. Verneuil's usual method was applied (without crucibles). The authors regarded the single crystal of composition $5Al_2O_3 \cdot 4SiO_2$ thus produced as an individual mineral and named it *praguite*. Praguite is one of the members of the solid solution series with sillimanite. Mullite is situated exactly in the middle of the interval, although mullite lattice minerals are formed in both directions. Neuhaus and Richartz (1958), on the contrary, contend that solid solutions are formed only between sillimanite and mullite and regard also these phases as quenched pseudo-solid solutions and not as real phases of molecular distribution.

Gelsdorf and Schwiete (1956) investigated the extent to which foreign substances can be intercalated into the lattice of synthetic mullite, without changing the lattice or forming a separate phase. In case of reagent-grade and thoroughly mixed starting materials the lattice of mullite can receive 6, 3 and 1.5 per cent of alumina, iron oxide and titania, respectively, without any considerable change except some small distortions. By the intercalation of the two latter oxides the lattice extends. CaO, MgO, Ga_2O_3 and GeO_2 cannot be intercalated, as proved by a later investigation of Gelsdorf and co-workers. This holds true also for FeO (Brownell 1958).

The mullite formation of artificial Al_2O_3—SiO_2 mixes was studied by Beznosikova and Poluboyarinov (1955), who used alumina, quartz, clay, kaolin, silica gel (precipitated from sodium silicate) and similar substances for starting materials. The experiments have shown that the temperature of mullite formation is only slightly modified by the sort and dispersity of the starting material, but it is greatly affected by contaminating admixtures, primarily by fluxes.

Shuliko and Poluboyarinov (1958) synthesized mullite from finely dispersed mixes, using a great variety of starting materials as e. g. alumina, corundum, kaolinite, amorphous silica, quartz, clay, etc.

As already discussed, almost every author dealing with the problem has stressed the necessity of the thorough intimate mixing of starting materials. Grofcsik (1957) e. g. says that the mix of fired alumina hydrate and finely ground quartz does not yield a starting material of high reaction capacity even if revolved for 480 hours in a ball mill or worked for the same time in a vibratory mill. All batches prepared in this way yield mullite only above 1000° C, irrespective of the grinding being made dry or wetted with water or some organic dissolving media.

It has been known for long that it is gels and not artificial mixes that give a suitable, finely dispersed material of high reactivity, when used as starting substances.

Investigations in Gels

Insley and Ewell (1935) examined the thermal reactions of kaolin clay minerals in detail, and compared them to the thermal characteristics of co-precipitated gels. The gels were prepared by co-precipitation from sodium silicate and aluminium chloride, followed by an electro-dialyzation process in order to expel sodium ions. These co-precipitated mixed gels showed an exothermic process at 950 °C of a similar character to that of kaolinite, but whereas for kaolin the authors found the exothermic peak to be caused by the production of γ-alumina, they ascribed the exothermic process of synthetic mixes to mullite formation. This has led the authors to the general conclusion that the nature of thermal products depends on the nature of the starting material. It is, however, very probable that gels produced by Insley and Ewell were not of chemically pure quality and contained a slight quantity of alkali. Grofcsik (1957) has proved that if a gel is produced from sodium silicate, the sodium ions, adsorbed at the surface of the gels, are bound by very strong forces and are not dializible even by a high voltage.

McAtee and Milligan (1950) prepared artificial mullite from a mixture of SiO_2 and Al_2O_3 gels. As shown by their investigation, the chemical formula of mullite is $3Al_2O_3 \cdot 2SiO_2$; at least this is the ratio where gels give the highest quantity of mullite. The starting materials were amorphous even at 1100 °C; at a higher temperature they reacted and mullite was formed, as a main constituent. In samples of high silica and high alumina content, cristobalite and corundum crystals were also detected as accessory phases. The authors did not obtain solid solutions; this result, however, is at variance with the results of several authors, e. g. Posnjak and Greig (1933), Budnikov and co-workers (1953), Rooksby and Partridge (1939) Toropov and Galakhov (1958), etc.

Letort (1952) has revealed by X-ray and infrared spectrography methods that mullite is formed from Al_2O_3—SiO_2 mixed gels. The static heat treatment he used resulted, after a firing of 7000 hours, in mullite formation at a temperature as low as 750 °C. Clays and kaolins show no mullite formation even after a firing period of several years. It is obvious that the static heat treatment applied by Letort is not comparable to dynamic heat treatment used in differential thermal studies. The different behaviour of gels and clays (or kaolins) show that results obtained with gels can be used for the explanation of thermal processes of kaolin only with precaution.

In all experiments described above gels precipitated from alkali silicates were used. Such gels, however, cannot be purified even by most careful after-treatments; Grofcsik and Vágó (1952) proposed a better method to achieve the co-precipitation of the gel from ethyl orthosilicate and aluminium sulphate solution (of calculated concentration) by ammonium hydroxide. This gel is free of alkalies and, after a moderate firing, gives a very pure starting material of high reactivity. The DTA examination of this material has shown a very distinct exothermic reaction at 950 °C. A typical solid-state reaction forms a crystalline phase at this temperature. Heated to the temperature of the exothermic effect and analyzed by X-ray, the gels of the ratio $3Al_2O_3/2SiO_2$ have shown the presence of mullite only. Methods comprising the use of organic silica compounds were patented by Bearer (1953) and by Jones (1954).

The staff of the College of Mineral Industries at the Pennsylvania State University, directed by Osborn and Roy, have developed the ethyl orthosilicate method in detail and made it generally applicable. The silicon-bearing material used in this method (Roy 1956) is ethyl orthosilicate or some other organic silicon compound; the other substances are added in the form of nitrates solved in water. In the presence of a few drops of hydrochloric acid as catalyst, silicon dioxide is precipitated from ethyl orthosilicate (especially if warmed). Nitrates are adsorbed on the surface of this gel. By evaporating the excess water and the ethyl alcohol formed during hydrolysis, a jelly-like gel is formed, which can be fired at a relatively low temperature (450° C) into oxides. This crumbly substance is an ideal starting material of high reactivity and, as confirmed by X-rays, is completely amorphous, i. e. without any crystalline phases acting as nuclei and disturbing reaction sequences present. Under hydrothermal conditions kaolinite, but no halloysite, is easily synthesized from gels prepared by the method described. Roy and Osborn (1954) found an interesting new phase, hydralsite. Hydralsite, of the formula $2Al_2O_3 \cdot 2SiO_2 \cdot H_2O$ can be obtained from mixed gels (synthetically) and by dehydration of kaolin clay minerals. Most probably, hydralsite occurring in nature has been confounded with pyrophyllite, a mineral of similar structure. Above 575 °C under hydrothermal conditions (700 atm. pressure) only mullite is stable.

Keler and Leonov (1955) investigated thermal processes by using artificial allophanoids as starting materials, and found these processes to be of the same character both with natural and with artificial minerals. Mineralizers act in the same way.

Nikitin (1955) examined the thermal reactions of natural kaolinite and of artificial $Al(OH)_3$ and $Si(OH)_4$ gels by water sorption. After heating the sorption characteristics of natural kaolin differed from those of artificial gels. From this difference Nikitin has drawn the conclusion that meta-kaolinite is not a simple mixture of oxides but an individual mineral.

Horte and Wiegmann (1956), Wiegmann and Horte (1956*a*, *b*) prepared a mixed SiO_2—Al_2O_3 gel of very high reactivity from silicon tetrafluoride and aluminium trichloride by co-precipitation with diluted ammonium hydroxide solution. Between 900 and 1000 °C these gels have a strong exothermic effect as shown by DTA investigations. An X-ray examination of the product showed silicate formation in the heated substance; owing to the similarity of the two phases, the authors could not determine whether it was sillimanite or mullite. In order to determine the nature of the product they made gels of different Al_2O_3—SiO_2 ratios and measured the area under the exothermic peak planimetrically, with the presupposition that the heat of reaction is the highest if the total substance is converted to a compound and lower if either silica or alumina is in excess. According to their results, the equimolar mixture of the two gels gave the highest heat of reaction, while that of mullite ratio showed a heat of reaction lower by 1/3.

Demediuk and Cole (1958) repeating Wiegmann's and Horte's investigations described above have examined the thermal characteristics of co-precipitated gels. The planimetering of areas under the peak, however, has shown a maximum heat of reaction at 0.67 $SiO_2 : Al_2O_3$ ratio, i. e. at the composition of mullite.

The investigation of the phase composition of the product has revealed some silicate and amorphous silica and some silicate and γ-alumina with SiO_2/Al_2O_3 ratios of above and below 0.67, respectively. The nature of the silicate has been investigated also directly by X-rays, using a precision method (Guinier type focussed camera of 114.6 mm diameter).

West and Gray (1958) have described a maximum heat of reaction at a mixture of the ratio 0.5 of SiO_2/Al_2O_3. The data originally published by Segawa (1949) have thus been confirmed.

The difference of investigation results is probably due to the non-identity of the starting materials used by various authors; it is difficult to precipitate the gels in a completely amorphous state and especially alumina is frequently present partly in the form of boehmite.

Bidet and Jouenne (1958) made a suspension in water from amorphous alumina and silica gels and found the two substances to react as low as at room temperature and to form a product similar to that of metakaolinite. At about 960 °C the mixed gels yield mullite by an exothermic reaction. At about 1215 °C a second exothermic reaction takes place, caused by the formation of secondary mullite from silica and γ-alumina. Insufficient mixing or alkali ions prevent the reactions. Also Bidet and Jouenne confirm that the thermal processes of kaolinite and those of gels are not of the same character.

CHAPTER 10

PHYSICAL CHEMISTRY OF ALUMINO-SILICATE FORMATION

A) THERMODYNAMICS

It is well known from the phase diagrams of the system Al_2O_3—SiO_2 and from Greig's (1926) investigations that the most stable anhydrous alumino-silicate of the system is mullite; the three other phases are unstable (provided the pressure does not surpass a few hundred atmospheres).

"Stability", however, is of little meaning without a thermodynamic support since the quantitative indices of stability can only be obtained in a thermodynamic way. The best quantitative characteristic of stability is the *free energy* (F; also called thermodynamic potential) which represents the maximum energy to be converted into *work* under given circumstances. Consequently, the dimensional formula of F is identical with that of work: calories per mols. According to the international convention, thermodynamic processes are viewed from the angle of the *system* (and not of the surroundings; the exothermic process, being a loss of energy, has a negative sign). With the increment of the negative value of ΔF the probability of a reaction increases. Since F can not be measured directly, its changes under isothermic conditions are computed with equation:

$$\Delta F = \Delta H - T \Delta S \qquad (T = \text{const})$$

where

H — enthalpy (heat content) [$\text{kcal} \cdot \text{mol}^{-1}$]

T — absolute temperature [°K] and

S — entropy [$\text{kcal} \cdot \text{mol}^{-1} \cdot {}^{\circ}\text{K}^{-1}$]

The values of H are obtained from heat-of-solution measurements. ΔS is — in case of solid crystalline substances — negligibly low, so the upper equation is well approached by the formula

$$\Delta F \approx \Delta H$$

In case of silicates and alumino-silicates only hydrogen fluoride can be used as a solvent. Hydrogen fluoride, however, dissolves alumino-silicates, especially mullite very slowly (cf. the mullite determination technique of extracting non-mullite matter by H_2F_2). Athigher temperatures the dissolving velocity increases and the measurement can be performed in a suitable heat-of-solution calorimeter, which operates at higher temperature, e. g. 70—75 °C, but even here the process will be too slow to ensure really adiabatic conditions (isothermal calorimeters are not used with silicates). Heat-of-solution methods being insufficient in such cases, the thermochemical and thermodynamical data, given by heat-of-solution measurements, are uncertain and must be used with caution. A good example for the necessity of caution is the history of research into the free energy resp. the heat of formation of alumino-silicates.

The heat of solution of alumino-silicates was first determined by Neumann (1926). Three years later these measurements, repeated by Klever and Kordes (1929), included also the determination of the heat of solution figures of silica and of alumina hydrates with the aim to determine the heat of formation of alumino-silicates. The heat of solution of SiO_2 and of Al_2O_3 was determined by dissolving quartz and alumina hydrates in hydrogen fluoride; in the latter case the heat of solution vs. water content curve was extrapolated to zero water content. Even the rightness of extrapolation as a method may be questioned; in addition to this, the experimental method gives the heat of formation of less stable γ-alumina than stable γ-alumina (corundum); the two sources of errors may cause an inaccuracy of the thermochemical data approaching one order of magnitude.

The free-energy-of-formation data of the three Al_2SiO_5 alumino-silicates are, according to investigations by Klever and Kordes (1929), at room temperature (298° K) [kcal · mol^{-1}]

$$\Delta F_{\text{sillimanite}} = -45.95$$
$$\Delta F_{\text{andalusite}} = -39.35$$
$$\Delta F_{\text{kyanite}} = -35.75$$

These data hold true when the minerals are formed from constituent oxides and are given with an accuracy of ± 3 kcal · mol^{-1}.

Although, as compared to those of other substances, e. g. of calcium silicates, these free-energy-of-formation data seem to be too high, they are quoted in a number of papers as e. g. in those of Richardson, Jeffes and Withers (1950); Tripp and King (1955); Wygant and Kingery (1952), etc.

Their excessively high value can readily be proved (Flood and Knapp 1957) by finding reactions which (i) have aluminium silicates and some other oxides as reactants, (ii) yield products of exactly known free energy and (iii) take place easily. The calculation of Flood and Knapp neglect a number of points, e. g. the change of bond types during the reaction. Hence their values, being approximately one thirds of those given by Klever and Kordes, may be considered only semiquantitative data yet can be supported by the thermodynamic data of other silicates and be fitted into the proper sections of free-energy-of-formation vs. ionic-potential curves.

There is another way to obtain stability relations from thermochemical resp. thermodynamical investigations: by regarding as the most stable the compound which in a system shows the highest heat of reaction if formed from its constituents. For instructive discussions concerning this problem see p. 98 (Segawa 1949, Wiegmann and Horte 1956, Demediuk and Cole 1959, etc.).

The dehydration (dehydroxylation) of *kaolinite* has been investigated from the point of view of thermodynamics and thermochemistry by several authors. Cohn (1924) was the first to determine the thermal effects of kaolin quantitatively. According to his measurements, the endothermic reaction of kaolinite is accompanied by a heat consumption of 100 kcal/g and the first exothermic reaction gives a heat evolution of 15 kcal/g. These data were substantiated by McGee's measurements (1926) yielding of 95 kcal/g for the endothermic reaction-heat consumption and of 16.5 kcal/g for the first exothermic reaction-heat evolution.

The product formed by the endothermic process has been investigated very thoroughly (cf. Chap. 8).

The nature of meta-kaolinite, however, can be — at least theoretically — best cleared up by a thermochemical test, i. e. by measuring the heat of solution of meta-kaolinite and that of a γ-alumina-silica mix; if these two data differ, a compound is formed. Klever and Kordes (1929) used this method when examining the decomposition of kaolinite. They measured the heat of solution of a mix which contained one mol of γ-Al_2O_3 and two mols of SiO_2 (quartz) and of meta-kaolinite 161 and 179 kcal/mol, respectively. The 18 kcal/mol difference is the heat of formation of the compound meta-kaolinite formed by the endothermic process of kaolinite. This heat effect, however, being very near to the error limit of experiments, gives no firm reason for the existence of meta-kaolinite. The heat of reaction of the first exothermic effect was found to be 335 kcal/mol, i. e. 1.5 kcal/g by Mchedlov-Petrosyan (1950). This is only about one tenth of the value measured by McGee (1926). The high activation energy of the reaction $3\,\gamma\text{-}Al_2O_3 + 2SiO_2 = 3Al_2O_3 \cdot 2SiO_2$ (a supposed value of about 200 kcal/mol) is only partly responsible for the difference. It is very probable that the bulk of error is due to imperfect measuring technique. Thermochemical data, if gained from the peak areas of differential thermal analysis curves, are, according to Shorter (1948), always inexact because of the influence of the heat conductivity (resp. the varying packing density) of the substance in the vicinity of the welded point of the thermocouple.

Avgustinik and Mchedlov-Petrosyan (1952) calculated the enthalpy changes of a number of important reactions, using Mchedlov-Petrosyan's heat-of-reaction data discussed above. The entropy changes during the reaction being low, the free-energy changes are numerically equal to the enthalpy changes, as confirmed by Greig (1926). They have found that the formation of mullite is more probable than that of sillimanite, irrespective of the starting materials. The error of these considerations, however, is of double nature: the substance is viewed only from a "chemical point", i. e. energy differences between the different mineralogic bond types are omitted, on the one hand, and no allowance is made for the formation of non-stoichiometric compounds, i. e. solid solutions, which may and are formed in the system, on the other. Mchedlov-Petrosyan and Babushkin (Mtschedlow-Petrossian and Babuschkin 1958) who considered also this possibility came to the same result.

As can be seen from the above, the thermodynamic investigation of the mullite problem has so far not yielded definite results, much remains to be done in order to give a suitable thermodynamic corroboration to these rather complicated processes.

B) CHEMICAL KINETICS

The chemical kinetics of mullite formation is an almost unknown territory, although its significance would deserve much more detailed investigations. Some reactions of mullite formation are very rapid, almost instantaneous, some are slow, almost imperceptible. The theory of *phase equilibria* gives very little information on reaction velocity; this enhances the importance of studying the chemical *kinetics* of mullite-forming reactions. Under equilibrium conditions, mullite is the stable final product, but the reaction may be imperfect doing to the non-equilibrium conditions of firing. The firing of mullite-containing ceramic materials is characterized exactly by such non-equilibrium reactions. Generally, the reaction velocity is determined by the following factors: *temperature*, *concentration* of starting and final products, and difference between the *free energy* of starting and final products; if, however, one or more of the reactant phases are *solid*, all these effects become of second order, the effect of temperature included, and the most decisive parameter will be the *area of contact surface*.

According to Arrhenius's classical theory, the velocity of reactions is determined by the collision frequency, if the reactants are of gaseous or of liquid state. The collision frequency is proportional to concentration; this, however, is not the only factor. The presence of "*active*" molecules, i. e. of those having an energy higher than the average, cannot be excluded from the actual processes. These active molecules may start reactions.

In case of gaseous reactions, the number of molecules taking part in the reaction is very important. From this point of view first-, second- and higher-order reactions may be distinguished. In case of a *first-order (unimolecular)* reaction the concentration of reactants decreases exponentially with time; in case of a *second-order (bimolecular)* reaction, on the contrary, the concentration of reactants is inversely proportional to time. The concentration of reactants, however, will not follow such simple rules in case of reactions of *higher-order*, since several reactions, usually running simultaneously, have an influence on one another to such an extent that the concentration vs. time function will be very complicated. (An exception: if one of the concurring processes is very slow as compared to the others the velocity of this slow reaction will determine the total complex reaction velocity.) The most important factor of gaseous reactions is collision frequency; the molecular energy term is predominantly that of *translation*. (The "order of reaction" can be characterized by the number of molecules participating in the reaction, strictly speaking, only in case of gaseous reactions but, formally — to judge from the run of the concentration vs. time curve — these terms may be extended to solid reactions.)

When reactions involving solid phases are considered, *vibration*, i. e. the thermal movement of the ions, etc. will be of utmost importance, for the reaction will only take place if this vibration exceeds a certain measure; and the ions cannot move quite free even if the bonds are broken by vibration. In this case the energy term is *diffusion*. These reactions are obviously much slower than gaseous or liquid reactions.

Among reactions between solid substances the two most important types are those of internal rearrangement and of external interaction. In both cases the reactions are affected by the same forces: ions (or atoms) must leave their original positions to migrate into new ones. The process may take an easy or a difficult course, depending on the packing density of the starting phase and on the relative difference between the positions of the original phase and the new one.

Internal rearrangements. Starting and final composition being the same with these reactions they can include only polymorphic transformations. Should the degree of rearrangement be low, without any break of bonds and with a rearrangement only in space, the energy required is insignificant. Such rearrangements taking place at a definite temperature in a very short time are *enantiotropic transformations (inversions).* The transformation of quartz at 575° C is an instructive example: the enthalpy change during this process is very low, approximately 0.003—0.006 kcal/mol.

In case of extensive rearrangement, the structures of the starting and the final products differ to a high extent and the reaction involves a considerable change of energy *(conversions).* There is a minimum temperature limit necessary for transformation which, in this case, is a slow process even well above the limit. An example of conversion reaction: the transformation of quartz into tridymite or cristobalite involves an energy change of about 6 kcal/mol which is one thousand times that of inversions.

A high absolute value measure of ionic migration is not a precondition, not even for conversion type reactions. Meta-kaolinite may therefore transform into mullite in the given structures as described by Brindley and Nakahira (1959*b*): during transformation, ions are running in "channels"; at about 1000° C SiO_4 groups migrate around the octahedral AlO_6 layer or slowly diffuse from the lattice. The process of diffusion is very slow, not completed even within geological eras (Jagitsch 1949).

Reactions of *external interactions* are similar to conversions accompanied by high-degree rearrangement. In these reactions the ionic migration passes through *lattice defects,* along the contact area. The most important rate-determining factor, besides the extension of the contact area, is the number of lattice defects since no such reaction can proceed without defects being present. Lattice defects are always present above the temperature of absolute zero *(Schottky's law)* and they grow in number at higher temperatures. Ion migration being aggravated in dense areas, the area and the nature of the contact are also significant factors. Migration will tend, first of all, towards places where lattice defects are present in larger numbers. Free energy is the driving *force* also of these reactions and diffusion is their driving *mechanism.*

In consequence of insufficient "screening" the outermost layer of solid substances is always distorted (as compared to the inside of the crystal, though lattice defects are present also in the latter). As such places make ion migration always possible the contact area is the starting point for the forming of diffusion layers. Rising temperature accelerates the progression of *diffusion layers* by increasing (*i*) the mobility of ions and (*ii*) the number of lattice defects (Schottky's law). Diffusion layers, however, are usually not wide, especially not at relatively low temperatures. According to calculations made by Jagitsch (1949), the diffusion velocity of sodium oxide in meta-kaolinite is very slow; the diffusion layer of the product (carnegieite) is only 1.8 cm at 500° C and not much thicker at 700° C after 108 years. At temperatures of polymorphic transformations (Hedvall effect) diffusion velocity and thereby also reaction velocity considerably increase. According to their function, there are three types of diffusion layers: *a)* as a *barrier* it may slow down the rate of reaction; *b)* as an *intermediate phase* it may propagate the reaction at a steady linear rate and *c)* as a *catalyst* it may accelerate the reaction.

Connexions between the width of the diffusion layer (y) and the rate of reaction $\left(\frac{dy}{dt}\right)$ are

in case *a)*

$$\frac{dy}{dt} = \frac{k}{y}$$

in case *b)*

$$\frac{dy}{dt} = k$$

and in case *c)*

$$\frac{dy}{dt} = k \cdot y$$

k being a constant.

By integrating these differential equations, the width of diffusion layers are

in case *a)* $y = \sqrt{2\,k \cdot t}$

in case *b)* $y = k \cdot t$

in case *c)* $y = e^{kt}$

Ceramic reactions usually involve *a*-type reactions, i. e. the reaction velocity is decreased in inverse proportion to the width of the diffusion layer, but in some cases reactions of type *b* may also occur (e. g. polymorphic transformations). Reactions of type *c* (autocatalytic reactions), though rare in ceramics, frequently occur in oxydation processes.

The rate-determining constant k changes with temperature. This change is usually characterized by equation

$$\ln k = -\frac{E}{RT}$$

hence

$$k = e^{-\frac{E}{RT}}$$

where E — constant, called *activation energy* of the reaction,
T — temperature, °K.
R — gas constant.

If the temperature function of k is exactly exponential in a reaction, it is called (just as in case of gaseous reactions) a reaction of *first order*.

Although in case of ceramic reactions the process is complicated by the effect of the *form factor* of the reacting particles and also by the *formation of crystal nuclei*, the considerations described above are still valid. The formation of nuclei as well as the starting of the reaction need a definite amount of energy called *activation energy*.

The presence of fluxes obviously changes the pure solid state of reactions; the presence of a liquid phase will raise reaction velocity. Pole and Taylor (1935) are of the opinion that the absence of fluxes will render mullite formation incomplete, as there will always remain some free alumina in the compound.

Chemical Kinetics of Kaolinite Dehydroxylation

As in all similar measurements, investigations into the chemical kinetics of kaolin dehydroxylation have been aimed at the determination of the reaction velocity constant k. The temperature function of k permits an easy determination of the activation energy and of the "order" of reaction.

By using the method of isothermal heating (a static method) Murray and White (1949, 1955) have come to the conclusion that the dehydroxylation of different clay minerals is a reaction of *approximately first order*, i. e. that the exponential curve of velocity constant k, if plotted as a function of (absolute) temperature, complies with the Arrhenius equation. A thorough evaluation, however, has shown that the $\ln k$ vs. $1/T$ plot is not perfectly linear, but shows a slight aberration from first-order reactions. Demidova and Goncharov (1951) have come to the same conclusion.

The activation energies of the dehydroxylation of English "Supreme" kaolin, of Newton-Abbot clay, of Wyoming bentonite and of Eureka halloysite were measured by Murray and White (1949) as 37.97, 34.31, 57.64 and 36.74 kcal/mol, respectively.

According to Brindley and Nakahira (1957), the velocities of the dehydroxylation reactions of kaolinite and halloysite follow the Arrhenius equation *exactly ;* the inaccuracy in previous experiments originated in the inadequate size, shape and packing of the samples. Brindley and Nakahira used disc-shaped samples of different widths and examined the k constant of the isothermal dehydroxylation process of these discs at different temperatures. The reaction velocity constants were expressed by extrapolating them to a sample width of zero. The temperature function of this extrapolated constant followed the Arrhenius equation exactly both in case of kaolinite and of halloysite, showing activation energies of 65 and 55 kcal/mol, respectively. The isothermal plot of the decomposition degree vs. time function yields an *exponential* curve. In case of bauxite, however, the sigmoid curve shows the presence of concurrent, simultaneous reactions instead of the single dehydration reaction of kaolinite and halloysite.

The dehydroxylation reaction of kaolinite is very sensitive to effects due to *water vapour*, which may easily cause rehydration. The dehydroxylation reaction is probably not simply

$$(OH) + (OH) \rightleftarrows H_2O + O\uparrow$$

but rather

$$(OH) + (OH) \rightleftarrows (OH)^* + (OH)^* \rightleftarrows H_2O + O\uparrow$$

where (OH)* means an activated transition state. This transition phase is very sensitive to water vapour. Even very low water vapour pressures may have a detrimental influence on the process in the direction of the upper arrow.

The phenomenon of rehydration was thoroughly studied by Evans and White (1958). They have concluded that the hydroxyl ions of rehydrated kaolin are less firmly bound than those of the original kaolin. Particle size distribution and diluting by inert substances do not influence the conditions of isothermal decomposition. The decomposition of loose clay powder is always a reaction of first order although its velocity is a function of layer width.

All investigations mentioned above were made by measuring the *isothermal loss of weight* as a function of time. This technique certainly has its drawbacks: there is a loss of weight before the whole sample reaches the desired temperature. The application of a *dynamic* technique, instead of measuring the isothermal loss of weight, e. g. the evaluation of differential thermal curves according to Vold's (1949), method, seems to be more promising. Measurements along such lines have yielded the following values for the activation energy of the kaolinite dehydroxylation process: 55 kcal/mol by Allison (1954), 44 kcal/mol by Sabatier (1955), 44.83 kcal/mol by Murray and White (1955) as against the mentioned value of 65 kcal/mol measured by Brindley and Nakahira (1957). Since the starting point of the reaction is not well defined in differential thermal analysis technique, and since the exact heat capacity of the sample, indispensable for calculations, is generally not known, it is rather difficult to evaluate the DTA curve in this respect.

At present thermo-gravimetry is the most practical method for the determination of chemical kinetic data. This method requires different calculations from those applied for the determination of the isothermal loss of weight. A useful method was suggested by Freeman and Carroll (1958) who deducted the following formula

$$\frac{\dfrac{-E}{2{,}3\,R} \cdot \Delta T^{-1}}{\Delta \log (W_c - W)} = X + \frac{\Delta \log \dfrac{\mathrm{d}W}{\mathrm{d}t}}{\Delta \log (W_c - W)}$$

where E — activation energy,
X — order of reaction,
W — loss of weight after t time,
W_c — loss of weight after completion of the reaction,
R — gas constant,
T — temperature, °K.

Thus, by plotting the graph

$$\frac{\Delta \log \frac{\mathrm{d}W}{\mathrm{d}t}}{\Delta \log (W_c - W)} \quad \text{vs.} \quad \frac{\Delta T^{-1}}{\Delta \log (W_c - W)}$$

we get a linear pattern from which the order of reaction (X) and activation energy (E) are easily derived. The TG curve will give ($W_c - W$) while the $\mathrm{d}W/\mathrm{d}t$, rate of weight loss can be best obtained from a differential thermogravimetric curve or from a simple thermogravimetric one. The thermal dehydroxylation process of kaolinite was measured by Jacobs (1958) as a reaction of exactly first-order having an activation energy: $E = 37.8$ kcal/mol. For the time being, this value may be considered the most exact.

CHAPTER 11

MINERALIZERS AFFECTING MULLITE FORMATION

It has been known for long that some materials have an influence on the quality and/or the quantity of the product formed by the firing of clays or clay-bearing bodies. Even a low quantity of such foreign materials, artificial or natural, may change the properties of the fired product to a great extent.

According to a widely accepted hypothesis, the quantitative phase distribution of the product changes under the influence of foreign substances. Admixtures, the hypothesis says, do not act directly but by changing the *quantity* of one or more phases in the product. Admixtures increasing the quantity of a phase in the product are called *mineralizers*.

Several authors claim to have succeeded in increasing the mullite content of some ceramic wares or experimental samples by the use of certain mineralizers. The data published so far on these questions are, however, extremely contradictory; it even happens that different authors invest the same material with diametrically opposed mineralizing effects.

The reading of these papers inevitably suggests that there must be a basic irregularity or at least some misunderstanding in the interpretation of the mineralizing effect. Without averting this misunderstanding there is little hope for a uniform opinion to form concerning the right evaluation and mechanism of the mineralizing effect.

Mullite crystals often grow in size under the effect of mineralizers and become well recognizable by microscope or less soluble in hydrogen fluoride. This increase of crystal size may be due to firing time or to temperature. The confusion is only enhanced by the arbitrarily chosen firing temperatures, different in almost every case described.

Many papers deal with the problem of mineralizers. McVay and Hursh (1928) have already noticed that after long service refractory bricks made of diaspore get enriched in alkali oxides and vanadium pentoxide on the surface. The infiltration of some components of coal ash shift the mullite zone, and the quantity of mullite crystals increases. In the hot zone, however, mullite decomposes into corundum and into two sorts of glass of a high and a low index of refraction, respectively. Magnetite is, according to these authors, a good mineralizer of such systems. Budnikov and Khizh (1930) have come to the same conclusion by the microscopic investigation of a fireclay wall after six months' service. The mullite crystals they had investigated contained a number of inclusions filled with wüstite.

Yoshioka and Isomachu (1930) examined the factors affecting mullite formation by dissolving in hydrogen fluoride. Admixtures, added in a quantity of 1 per cent, have a great influence on the quantity of mullite formed during firing. The sequence of efficiency (at a firing temperature of 1400 °C with a firing time of 1 hour) is: Fe_2O_3, B_2O_3, steatite, orthoclase talc, CaO, CaF_2.

Nakai and Fukami (1939) made careful investigations with a high number of parameters: the mullite content was determined by hydrogen fluoride extraction and the material remaining undissolved was chequed also by X-rays. The starting materials were Korean kaolin, a kaolin-alumina mix and a quartz-alumina mix; the quantities of mineralizers added to the batches were 1/2, 2 and 5 per cent. Firing temperature ranged from 900 to 1450 °C. Substances of very different nature were used as mineralizers; in most cases they were oxides, but some tungstates, molybdates, nitrates were also investigated. The authors state that every substance has its temperature interval of optimum mineralizing effect; the most effective low-temperature (900—1000 °C) mineralizers are molybdenum and boron, the one for high temperature (above 1300 °C) is mangan. For general use copper oxide is recommended.

Parmelee and Rodrigues (1942) again dissolved fired products in hydrogen fluoride for determining the mineralizing action of various admixtures upon mullite formation. Although the authors admit that this method of mullite determination gives but relative values (the so-called "technical mullite quantity") they consider it suitable for obtaining technical indices. They classified the oxides according to their efficiency as follows: Zn, Li, Mg, Fe, Mn, Ce and Mo are *good*, Na, K, Ti, and Sn are *bad* mineralizers while B and Ca are of *medium* value. Li and Mg are most effective at high temperature.

Akiyama and Kadogawa (1943) investigated the mineralizing efficiency of AlF_3, $AlCl_3$, $Al_2(SO_4)_3$, NaCl, Na_2CO_3 and HCl. Parameters: quantity of admixtures 1—5 per cent, firing time: 2 hours, firing temperature 1430 °C. Method of phase composition control: microscope and X-ray patterns. The most effective mineralizers are, according to the authors, Na_2CO_3 and (in a lower degree) $Al_2(SO_4)_3$.

Palmeri (1951) fired kaolinite between 945 and 1350 °C with and without admixtures. The percentage of admixtures was a constant 3 per cent. The mullite quantity of the product was determined by the H_2F_2 solution method combined with the optical, electron-optical and X-ray control of the solution residue. If the firing lasted 30 hours or more the first mullite reflections of the solution residue were observed just above a firing temperature of 945° C. Sequence of effectivity of mineralizers used: CaF_2, B_2O_3, CaO, LiCl, MnO_2 and finally MgO.

Skinner and co-workers (1953) investigated the mineralizing effect of TiO_2, Fe_2O_3 and of alkali oxides. Their most significant statement is that the mineralizing effect of TiO_2 greatly depends on the Al_2O_3/SiO_2 ratio of the batch; the effectiveness of TiO_2 is very high; in certain cases the adding of 5 per cent TiO_2 may be more effective than 10 or more per cent of Al_2O_3. Iron oxide is a good mineralizer too, but only if added in a quantity below 5 per cent. Alkali oxides have no increasing influence on the quantity of mullite, they even spoil the mineralizing effect of titanium oxide and of iron oxide.

There is a great number of other materials whose mineralizing effect has been examined: oxides of iron, barium, lithium, copper and of boron as well as iron tungstate by Ushakova (1953); zinc and titanium oxides, lithium carbonate, talc and metallurgical slags by Budnikov (1954); thorium oxide, copper oxide, fluorspar and topaz by Chowdhury-Roy and Singh (1954).

Keler and Leonov (1955), investigating the mullite quantity formed by the firing of kaolinite and artificial allophanoids, also examined the effects of mineralizers. They found that the mullite percentage might be increased by adding MgO, CaO, MgF_2 and CaF_2.

Moore and Prasad (1955) fired kaolin-alumina mixes, corresponding to the composition of sillimanite and mullite in a temperature range of 1300—1600 °C for 24 hours. The mineralogical composition of the product was determined by quantitative X-ray analysis. The mineralizers used were: salts of sodium, lithium, potassium, magnesium and calcium, and oxides of mangan, titanium and iron. The authors came to the conclusion that mullite formation was enhanced by practically any admixture of low concentration; mineralizers, however, act as retarders if present in large quantities.

Nazarenko and Sviridenko (1956) investigated the mineralizing effect of LiF, $MgCO_3$ and TiO_2 in detail, using them in an amount of 1/2—2 per cent, at a firing temperature of 1500 °C for a time of 2—10 hours. Hydrogen fluoride extraction was the method of mullite determination: 76—78 per cent of the samples fired without a mineralizer was found insoluble. The percentage of the insoluble substance was not influenced by adding TiO_2, but was increased by adding $MgCO_3$ (i. e. $MgCO_3$ acted as a mineralizer). The behaviour of lithium fluoride was unusual: if added to the batch in a quantity of 1/2 or 2 per cent, it decreased the insoluble residue by 3 per cent; an addition of 1 per cent, on the other hand, decreased the insoluble residue to 15—20 per cent.

It was Budnikov who first tried to set things right in this chaotic problem of mineralizers by logically designed experiments and by a theoretical support. Budnikov and Shmukler (1946) undertook a series of experiments under the following circumstances: material: clays, kaolins; firing temperature: from 1000 to 1600 °C; firing time: 1, 3 and 18 hours; mullite-determination method: dissolving in hydrogen fluoride, followed by an X-ray and a microscopic control of the residue. Their most important achievement is to have noticed that the mineralizing effect is a function of r/e (r: ionic radius, e: ionic charge), i. e. that the systematic order of mineralizers following the decreasing sequence of r/e is, at the same time, the order of effectiveness. The mullite percentage, as determined by the extraction principle, was, as a rule, 7—9 per cent lower than set up by theory. No doubt, Budnikov's initiative has certain merits, although his results were discredited later by Avgustinik, Nazarenko and Sviridenko (1954) whose hypothesis is diametrically opposed to the former. The latter say that in case of identical charge the mineralizing effect grows proportionally to the decrement of the ionic radius. When repeating their experiments Nazarenko and Sviridenko (1954) came to the conclusion again that by planimetering the quartz content of SiO_2—Al_2O_3 batches which contained mineralizing admixtures, the mineralizers of high charge and high ionic radius proved the most effective.

Hamano (1957), when firing a mix of felspar+kaolinite, observed that the mullite crystals of the albite-bearing body were high. He explained this effect by the viscosity of the melt. The microscopic determination of mullite, however, may involve errors; Bor (1950) e. g. has proved that the elongated crystals, frequently occurring in the hot zone of the refractories of glass kilns and having optical properties, similar to those of mullite, are in fact not mullite, but so-called β-alumina, $11Al_2O_3 \cdot Na_2O$.

Volatile materials may also act as mineralizers. Ao (1933) and later Osborn (1933) described water vapour as a very effective mineralizer and this was confirmed also by Nemetschek (1958) who observed that without the presence of water vapour mullite could not be recognized even under an electron microscope. Tanaka (1951) recommended a constituent of lower volatilization degree. According to his opinion, 0.3 per cent boric acid raises the strength of porcelain by 20—25 per cent on account of the increased mullite quantity of the body.

It has been observed that admixtures may not only increase but also decrease the quantity of mullite. Kraner (1938) e. g. has found that the mullite crystal formation of cast mullite refractories is prevented by the addition of 4.5 per cent sodium carbonate and of 2 per cent lithium oxide; calcium oxide above 10 per cent is of a similar effect. In such cases the only crystalline constituent of the refractory is corundum. The fact that CaO prevents mullite formation was confirmed later also by Nemetschek (1958).

Having spent some time in a thorough and critical study of literature data as well as in laboratory and plant experiments, Grofcsik (1957) came to the idea to ascribe the contradictory results to the incorrect and unsatisfactory determination of the mullite content in the samples. Usually this determination is made by the hydrogen-fluoride dissolving method or, sometimes, by planimetering under microscope. As, however, both methods, especially the former, may involve a number of methodologic errors, the results cannot be accepted (cf. Chap. 2). The author used fired kaolins, clays, gel mixtures and technical fireclay products as samples in the presence of various mineralizers and found that neither the presence of admixtures, nor heating time, nor heating temperature (above 1000° C) influenced the *quantity* of mullite in the fired product, as determined by the internal standard X-ray method of the author (cf. Chap. 2). It is always the *stoichiometrically* maximum *quantity* of mullite, formed from Al_2O_3 and SiO_2 present, that is produced from every mix if the temperature and time of firing is sufficient for the solid-state reaction of mullite formation (Table IV).

Admixtures (as well as heating time and temperature) change the *size* and the *specific surface* of the mullite crystals formed in the samples. Particle size may vary under the effect of admixtures to a very high extent; since particle size increases and specific surface decreases under the effect of the additives. The extent measure of changes may reach more than two

TABLE IV

Composition, measured and calculated mullite percentages of samples, made of co-precipitated alumina-silica gels and different mineralizers

Sample No.	Mineralizer 1 per cent	Al_2O_3 percentage of gel	Mullite percentage	
			measured	calculated
37	—	71.8	99	100
38	Ca	71.8	97	99
39	Ni	71.8	96	99
40	Co	71.8	98	99
41	Mg	71.8	98	99
42	Fe	71.8	97	99
43	Li	71.8	96	99
44	Sn	71.8	96	99
45	TiO_2	71.8	97	99
46	Mn	71.8	97	99

All mineralizers (except TiO_2) have been added as solutions

orders of magnitude. This is why the apparent mullite quantity, determined by a dissolving process, shows high variations, even if the actual mullite quantity remains unchanged.

The mineralizing effect of various additives results in size enlargement resp. specific surface reduction. Contradictory literature data are due to the misunderstanding of this effect.

Strictly speaking, there are no mineralizers at all, i. e. there is no material that would increase the mullite *quantity* of the fired product if added to the raw mix. The addition of some materials, on the other hand, may be very advantageous in some instances from the point of view of ceramic technology or for the physical and the mineralogical composition of the product. Nor can the probability of some disadvantageous effect be definitely excluded. None of these effects is, however, a consequence of changes in mullite *quantity*.

PART FIVE

THE SIGNIFICANCE OF MULLITE

8*

CHAPTER 12

THE SIGNIFICANCE OF MULLITE IN ALUMINO-SILICATE REFRACTORIES

Fired alumino-silicate refractories are classified according to their alumina content into three groups: semi-acid, fireclay, and high-alumina products, with an alumina percentage of 15—30, 35—40, and above 45, respectively. The phase compositions, melting points, etc. of the products can be read from the Al_2O_3—SiO_2 phase diagram (with the presumption, that non-alumina, non-silica contaminations do not affect the properties). As can be seen from the diagram, up to about 1800 °C only one stable solid crystalline phase is present in the alumino-silicate refractories and that is *mullite*. At the same time also silica is formed from clay minerals.

The percentage of the melt phase increases with temperature. For example:

In isopleth of 45 per cent alumina and 55 per cent silica, melt percentage increases from 38.5 per cent (at the eutectic temperature 1545 °C) to 45 per cent (at 1700 °C), as calculated by the lever rule. At the latter temperature only mullite is present without any melt if the calculation is performed with the 72 per cent isopleth.

When studying phase diagrams, it must be born in mind that all of them hold true only when using samples of ideally pure and homogeneous substances. In practice, however, there are many factors which change the data as compared to the phase diagram as e. g. contaminations, accessory constituents, inhomogeneity due to a relatively coarse particle size, insufficient firing time yielding no equilibrium, etc.

A) FIRECLAY REFRACTORIES

The most common contaminations of raw materials in fireclays used for the production of refractories are Fe_2O_3, SiO_2, TiO_2, CaO, MgO, K_2O, Na_2O, in a quantity totalling between 2—5 per cent. With SiO_2 these contaminations form a silica-rich vitreous phase. Several authors have been interested in the function of this vitreous phase.

Halm (1948, 1951) has proved that the crystallization of mullite is facilitated by the presence of the vitreous phase; this, however, is not formed at low temperatures, its lowest temperature limit being above 1250 °C. Mullite, however, is formed even below this temperature, without the presence of glass, a fact indicating that the equilibrium tends towards mullite in the solid state already. This is obvious because phase diagrams give only information concerning the solid—liquid phase transition, but have nothing to say on reaction velocity. The *trend* of mullite formation is present at all temperatures below 1810 °C but the energy of the thermal movement is not sufficient to surpass the barrier of activation energy. The theoretically maximal quantity of mullite is formed from clays, co-precipitated gels, etc. at a temperature as low as 1000 °C (Grofcsik 1957).

Biagotti and Grungo (1951) and Massazza (1955) consider the presence of the vitreous phase to be essential in fireclay bricks since this phase facilitates the dissociation of mullite into corundum and high-alumina glass. Rose and co-workers (1957) describe the role of alkalies and iron(III) oxide in the formation process of mullite and the vitreous phase. Also Partridge (1953) discussed the vitreous phase of fireclay refractories, but without adding any new results (they had been described by Bowen and Greig already); his statement that clay decomposes into a mixture of amorphous silica and alumina is contestable. Among the usual contaminations K_2O and Al_2O_3 are the best to promote the formation of the melt phase.

Alumino-silicate refractories may be classified into such three-component system as Al_2O_3—SiO_2—K_2O, or Al_2O_3—SiO_2—CaO or Al_2O_3—SiO_2—MgO, or rather into polycomponent systems because of the contaminations. Since, however, the quantity of accessory components is generally low, the binary system seems sufficient to give approximate results (by the presupposition that the contaminations do not exceed 4—5 per cent). Polycomponent systems, containing only a low quantity of such fluxing agents, give diagrams that are confused to unapplicability (Savioli 1953).

Kienow (1959) has studied the system SiO_2—Al_2O_3—Fe_3O_4 and described that in certain cases oriented crystals of a ferroginous spinel grow upon mullite crystals. Crystal forms depend primarily on the viscosity of the melt and on its chemical composition. In melts of high viscosity, no oriented spinel-crystals are formed; with very low viscosity and with a high percentage of silica, interlaced fan-like crystals of spinel-mullite appear in the melt. Mullite-silica mixes have a tendency to segregate below the eutectic temperature. Spinels of high iron oxide content may deposit upon the surface of quartz or of some modifications of quartz, where in certain cases they form a protective layer against corrosion.

According to Konopiczky (1954, 1955) it should be born in mind that fluxing agents even of low quantity decrease the viscosity of the melt to a considerable extent, whereas they increase its quantity but slightly. The phase percentages of fireclay products (mullite, vitreous phase, occasionally cristobalite) are easy to calculate according to the system Al_2O_3—SiO_2—K_2O, by adding TiO_2 to the quantity of Al_2O_3 and Na_2O to K_2O (the latter always occurring in larger quantities in fireclay refractories). Fe_2O_3 has a special function, not yet explored. Konopiczky recommends a special method for the calculation of phase percentages.

Equilibrium conditions can hardly be realized in the system Al_2O_3—SiO_2 (which contains a small quantity of other oxides too) under industrial firing and cooling circumstances. The reaction of the fireclay batch is usually hindered also by the somewhat coarser particles giving a low contact area. This is why there is always a deficiency of mullite content in fireclay refrac-

TABLE V

Investigation data of refractories

No	Name	Chemical composition	PCE refractoriness	Refractoriness under load 2 kg/cm^3	Firing temperature °C	Mullite percentage	
						theoretical	measured
1.	"Petény" clay	SiO_2 54.88 Al_2O_3 28.63 TiO_2 0.90 Fe_2O_3 2.39 Loss-on-ignition 10.59	30	1400	1350	44.4	39
2.	id.	id.	30	1400	1000	44.4	37
3.	Ladle brick, Soviet-made	SiO_2 56.38 Al_2O_3 41.33 TiO_2 1.12 Fe_2O_3 0.95 Loss-on-ignition 0.19	33/36	1490	unknown	57.2	48
4.	Normal fireclay brick made in "Budapest" Refractories Factory	SiO_2 55.33 Al_2O_3 42.86	33	1380	1390	59.5	56
5.	Experimental fireclay-brick laboratory made	SiO_2 58.47 Al_2O_3 37.56 Fe_2O_3 2.78	31/32	—	1000	52.2	47
6.	id.	id.	31/32	—	1300	52.2	44

tories as compared to the theoretical mullite content (Grofcsik 1957). Shears and Archibald (1954) have described that the quantity of mullite in fireclay products of usual composition, preparation and firing will be below the theoretical value. The adding of fluxes, which decrease the viscosity of the melt, is a very important factor in reaching equilibrium conditions; this, however, decreases refractoriness. Also firing time and temperature have a considerable influence on the formation of mullite and of the melt phase. Dilatometric investigations of fireclay products fired at relatively low temperature usually show a more or less defined cristobalite and/or mullite effect, indicating the presence of silica (formed simultaneously with mullite). In case of higher firing temperatures a high-silica glass is formed, which will make dilatometric curves more uniform and after-shrinkage lower.

It is obvious that the firing temperature of fireclay products must be higher than the temperature of mullite formation. The clinkerization of bond clay begins only above 1000 °C; the exact temperature depends on the chemical-mineralogical composition of clay. The formation of the liquid phase calls forth an intensive clinkerization. The temperature of intensive clinkerization, however, must not be exceeded too much, since this would increase the quantity of the liquid phase too much, and cause a deterioration of the technical properties of fireclay, first of all in its refractoriness under load. Freberg (1939) says that the mullite phase is formed from the decomposition products of kaolinite below 1200°; a higher firing temperature will only make mullite crystals larger. Large mullite crystals can be produced by firing at a high temperature, by a long endurance at the maximum firing temperature or by a slow cooling.

Some technical experts advise fireclay products to be fired above 1350° C but at least at 1300° C. The above considerations contradict this opinion. Miehr and co-workers (1927) were also mistaken in requiring 1600° C and 1500° C for perfect mullite formation and mullite crystallization in case of very pure and less pure fireclays, respectively.

It is not a maximum but an optimum temperature the melt requires for the formation of mullite and for the embedding of mullite crystals. This temperature depends on the composition of the raw material and on particle size. Perfect formation and the size of mullite crystals are affected also by some accessory oxides present in the batch as natural (or artificial) admixtures and acting as catalysts. Iron oxides e. g. have a considerable influence on the crystal growth of mullite (Budnikov and Khizh 1929).

The softening of the glassy matrix of fireclay begins at the eutectic temperature, independently of the mullite : melt ratio. A further decrease of the viscosity of the melt will shift the mullite crystals and the *deformation* of the fireclay product will begin. This is why fireclay brick must not be used up to its PCE, but only to its refractoriness-under-load temperature (T_a). Naturally, the better a fireclay product, the higher its mullite content because this means a low glass content at the same time. A high quantity of mullite in itself is not sufficient as the vitreous phase has a more definite determining force as to the properties of a fireclay brick. The cause of strength is, according to Budnikov and Gevorkyan (1950), the vitreous bond reinforced by a mullite skeleton; mullite crystals, being usually distributed in the glassy matrix as individual insulated crystals or as crystal groups, cannot increase the resistance of the fireclay product to softening, thermal shock, corrosion, etc. The right process of technology must be chosen with due regard to all factors and must not be based on mullite quantity only (Święçki 1955).

B) SINTERED HIGH-ALUMINA REFRACTORIES

The recognition of the properties of mullite and of their role in fireclay refractories has led to the statement that an alumino-silicate refractory of technical properties surpassing those of fireclay can be produced by reducing the amount of the vitreous phase and by simultaneously increasing that of mullite. These considerations have induced the production of *high-alumina refractories.*

Mullite is the single stable solid crystal phase in high-alumina products below 72 per cent alumina content. Silica above 28 per cent reacts with the accessory minerals of the raw materials and gives a vitreous grog, softening at high temperature, just as in fireclay products. Getting nearer to the composition of mullite, the percentage of the vitreous phase decreases, and the technical properties of the high-alumina product improve. With an alumina content above 72 per cent a liquid is formed (in the absence of fluxes) only above 1810 °C. Below this temperature, only mullite and corundum are present. The resistance of high-alumina refractories to the attack of acid and basic slags is gradually improved by an increased alumina percentage; this property shows a sudden improvement in the so-called *corundum refractories* with 98—99 per cent alumina content.

As a consequence of alumina reacting at high temperature like an acid, high-alumina refractories will be less resistant to basic slags than magnesite, chrome-magnesite and dolomite refractories.

Though mentioned in the literature, the slag resistance of alumino-silicate refractories has not yet been cleared up. Rigby, White and Green (1939) e. g. investigated the effect of blast-furnace slag upon a superduty high-alumina brick and found three layers: the hot-end layer contained a high percentage of the vitreous phase with embedded anorthite crystals; the middle layer was primarily built of mullite, while the cold-end layer remained unchanged. The study on the thin sections of a glass-melting mullite pot describes even four layers: the inner layer is mainly vitreous; the second layer, when put under the microscope, shows interlaced mullite-crystals embedded into glass; the third corroded fireclay particles with mullite crystals and tridymite, while the fourth layer consists of unchanged mullite.

Belyankin and Bezborodov (1930) described the new formation of minerals upon the areas of alumino-silicate refractories, which get in contact with glass melts, slags, fly-ash, etc. The mineral paragenesis revealed the mineralizing effect of these technical substances to be similar to that of contact-metamorphic rocks. The most common new formations are plagioclase, β-calcium silicate, gehlenite, pyroxens, magnetite, mullite, corundum and (sometimes) carnegieite. Steinhoff (1954) has proved that the so-called "white layers" of glass tank blocks are formed by adjacent mullite needles. This layer has a high resistance to the diffusion of alkali ions. Filonenko and Lavrov (1953) have investigated glass tank blocks microscopically and observed that by heating refractories which contain mullite in bulk and Na_2O to 4—6 per cent to a temperature of 1820° C, corundum crystals are formed, considerably increasing in percentage at a heating of 1830° C. Mullite decomposes into corundum and into a high-silica vitreous phase. The effect of alkali vapours upon high-alumina bricks is, according to Brisbane and Segnit (1953), well explained by the Al_2O_3—SiO_2—K_2O equilibrium diagram. Corundum and glass are formed primarily in grog, mullite and glass in the matrix. The temperature of melt formation depends on the SiO_2/Al_2O_3 ratio. If the silica content surpasses that of mullite, a melt-phase forms at a temperature as low as, 1000° C if it is equal to that of mullite, the melt-phase appears at 1315° C only. Consequently, it is advantageous to increase the alumina content of the raw materials.

Vitreous silicate phases, owing to the fly-ash of industrial plants, often contain, mainly in the grog, mullite crystals as Meldau and Stach (1930) detected by photo-micrographs and X-rays.

Through microscopic methods Budnikov and Khizh (1930) observed a high quantity of mullite (containing inclusions of wüstite) in a refractory lining after 6 months' service. Melted aluminium reacts, according to Brondyke (1953) with all sorts of alumino-silicate refractories according to the equation

$$4Al + 3SiO_2 = 2Al_2O_3 + 3Si.$$

This reaction is not influenced by the partial or a complete transformation of silica into mullite.

Several papers deal with the manufacturing process of fireclay and high-alumina refractories. Their complete reviewing has been excluded from this monograph since they are mainly of technological or manufacturing interest, but their theoretical considerations have been summed up. The significance of mullite in high-alumina refractories will be dealt with in a more detailed manner.

Raw-material Problems in High-alumina Refractories

The following substances are generally used as raw materials for high-alumina refractories: 1. natural alumino-silicates; 2. natural alumina hydrates; 3. artificial alumina and 4. refractory bond clay.

Natural *alumino-silicates* (andalusite, kyanite, sillimanite) transform into mullite at 1380—1550 °C according to the following equation:

$$3Al_2SiO_5 = 3Al_2O_3 \cdot 2SiO_2 + SiO_2$$

Theoretically 88 per cent mullite and 12 per cent silica is formed by this equation. If, however, there are some accessory constituents (usually fluxes) in the batch, the product contains a high-silica glass besides mullite, with the amount of the vitreous phase considerably lower than in fireclay products, as can be seen from the above formula.

As minerals of the sillimanite group, unfortunately, always contain contaminations from the original rock and its accessorial minerals, it is essential to concentrate the rocks (with the exception of a few occurrences). Concentrated products generally have an alumina content of 58—62 per cent (Dixon 1958; Kawai and Shinohara 1942).

Sövegjártó (1956), investigating 120 thin sections of various high-alumina products manufactured from kyanites of Korea, Moçambique, India and Kenya, derived the following characteristics: 1. kyanite decomposition always begins at the surface of the particles; 2. the needles of mullite are always perpendicular to the original surface; 3. bonds of mullite interlace always at a definite angle, usually at 50°.

Volume changes due to the transformation of natural anhydrous alumino-silicates into mullite are of high importance from a technological point of view. All minerals of the sillimanite group have a specific gravity above 3 g/ml, while that of the fired product (mullite + amorphous matter) is below 3 g/ml (cf. Table 3). The increase in volume (expansion) due to a decrease in specific gravity being considerable, all minerals must be prefired before being manufactured into a refractory product (with the exception of some very pure sorts of andalusite). Prefiring temperature should be PCE 13 and 20 in case of kyanite and sillimanite, respectively. In case of unsatisfactory prefiring, the product will scale with a simultaneous reduction in strength. The importance of prefiring was especially emphasized by Dietzel and Knauer (1955).

Mullite is formed from kyanite as low as at 1200 °C; when heated to 1600 °C a dense network of mullite crystals appears, surrounded by a vitreous mass (Rao and co-workers 1953).

In order to ensure shaping, some good-quality *fireclay* is added to prefired semi-product ground to suitable particle size. The percentage of bond clay is usually 5—10 per cent, the minimum firing temperature 1500 °C. The properties of the product are determined by its mullite: vitreous phase ratio which again depends on the alumina and flux content of the raw material concentrate.

According to Forkner and Whittemore (1959) several manufacturers in the USA add "mullite", obtained by the firing of kyanite concentrate (with 600 mesh particle size) in a percentage of 20—50. This mullite concentrate is used also in the manufacture of sanitary ware.

High-alumina refractory products, manufactured from minerals of the sillimanite group, are usually called "*sillimanite refractories*" even now, although it is well known that they contain no sillimanite, but mullite. Recently, the name "*mullite refractories*" has become more common besides a number of fancy and advertisement names as e. g. *Silmax*, *Mullital*, *Vitrox*, and others.

Natural alumina hydrates (hydrargillite, boehmite) transform first into γ-, later into α-alumina when fired. Artificial alumina hydrate transforms into α-alumina as well. The volume of alumina hydrates is greatly reduced when fired. Shrinkage percentages are 60, 33 and 13 per cent for pure hydrargillite, pure boehmite and γ-alumina, respectively. Natural alumina hydrates are the chief constituents of bauxite, the accessory minerals present are iron oxide, iron hydroxide, quartz, calcite and sometimes also kaolinite and other minerals.

Some low-iron *bauxite* sorts of suitable composition were tried as raw materials for high-alumina refractories. Bauxite was prefired (because of the high degree of volume change), shaped and fired after the addition of about 10 per cent fireclay as a bond. Bauxite refractories, however, have not shown good results; the firing shrinkage being incomplete even at high temperatures, the products are porous, their refractoriness-under-load properties unsatisfactory in spite of their high alumina content. The reason is to be found in the iron oxide content; even so-called low-iron bauxite contains a pretty high quantity of iron compounds (5—10 per cent), which make refractory properties poor. Bauxite could not be de-ironed, because the iron-bearing compounds are of very fine distribution and would not be removed either by sedimentation or by flotation, only by very expensive chemical methods.

Diaspore, a detrital rock, could be applied better. As shown by Evers (1930), Missouri diaspore (USA) has the following composition (weight percentage): 72% Al_2O_3, 6.56% SiO_2, 3.65% TiO_2, 2.37% Fe_2O_3, 1% alkali oxides, 13.88% loss on igniton. Its refractoriness is PCE 40. Diaspore refractories have proved well in the USA and are manufactured from a batch containing about 60 parts of prefired, 40 parts of unfired diaspore and about 10 parts of refractory bond clay.

Diaspore is widely used also in the USSR. According to Budnikov (1950), a concentrate, dressed from Ak-Tashsk raw diaspore, has the following characteristics: chemical composition (weight percentage): 70—72% Al_2O_3, 20% SiO_2, 3—5.5% fluxes. Refractoriness: PCE 38—39. Ak-Tashsk diaspore concentrate is characterized by its low shrinkage on firing; this shrinkage passes at a high temperature (above 1500 °C) into a slight swelling, owing to the quartz → cristobalite transformation. The refractory product made of Soviet diaspore has a PCE refractoriness of 37—38, and a refractoriness-under-load of 2 kg/sq.cm, t_a — 1500—1550° C.

The fragments of *electrocast mullite and corundum refractories* (Rybnikov 1949) and *technical alumina*, made by the firing of technical alumina hydrate (Poluboyarinov and Popilski 1948), can also be used as a raw material of high-alumina refractories. The latter material is mineralogically α-alumina; its chemical composition being (weight percentage): 99.0—99.5% Al_2O_3, 0.25—0.1% SiO_2, 0.5—0.3% Na_2O and about 0.1% other oxides. As can be seen from these data, the purity of artificial alumina is superior to every natural substance and has a refractoriness of PCE 42.

Natural alumino-silicates, as mentioned, have a maximum alumina content of 60—62 per cent. For the manufacture of a refractory, containing only mullite, it is essential that alumina should be added in order to increase the Al_2O_3 content to approximately 72 per cent. No higher enrichment of alumina is necessary since — as Poluboyarinov and Kalliga (1951) have proved — the adding of alumina increases the refractoriness-under-load only until the composition of mullite is reached. Beyond this it becomes uneffective, as it is the partial melting of the mullite phase itself that will soften the product.

Skinner and co-workers (1953) examined the effect of TiO_2, Fe_2O_3 and of alkali oxides upon the mineralogical and physical properties of sintered high-alumina and mullite refractories. According to their results the mineralizing effect of TiO_2 greatly depends on the Al_2O_3/SiO_2 ratio of the product.

The adding of 5 per cent titanium dioxide may prove better in some cases than the alumina content increased by 5—10 per cent. A mix, containing 5 per cent TiO_2, 65 per cent Al_2O_3 and 30 per cent SiO_2 gives the maximum percentage of mullite. Fe_2O_3 is of similar effect, but only up to 4—5 per cent. The effect of TiO_2 is less affected by alkalies than that of Fe_2O_3. Heeley and Moore (1952) described similar results.

According to Litvakovski (1950), by the addition of about 8 per cent of zirconia to a refractory of 68 per cent mullite content, the texture is made much more uniform; at the same time the viscosity of the melt is reduced and softening temperature gets higher.

In lack of natural raw materials, it is most practical to use technical alumina (produced from bauxite) as a raw material for high alumina refractories and to manufacture so-called *synthetic mullite products*.

The essential points in the manufacture of *sintered* mullite refractories can be summarized in the following: briquets, pressed from a mixture of technical alumina hydrate, refractory clay and sand are fired at 1500—1600 °C, crushed, ground to a suitable particle size, mixed with 10—15 per cent of refractory bond clay; the body gained is shaped into bricks and refired at 1400—1500 °C (Poluboyarinov and Popilski 1949).

The formation of mullite being primarily a solid-phase reaction, the area of contact surface should be as high as possible. The raw materials of the briquet should be ground in the form of a slurry in a *ball mill*. The reactions in these mixes are represented by the following formulae:

Below 1400 °C

$$Al_2O_3 \cdot 3H_2O \rightarrow \gamma\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3$$

$$3(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O) \rightarrow 3(Al_2O_3 \cdot 2SiO_2) \rightarrow$$

$$\rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2$$

Above 1400 °C

$$3\,\alpha\text{-}Al_2O_3 + 2SiO_2 \rightarrow 3Al_2O_3 \cdot 2SiO_2$$

The refractoriness-under-load of these products is approximately 1500 °C. Synthetic mullite can be produced from other materials too; according to Jones' patent (1954), e. g. from a mixture of alumina and ethyl orthosilicate.

Contrary to the method of Poluboyarinov and Popilski (comprising a wet grinding) Zhikharevich and Krushel (1951, 1956) elaborated a method in the Institute of Refractories Research, Kharkov, which comprises dry grinding with a periodic ball mill. The raw materials of the briquet are ground to extreme fineness (maximum and average particle sizes are 2.5 and 1.5 microns, respectively). Mixes in which the particle sizes are quite uniform, give a mixture easily pressed to a briquet and clinkerized as low as at 1500—1600 °C. No doubt the dry process offers a simplified form of technology.

Popilski (1952, 1953) discussed the economic production of high-alumina refractories from technical alumina.

Boron-bearing alumino-silicates *(dumortierite)* may also be used as raw materials for high-alumina refractories. Albrecht and co-workers (1955) patented the process which comprises the release of boron trioxide during firing.

Some experiments concerning the manufacture, properties and improvement of high-alumina products were described by Richter (1957), Kawai and Furukawa (1943), and by Kitaigorodski (1946). Such superduty refractories are widely used also in non-ceramic, non-metallurgic industries, e.g. in chemical and hydrocarbon industries (Turner and co-workers 1952).

C) MELT-CAST MULLITE REFRACTORIES

Mullite refractories are manufactured also by fusion in an electrically heated kiln and by *casting* into a suitable form. The best representative of such electrocast mullite refractories is the *Corhart* block manufactured first in the USA by two companies (Corning and Hartford). A batch of 72 per cent alumina content was melted in an electric furnace and the melt was cast into a sand form; a well-defined cooling schedule resulted in a refractory block of closely interlacing mullite crystals and of very dense texture. The outstanding properties of such refractory blocks are given by Knuth (1935) in the following: bulk density 3000—3100 kg/cu.m; porosity 5—7 per cent; water absorption capacity 0.5—2 per cent; heat conductivity 0.0101 cal/cm.hr.°C (measured at 1200 °C); pyrometric cone equivalent 38, refractoriness under load above 1800 °C; temperature of melting 2200 °C. The chemical composition of Corhart refractories comes near to that of mullite.

Recently, cast-mullite and mullite-corundum refractories have been manufactured by other companies too. The crystallization of a melt, with an alumina content of 70—72 per cent as a minimum and a silica content of 25—28 per cent as a maximum, has been controlled. *Bauxite* is also frequently used as a raw material because here the iron oxide content of bauxite, unlike in the case of sintered high alumina bodies, has no disturbing effect, for at the high temperature of the kiln it gets converted with the coke, added to the batch, into ferro-silicon which, owing to its high density, flows into the bottom of the kiln and may be drawn off separately.

Mullite is melted in an electric arc furnace. The gross process taking place in the furnace can be summarized according to Budnikov (1950) by the following equation

$$3Al_2O_3 + 3SiO_2 + Fe_2O_3 + 5C = 3Al_2O_3 \cdot 2SiO_2 + Fe_2Si + 5CO.$$

As can be seen from the equation, the iron oxide content of bauxite is limited. Bauxites of Fe_2O_3 content higher than 10—15 per cent must not be used for the production of electrocast mullite refractories.

The contaminations of bauxite, as titania, calcium oxide, magnesia and alkaline oxides form, together with a slight content of iron oxide, a melt and after the crystallization of mullite remain in a vitreous phase. If the iron oxide content of the batch is too high, it reduces a higher quantity of silica and causes a higher percentage of glass and, besides mullite, a crystallization of corundum in the product.

Electrocast mullite products can be manufactured from other high-alumina raw materials too, e. g. from a mix of alumina and kaolin. The technological process is always the same: melting in an electric arc furnace, casting into a suitable form, and controlled cooling. Patents concerning electrocast mullite refractories are summarized by Wickert (1951) and Reinhart (1952). The discussion of the latter are limited to European patents.

High-quality electrocast mullite refractories are of a uniform texture, fibrous or fine-grained, with a mineralogical composition of 70—80 per cent of mullite, 10—15 per cent of corundum, 10—15 per cent of vitreous phase; bulk density 3300 kg/cu.m; apparent porosity 1 per cent; compressive strength 300—400 kg/sq.cm; refractoriness under load 1700 °C; thermal dilatation between 20—1000 °C 0.60—0.65 per cent.

Poluboyarinov and co-workers (1955) discussed the structural changes of mullite-corundum bodies, due to phase changes.

The uniform, possibly fine-grained texture can be easily achieved by the addition of a small amount of zircon or zirconia to the batch. This additive was used first with Corhart blocks.

Galdina (1951) dealing with the effect of admixtures upon the texture of electrocast mullite has observed that iron, titanium, calcium and alkalies give a vitreous, prismatic texture. As a consequence of the high amount of glass, pores and voids are formed in the block, and the percentage of the crystalline phase is obviously reduced. These effects are partly eliminated by the addition of ZrO_2.

Some contributions deal with the problem of zircon-mullite cast refractories: Belyankin and Lapin (1951) investigated the effect of ZrO_2 by microscopic methods; Solomin and Galdina (1953) examined the effect of the technological process upon the composition of cast zircon-mullite blocks; Partridge and Busby (1954) and Kitaigorodski and Batanova (1955) described the use of this type of refractories as glass-tank blocks. Tubes made of this material have proved especially good if used in furnaces operating *in vacuo* at high temperatures, according to Gulbranzen and Andrew (1949). Geiger and co-workers (1948) described some other applications.

The refractory properties of electrocast mullite blocks are favourable even if they have a relatively high silica content; these products have also another precious property: that of high corrosion resistance. The qualities mentioned make them most useful as glass tank blocks. Although the refractoriness-under-load characteristics of such blocks are rather poor, for a number of industrial purposes they may be applicable. The only crystalline component of such high-silica electrocast mullite refractories, which contain the excess of silica in an amorphous or vitreous form, is mullite.

The third group of high-alumina refractories are that of chemical bond. Knauft and co-workers (1957) consider zircon-mullite refractories of chemical bond especially useful for glass industry.

Vinogradova and co-workers (1956) manufactured a mullite-corundum refractory. The alumina + titania content of this product is about 77 per cent. Physical properties: porosity 15.2 per cent; bulk density 2760 kg/cu.m; compressive strength 682 kg/sq.cm; refractoriness-under-load 1520 °C. The method of production is a developed form of the Poluboyarinov and Ryakhovskaya (1954) method.

A further additive to mullite or corundum is silicon carbide which gives products of excellent slag resistance, refractoriness and shock resistance. Such products can be manufactured, according to Budnikov and Khramova (1952), from batches containing 75 per cent mullite and 25 per cent silicon carbide or 60 per cent corundum and 40 per cent silicon carbide. The mineralogical composition of the product is not changed either by oxydation or by reduction.

CHAPTER 13

MULLITE IN CERAMIC WHITEWARES

Oschatz and Wächter (1847) were the first to mention the crystals of porcelain. They made microscopic investigations to determine that the vitreous matrix of porcelain contains closed pores and is interwoven with minute crystals. These crystals were regarded as devitrification products of the glassy matrix of the porcelain body. Seger (1896), on the other hand, was of the opinion that a felspar melt can dissolve a high amount of quartz, while kaolinite, with its amount and refractoriness, is the rigid support of porcelain, which makes the body dense and fills the pores of molten felspar. Neither of the authors mentioned any crystallization process.

Crystallization was discovered by Glasenapp (1907). According to his opinion, the firing of kaolin or clay yields first an amorphous aluminosilicate, "anhydrous clay-substance" ($Al_2O_3 \cdot 2SiO_2$) which later dissociates into two parts, one being poor and the other rich in silica. According to his theory, "all sorts of clays become crystalline at a higher temperature as a consequence of the dissociation of clay substance".

Vernadský (1890) dissolved Sèvres china in hydrogen fluoride and analysed the undissolved residue chemically. The alumina percentage of this material was 70.3, and the formula of this crystalline product of porcelain (sillimanite, according to the author) was given as $11Al_2O_3 \cdot 8SiO_2$. The formula was later modified by Vernadský (1924) to $4Al_2O_3 \cdot 3SiO_2$.

Our present knowledge of the porcelain structure is based upon the work of Mellor (1907) and Zoellner (1908) who, naturally, identified mullite crystals as sillimanite. Zoellner dissolved china particles in cold hydrofluoric acid of 25—33 per cent concentration for some days. This operation dissolved the vitreous matrix of the particles, but the "sillimanite" crystals of larger size remained intact and the china particles did not lose their shapes after the experiment though they became easy to crush when slightly pressed.

Zoellner repeated his experiments with hard porcelain (fired at PCE 14) and also with Seger's soft porcelain. The latter material behaved similarly but lost its shape after the experiment.

The important role of mullite in porcelain has been investigated by a number of authors. Zoellner (1908) assumed that the thermal shock resistance of porcelain might be enhanced by increasing the percentage of "sillimanite", which can be achieved by a long-lasting firing at high temperature. A multiple firing, however, is disadvantageous because, as shown by Geller

(1933), this would result in the growth of mullite crystals and large mullite crystals reduce the strength of porcelain.

The growth of mullite crystals in porcelain due to long or high-temperature firing and the consequent loss of strength have been investigated more exactly by Krause and Keetmann (1935, 1936, 1937). The growth of crystals (under isothermal conditions) follows an approximately logarithmic rate: at a firing temperature of 1400 °C, the average lengths of mullite crystals are 5; 7.2; 11 and 14.3 microns, corresponding to a firing time of 6; 60; 600 and 6000 minutes, respectively. All measurements were done under microscope.

Budnikov and Gevorkyan (1951) have examined the effect of heating time and stated that during this period a marked diffusion takes place in porcelain bodies, especially at the contact surface between crystal particles and liquid. Diffusion produces a skeleton of quartz and mullite crystals, which is of most favourable effect on the strength and other properties of porcelain.

Recently, the role of mullite in porcelain has been criticized. Some authors are of the opinion that the strength of porcelain is increased by a high quantity of mullite, while others disagree with this view. Wiedmann (1959) e. g. has proved experimentally that the increase of the kaolinite content of a porcelain body (at the expense of quartz content) causes an increase of strength, owing to the larger mullite content of the fired body. Mattyasovszky-Zsolnay (1957), on the other hand, refers to his experiments when expressing his contrary opinion.

Laboratory and plant experiments performed by Grofcsik (1959) have showed that bodies of a high *kaolinite* content yield a porcelain product of high mechanical strength. The former experiments of the author (1957) have proved that the total alumina content of kaolinite is transformed into mullite during firing; the increase of mullite percentage in the body means at the same time greater mechanical strength. Greater strength can, however, be reached by increasing the quartz content of the body too, but only if it is of optimum particle size. If the particle size is too coarse, the thermal stresses between quartz and the vitreous phase will cause micro-cracks; if it is too low, quartz particles will dissolve in the melt. Both effects reduce the mechanical strength of porcelain. Porcelain of high quartz percentage is unfavourable also from the point of thermal-shock resistance.

The strength of porcelain is determined, according to Budnikov (1950), by the vitreous phase. A fired porcelain product is composed of glass up to almost 50 per cent, so this phase, being the weakest constituent, is the most important strength-determining mineral. In order to increase the strength of porcelain, the Al_2O_3 content of the product, i. e. the kaolinite content of the batch must be increased and a long firing of high temperature applied. In consequence of this firing mullite will partially dissolve in the glass and increase the strength of the latter. The temperature of firing, however, should not exceed a certain optimum.

Mullite formation requires a slow heating and cooling rate. This is one of the most important factors according to Nandi (1950); a long heating at a high temperature increases only the size and not the quantity of mullite crystals. The technological process is also one of the quantity-determining factors. The mullite content of slip-cast or pressed products is always higher than that of extruded ones.

According to Morey (1934), the vitreous phase is important in porcelain for it assures the homogeneity of the mullite skeleton. The formation of the vitreous phase during firing can be influenced by the particle size of felspar. Though the mullite/glass ratio should be kept constant, large mullite crystals are disadvantageous, as proved later by Nazarenko and Razumova (1956).

In their latest contribution Toropov and Alekseeva (1959) examined the formation of porcelain micro-structure during firing. By a hydrogen fluoride etching technique of thick sections, observed in reflected light, Inzigneri and Peco (1955) have found that the transition layer between electro-porcelain and its felspar-bearing glaze contains a well-developed nest-like interwoven network of mullite crystals.

The mullite content is favourable not only for strength, but also for refractoriness. For special refractory purposes a so-called *mullite-porcelain* is manufactured, which incorporates the silica partly in form of crushed electrocast mullite (made from the mixture of kaolinite and alumina).

The nature and quality of raw materials greatly affect the mineralogical composition and the mullite content of china. Some of these effects may be calculated and one or several properties of the product predicted. Dietzel and Padurow (1954) e. g. have given a method to calculate the translucency of fired china.

The mullite content of vitreous china was determined by Kopeikin (1958) as a function of composition and firing temperature. His results were:

Composition	1	2	3	4
clay (%)	43	58	51	51
felspar (%)	30	21	37	30
quartz (%)	27	21	12	19
firing temp. (°C)	1250	1200	1300	1250
mullite (%)	15.7	22.5	27.3	18.1

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