MINERALOGISCHE ONDERZOEKINGEN AAN KLEIEN EN KLEIMINERALEN

I. General discussion of the mineralogical composition of clays and qualitative X-ray analysis of some Dutch clays.

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GENERAL DISCUSSION OF THE MINERALOGICAL COMPOSITION OF CLAYS AND QUALITATIVE X-RAY ANALYSIS OF SOME DUTCH CLAYS

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1. ON THE CRYSTALLINE NATURE OF CLAY.

a. The antithesis crystalline-amorphous.

The word amorphous literally means without form and recalls the days when a distinction was made between substances with form, crystalline substances, and amorphous substances. This distinction was thus originally based on the external properties of the substances.

The development of crystal optics has already given an insight into the special physical properties of a number of crystallized substances and has thus also offered an opportunity of determining the crystalline character of many substances independently of their external form. In particular, the combination of crystal-optical and microscopical methods, i.e. investigation with the aid of the polarising-microscope, furnished the proof of the crystalline character of many substances, whose individual particles could not be recognized as crystals. From these investigations are derived expressions like microcrystalline, cryptocrystalline, with which substances were described which were considered originally as being amorphous.

Besides crystal optics, physical crystallography uses quite distinct methods, which are of importance in all sorts of cases for distinguishing crystalline from amorphous substances.

Physical chemistry, too, has contributed a good deal to the elucidation of the antithesis crystalline-amorphous. As typical examples of amorphous substances may be considered the glasses.

With decreasing particle size of the substance to be examined the application of optical methods is limited by the relatively great wave-length of visible light. With the aid of X-rays, whose wave-length is considerably shorter, much smaller particles can be examined and tested as to their crystalline nature than is possible with optical methods. As a rough suggestion of a lower limit it may be said that particles consisting of less than some hundreds of atoms (or ions) are generally beyond the limit of direct X-ray examination.

With the aid of X-ray analysis, again, several substances originally considered as amorphous were recognized as being crystalline.

Although, therefore, the external form of the particles of a substance was originally taken to be characteristic of the crystalline state, gradually *the properties relating to its interior structure came to be* considered as of critical importance.

The crystalline state is really a certain regular arrangement of atoms (or ions) in a so-called crystal-lattice. Expressed more exactly, the crystalline state consists of a threefold periodical arrangement of atoms (or ions). Every crystalline substance, and also every modification of such a substance, has its own characteristic lattice-structure and it is an important problem of crystal chemistry to determine from X-ray and other data the specific structure for every material, further to study the properties of the substances in connection with the structure, and to explain, if possible, these properties from the lattice-structure.

As every crystalline substance has its characteristic lattice structure, its X-ray photograph is also characteristic, which makes X-ray analysis an important help in diagnosing all sorts of crystalline substances.

Whilst the crystalline state has been characterized sufficiently for our purpose owing to the threefold periodical arrangement of the atoms (or ions), the opposite, the amorphous state, gives rise to difficulties. *It would be consistent to give a definition expressing the aperio*dicity of the arrangement of the atoms (or ions). There is, however, no method that can detect the aperiodical arrangement of atoms (or ions) by direct examination and thus those substances might be called amorphous whose crystalline structure is not certain. We must here *refer back to the fact that substances whose grains are still finer than* the above-mentioned rough limit of some hundreds of atoms (or ions) are beyond the limit of X-ray examination. In such cases, however, it cannot be said with certainty that the particles of the substance concerned do not have a threefold periodical structure. Thus X-ray photographs of silica-gel, a material one is inclined to consider as amorphous, sometimes show X-ray patterus of cristobalite, a modification of SiO_2, sometimes however they do not. This can easily be explained by the consideration that the particles forming the silicic acid gel are only in a number of cases big enough to render the detection of their regular structure possible. The proof of this reasoning, however, cannot be given. On the other hand it is of little use to consider the silicic acid gel in one case as consisting of crystalline particles, and in the other as an amorphous mass.

If one adheres to the definition that a substance is amorphous so long as its crystalline nature is not proved, one should be prepared for a continuous decrease of the number of substances still to be considered as amorphous.

Although *in the case of extremely fine dispersion* some degree of uncertainty remains in distinguishing crystalline from amorphous substances, for a large number of substances their crystalline nature has of late years been demonstrated, thanks to X-ray examination. To these belong the clay-minerals which now come up for discussion in the following sections.

b. Conceptions of the nature of the clay material.

In soil science clay is usually defined as the fine fractions of the inorganic part of the soil, i.e. the particles with diameter smaller than 2 μ. The word clay, however, is also used to denote soils rich in inorganic material with particles of diameter smaller than 2 μ. In the following discussion, the fine particles meant will therefore be designated as clay fractions or clay colloids.

One of the present writers (EDELMAN, 1937) some time ago discussed former conceptions of the nature of the clay material. The following is mainly borrowed from that discussion.

Ceramic interests have led to the development of more scientific conceptions of clay. As kaolin is the most important constituent of ceramic clay, in the course of time the notions kaolin and clay have become more or less synonymous; clays which, from a ceramic point of view, were less valuable, were considered as impure kaolins.

The old conception that kaolin is the characteristic constituent of clays is also found in a more recent form, among others in VAN BEMMELEN (1910), who considered clays as a mixture of:

1. The weathering silicate A, soluble in HCl (by treatment according to a certain method), which constituent corresponds more or less with the alumosilica gel of later authors and which was supposed to be the bearer of the adsorptive properties of clay.
2. The weathering silicate B, soluble in H_2SO_4 (also by treatment according to a certain method), which constituent was supposed to be kaolin.
3. The mineral skeleton, insoluble in the acids mentioned under 1 and 2.

Although the distribution of kaolin cannot be considered at all universal according to present knowledge and although kaolin cannot be considered as the type clay mineral, the mineral still belongs to the chief constituents of clays in general.

It should be borne in mind, that the recent conception of this mineral is more precise than earlier definitions and that it is desirable to indicate the mineral in the modern narrower sense as kaolinite. The term kaolin may still be used for the ceramic material and in the sense of the more vaguely defined materials in the older literature.

Soil science has led to quite a different idea of the nature of clay. The term clay is now used in the sense of the finest fraction of the inorganic constituents of the soil, especially since it has become known more generally that the clay of the soil scientists had the capacity for base exchange. As formerly the zeolites were the only minerals known to possess this property, the supposition arose that the clay of the soil scientists contained zeolites, which gave rise to the use of the term soil zeolites for the clay fractions. Although the idea of soil zeolites may at present be considered as archaic, the term is repeatedly found in the modern literature.

About 1910, under the influence of the rapidly developing colloid-chemistry, another conception arose. In the laboratory so-called mixed gels of silicic acid and aluminium hydroxide or iron hydroxide can be prepared, which likewise possess the power to exchange bases. This fact soon gave rise to the idea that the finest fractions of the inorganic part of the soil consisted of these mixed gels. One of the principal advantages of this theory over that of the soil zeolites is that the zeolites have definite chemical formulae, which could never actually be found by converting chemical analyses of clay fractions of soil. It was the great variation in composition of the clay colloids and the lack of stœchiometric proportions which formed a strong support for the theory of mixed gels.

One of the results of the theory of mixed gels was that extensive investigations into the colloid chemical properties of these artificial mixed gels were instituted; these investigations are of great value as parallels to the phenomena in the soil and recently, especially owing to the investigations of MATTSON (1929–1935), they have become of fundamental importance for explaining the various soil types. For the sake of completeness it should be added that soil scientists have also occupied themselves with the permutites, artificial glass-like zeolites that have also been studied as examples of the complicated clay colloids without, however, having been identified with clay.

About 1928 the conflict of opinions seemed to be at an end; the inorganic soil colloids were considered to be amorphous and to have a varying composition, and the whole was considered as consisting of mixed gels, finely divided between coarser particles, the soil skeleton.

Apart from the question touched upon in section *a* (namely how far we are justified in considering the substance denoted as mixed gels as crystalline or amorphous) it may be said that at present the theory of mixed gels as a general conception of the essence of clay colloids is discarded. It is chiefly X-ray analysis that has been responsible for this great change in opinions. Important contributions have been made by HENDRICKS and FRY (1930) and by KELLEY, DORE and BROWN (1931). An earlier publication by GILE (1925) has evidently had little influence. X-ray examinations have shown that even the finest clay fractions give X-ray photographs, which, when compared with those of more or less well-known minerals, in most cases give rise to an unequivocal conclusion as to the mineralogical composition of the clay fractions concerned. Even if in this field much is still far from clear, the fundamental question whether the clay colloids are crystalline or not, has been answered, viz. in the affirmative.

Apart from the results of X-ray examination there are many other facts which are contrary to the theory of the mixed gels as a general conception of the clay colloids. Along purely chemical lines it can easily be established that the fine clay fractions are attacked much less strongly by bases and acids than the mixed silica-sesquioxide gels. It must be remembered also that pure minerals are still perceptibly attacked by acids and bases. The dehydration of mixed gels is quite different from that of clay colloids (PARAVICINI, 1932). That zeolites play no rôle appears, among many other things, from the fact that zeolites lose their base exchange capacity after heating up to 350°, which is not the case with clay fractions of bentonites and soils (KELLEY, DORE and BROWN, 1931).

Together with the development of the conception that even the finest clay fractions are still for a considerable part crystalline, the study of the clay minerals, a chapter of mineralogy, which formerly could hardly be studied, has also progressed, so that at present the chemical properties and the crystal structure of most of the clay minerals are known, although it must be admitted that there remain some unsolved problems with regard to the clay minerals themselves.

In the above it has already been pointed out that the very variable composition of the colloidal fractions of the clays has been considered as an important argument in favour of the theory of mixed gels. Of late years, however, the theories of isomorphous substitution within numerous groups of silicates have changed, especially as a result of the ideas of BRAGG (1932), in such a way that at present the lack of stœchiometric relationships in silicates is no longer considered at all abnormal, so that this support also fell away from the theory of mixed gels.

A summary of the arguments that are in favour of the crystalline nature of clay fractions of soils is found in KELLEY (*1935a*).

Some authors nowadays go so far as to deny the occurrence of amorphous substances in clay fractions (apart from the question discussed in section *a*). In our opinion such an extreme point of view is not justified. Miss NEEB (1935), for instance, has shown microscopically the presence of gel-like constituents in a number of soils (see also HELLMERS and KÖHLER, 1935). On theoretical grounds, too, there is no reason why at least some percents of amorphous substance might not be present in clay fractions. *In general, however, it can only* be a question of small quantities. Although even such small quantities will not be without influence on the properties of clays and soils, conversely it has become entirely impossible to consider the properties of clay colloids exclusively as a function of these small quantities of amorphous substances that are perhaps present in clay. The crystalline character of the constituents of clay fractions involves the view that the properties of the clay fractions concerned are functions of the lattice-properties of the constituent minerals (VAN DER MEULEN, 1935; EDELMAN, 1935; KELLEY and JENNY, 1936; MARSHALL, 1937). This means that it is necessary to identify these constituents and examine their properties. This double task is the basis of the investigations to be discussed in this publication and in following ones.

A result of the changed views as to the nature of clay has first of all been a very much increased interest in the already existing knowledge of the clay minerals. A number of summarizing publications bear testimony to this. Of these may be mentioned: W. L. BRAGG (1937), BRAMMALL and LEECH (1937), EDELMAN (1937), VON ENGELHARDT (1937*b*), URBAIN (1937), W. H. BRAGG (1938), CORRENS (1938*a*), DE LAPPARENT (1938), NOLL (1938).

2. PRINCIPAL METHODS OF MINERALOGICAL INVESTIGATION OF CLAY AND CLAY MINERALS.

a. Microscopical methods.

Microscopy is the obvious method for examining coarser material, e.g. clay constituents with a diameter larger than 5–10 μ. The sand fractions ($> 40\ \mu$) of Dutch soils have already been subjected to an elaborate examination (for a summarizing discussion of these examinations, see EDELMAN, 1938 *a* and *b*) with almost exclusively microscopical methods.

The only publication in which constituents of the fractions of 5–40 μ of Dutch soils are examined is that by F. A. VAN BAREN (1934). As the intermediate fractions are in many respects of interest, they will play an important rôle in the future mineralogical examination of Dutch soils, but the examination made in this respect at Wageningen is not yet finished.

The technique of the microscopical examination of the grain fractions mentioned above has been developed especially by CORRENS and his co-workers. From this school comes the greater part of the literature on the mineralogical composition of the intermediate fractions of clays, among others SCHLÜNZ (1933, 1935), CORRENS and SCHLÜNZ (1936), CORRENS (1935–1937), VON ENGELHARDT (1937*a*), SCHACHTSCHABEL (1937*b*), PRALOW (1937), CORRENS (1938*a*). The application of this part of the mineralogical examination of clay is retarded by the laborious character of the investigation, but important results may be expected in the future.

For material with particle size smaller than 5 μ direct microscopical examination is in general difficult or impossible. Yet, in favourable cases it is possible to carry out some important determinations. Thus a mean refractive index can be determined on flocculated colloidal material, but this is only of value if the colloidal material consists entirely or practically entirely of one single mineral. For this determination many immersion liquids are unsuitable, because certain clay colloids have a strongly adsorbing effect on these liquids, so that the R.I. is changed (CORRENS and MEHMEL, 1936; F. A. VAN BAREN, 1936).

With the use of the usually flat shape of the clay particles GRIM (1934) succeeded in orientating the clay particles on an object glass by means of sedimentation from a suspension. In this way at least one of the R.I.'s can be determined accurately, while sometimes, in the case where the particles orient themselves also according to their horizontal axis and the orientation is therefore complete, the optical sign can also be determined and the optic angle measured.

MARSHALL (1930, 1935*a*) has developed a method for determining the electrical double refraction of a clay suspension. This method is based on the possibility of orientating the particles floating in the suspension by means of an electric field, which makes it possible to measure the bi-refringence of the suspension. This electrical bi-refringence proved to be dependent on the adsorbed bases of the suspended clay. It may be remarked that MARSHALL did not take into account the possibility that the result of the measurement can be influenced by the water molecules, which, dependent on the hydration of the bases present in each of the cases examined, are adsorbed in different quantities by the clay particles. This seems more probable than MARSHALL's view, that the adsorbed bases themselves might be the direct cause of the difference in electric bi-refringence.

b. X-ray methods.

The fundamental principles of the X-ray method will not be described here; for this we refer to the numerous summarizing works in this field, e.g. W. L. BRAGG, The Crystalline State, I. General Theory, (London, G. Bell, 1933); F. HALLA und H. MARK, Röntgenographische Untersuchung von Kristallen (Leipzig, J. A. Barth, 1937); J. M. BIJVOET en N. H. KOLKMEIJER, Röntgenanalyse van kristallen (Amsterdam, D. B. Centen's Uitgevers-Maatschappij, 1938).

The powder method of DEBIJE-SCHERRER-HULL takes up a dominating position in the X-ray examination of clay. Only very rarely was it possible to find bigger crystals of clay minerals, which could be used for rotation photograph (Ksanda and Barth, 1935, for dickite, Hendricks, 1938*b*, for talc and pyrophyllite). Naturally these special cases are of great importance for determining the crystal structure of the minerals concerned, but for the examination of clay fractions which by definition consist of material with fine grains the method cannot, of course, be taken into consideration.

Clark, Grim and Bradley (1937, cp. also Grim, 1934, quoted in section *a*) succeeded in making X-ray photographs of aggregates consisting of orientated settled clay particles. The aggregates to a certain extent allow of rotation patterns to be made and can at least form a valuable supplement to the powder photographs. Their method certainly deserves to be followed, especially in connection with the study of the crystal structure of minerals which only occur in submicroscopic crystals.

The determination of the mineralogical composition of the clay fraction can be made by comparing the X-ray photographs of clay fractions with those of standard photographs of minerals which can be considered as constituents of clays. Geochemical considerations make it probable that numerous important constituents of the earth's crust cannot occur in clays. Theoretically it is not impossible that the minerals used by others and also by us as material for comparison do not comprise all the possibilities, but it must be considered as in a high degree improbable that well-known minerals hitherto left out of consideration should play an important part in clays. There is, it is true, some uncertainty as to the mutual relationships of a number of clay minerals in a narrower sense, but here the difficulty lies in the very fact, that the minerals concerned are limited in their occurence to the clays and comparison with standard preparations is therefore impossible.

Apart from its use in identifying the constituents of clay fractions, X-ray examination is of importance in studying the properties of the clay minerals themselves. The chief and most fundamental application in this connection is naturally the determination and closer study of the crystal structure which for some important constituents of clay fractions must still be called unsatisfactory. In addition, several other cases may present themselves in which X-ray examination is desirable or necessary, e.g. in verifying the purity of preparations to be used for scientific examination. It is exactly by the fact that clay fractions in general consist of different constituents that the results of several examinations, e.g. in the field of chemistry, cannot be considered as characteristic of the conduct of certain important constituents. In future this will undoubtedly be different owing to the possibility of X-ray checking.

c. Analytical-chemical methods.

Total analysis of clay fractions has received much attention, especially in Russia and the United States (ROBINSON and HOLMES, 1924; ANDERSON and BYERS, 1931; ANTIPOV-KARATAEV and BRUNOWSKII, 1936; BYERS, ALEXANDER and HOLMES, 1935). It is hoped that in this way a system of soils will be established, in which the ratios silica — sesquioxides and silica — alumina, respectively, determined in both cases on the clay fraction, might serve as a basis. It is no doubt of importance in all circumstances to know the composition of the clay fractions and the above mentioned ratios, but the value of the analysis is limited by the fact that many, perhaps most, clay fractions are mixtures of substances which should be known, before it can be decided to what extent systematics based on the total composition has any value. Considered in a broader connection it is therefore necessary to study the total analysis of clay fractions in the light of the results of other methods, especially those of X-ray examination.

A second cause of uncertainty in interpreting the total analysis of clay fractions lies in the bases adsorbed by the clay colloids. These bases are not always removed, or substituted by a base like ammonium, before the material is analysed.

If there is any certainty as regards the mineralogical purity of the preparation to be analysed, total analysis becomes a very valuable, even indispensible help in studying the substance concerned.

In case of a very small particle size another difficulty crops up in interpreting total analysis, viz. that the essential composition of a substance need not agree with the real composition. A possible example of this case is discussed in 3 c.

By the side of total analysis, rational analysis must be mentioned in this connection. An elaborate examination of Dutch clays, in which rational analysis plays an important part, is that of ROBORGH (1935). The mineralogical interpretation of the data obtained by rational analysis is very difficult. The attack by acids is not only dependent on the strength of the acid, the temperature, the time of action and the way, in which the extraction is made, but also on the particle size (the surface) of the material dealt with. It is therefore practically impossible to say what really happens to the material during the acid treatment. Probably a close study of the action of acids on fractions — lying between narrow limits — of the pure minerals will give a better insight into the interpretation of the results of rational analysis. As a mineralogical method rational analysis of clay fractions is for the time being only of limited importance.

d. Colloid-chemical methods.

It is not at all our intention to give in this section a survey of colloid-chemical methods which can give a decisive answer as to the nature of the material constituting the clay fractions. We only want to direct attention to the fact that there are colloid-chemical methods that are of importance for our purpose.

Titration-curves of clay fractions have repeatedly been published (see e.g. ANDERSON and BYERS, 1936; MITRA, 1936). From the data brought together in this way it appears that the titration-curves of different clay fractions can have an essentially different form. It would be of great importance to be accurately informed as to the buffer power of the pure constituents in order to have thus a basis for judging the conduct of mixtures of the clay minerals. The advantage of the titration of clay colloids above other methods of investigation is, that the time necessary for carrying out the titration is comparatively short. The exact interpretation of the titration-curves of clay colloids is far from simple, but as a rapid method for the characterization of a clay colloid the titration can yet be of value.

The relation between the adsorption capacity of clay colloids and the pH of the buffer solutions with which the adsorption capacity is determined, can also be characteristic of certain clay colloids. Here a publication by HARDON (1935) may be mentioned, in which widely differing curves with regard to this connection are given for characteristic examples of the main soil types of Java. One of the following communications from this series will refer to this important material of HARDON.

BÄR (1936, see also BÄR and TENDELOO, 1936) found for a number of clays a more or less linear relationship between the adsorption capacity and the pH. His view that this approximately linear relationship is actually linear, is hardly compatible with some of the curves of HARDON.

As was also the case with analytical-chemical methods, colloid-chemical methods for characterising clay colloids have hitherto been chiefly applied to material of heterogeneous composition. In this case, too, the investigation on guaranteed pure material will be able to clear up our views considerably. Here too the X-ray check on the preparations to be examined should not be neglected.

That very simple colloid-chemical phenomena can also be of importance for our purpose, is illustrated by a recent notice of NAGELSCHMIDT (1938*b*) on rod-shaped clay particles, suspensions of which may show negative streaming double refraction. This rod-shape is according to NAGELSCHMIDT probably characteristic of particles of minerals from the palygorskite series, although disk-shaped particles may also have aggregated into rods and in this way can show similar phenomena in suspensions.

An entirely different application of colloid-chemical methods is based on the fact that in principle it will be possible to separate clay minerals from each other by making use of their different colloid-chemical behaviour. Even though attempts in this direction have up to the present moment not yet led to a satisfactory result (e.g. Drosdoff, 1935; Urbain, 1937), all hope of success need not be abandoned beforehand.

e. Thermal methods.

With the aid of thermal methods the alterations of a substance which occur by heating are studied. The method which is mostly applied determines the loss of weight; as a rule this loss is caused by dehydration.

The dehydration process is *more or less characteristic* of each mineral, so that it is often possible to draw conclusions from the dehydration curve of a clay fraction as to the presence of certain minerals.

In dehydration, however, there may arise all sorts of difficulties which hamper the direct interpretation of the curve obtained. As a variable factor there is not only the particle size of the material, but also the vapour pressure during dehydration and the speed with which dehydration is carried out. By deminishing the particle size even the character of the curve may change. The latter phenomenon has been studied, among others, by Kelley, Jenny and Brown (1936) and can be explained by the consideration that with extreme crushing so many hydroxyl-ions come to the surface of the crystal fragments, that a large part of the water conducts itself as „adsorbed'' water and escapes at a relatively low temperature.

A further difficulty is that it is not certain at the outset that mixtures — and the clay fractions are often mixtures — during dehydration show a behaviour in agreement with the sum of the behaviours of the individual constituents in dehydration.

Notwithstanding these difficulties, examination of the dehydration phenomena is undoubtedly of value for characterizing clay fractions; the application, however, is hampered by the fact that the investigation takes much time.

In French literature frequent use is made of so-called thermal analysis. This method is based on the fact that during heating reactions occur in the preparation which are partly exothermic, partly endothermic. This can be established by gradually heating the substance to be examined in a furnace and continually comparing the temperature of the preparation with that of another substance, which shows no special reactions, placed in the same furnace. If an exothermic reaction takes place in the preparation, its temperature rises above that of the other substance; during an endothermic reaction the temperature of the other substance is higher. It will be clear that a distinct difference in temperature between the two substances can only arise if the heat effect is sufficiently great. This is at the same time the strong and the weak point of the method (DE KEYSER, 1937). The fact that this determination can be carried out quickly favours the application, but on the other hand its interpretation is limited. The above mentioned influence of the mixture on the course of dehydration can also appear in the thermal analysis of clay fractions.

f. The synthesis of clay minerals.

The synthesis of clay minerals is naturally not of direct importance for the examination of the clay fractions themselves, but it is of great importance for forming a correct idea of the circumstances in which clay minerals can arise and moreover it can give a decisive answer as to the variability of the composition of the mineral concerned.

The principal recent examinations of the synthesis of clay minerals have been carried out by NOLL (1934, 1935, 1936*a* and *b*) who succeeded in preparing a number of minerals within the system Al_2O_3 — SiO_2 — H_2O. His preparations have been verified optically and by means of X-rays, so that his identifications are irrefutable. The circumstances in which NOLL carried out his syntheses of minerals differ greatly from those which occur in soils and resemble more the hydrothermal process. There are, however, some parallels between nature and NOLL's experiments; thus the conclusion may be drawn, if only with reservations, that kaolinite arises mainly under acid conditions and montmorillonite under basic conditions.

Further, it is of importance that montmorillonite can be obtained in systems which contain no magnesium. This result means that, contrary to the assertion of some investigators montmorillonite need not contain magnesium.

Very interesting from a soil scientific point of view is a synthesis of montmorillonite by SEDLICKII (1937) consisting of an ageing, during a period of over three years, of a mixed silica-alumina gel of a suitable composition. This synthesis too has been verified by means of X-rays.

Further literature on recent synthesis of clay minerals is found in VON ENGELHARDT (1937*b*) and NOLL (1938).

g. Summary.

From the above it appears that many methods are more or less suitable for characterizing or determining clay colloids. At the same time, however, it appears that the X-ray method takes up a special place, not only because it allows of fundamentally important observations to be made, but also because, by the side of numerous other methods, it is indispensable for checking the purity of the material.

3. THE PRINCIPAL MINERALS OCCURRING IN CLAY AND SOME OF THEIR PROPERTIES.

All minerals occurring in clay may be called clay minerals but it is desirable to call those minerals which practically only occur in clays clay minerals in a narrower sense.

In this survey, however, the principal minerals of clay fractions in general will be discussed, and with special reference to the constituents of Dutch clays.

a. Quartz and silicic acid.

The occurrence of quartz in clay fractions is of importance for various reasons. First of all quartz disturbs the interpretation of the chemical analysis of the clay fractions, because the mineral increases the ratio SiO_2 — sesquioxides in a way which does not agree with the objects underlying the calculation of the ratios mentioned above. For these ratios are determined in order to get an impression of the ratio of reactive acid material to reactive acidoid material and this aim is not reached if a considerable quantity of non-reactive substances is present in the clay fractions.

Further, a result of the presence of the non-reactive quartz is that the adsorption capacity gives too low an estimate of the activity of the material that really causes the adsorption.

It would therefore be desirable not to reckon quartz in clays, but then objections arise in connection with the definition of clay. However, a distinction might be made as regards the clay fraction between reactive and non-reactive material.

In the X-ray examination of clay fractions quartz can comparatively easily be identified by comparing the X-ray photograph with that of a standard preparation. In Table I (p. 28) the second column indicates the values found by one of the present writers (FAVEJEE, 1939*a*) for the various interferences, and the third gives the calculated values for the sake of comparison.

It is possible to determine the content of quartz chemically, by an agent which destroys the other elements, but leaves quartz unattacked. Phosphoric acid (HIRSCH and DAWIHL, 1932) and perhaps the borofluoric acid recently recommended by LINE and ARADINE (1937) are suitable for this purpose.

The question how far quartz is formed in clay colloids, or, in the case of alluvial clays, is originally present as such, is not unimportant. Although it is very probable that the latter is often the case, naturally the possibility of the formation of quartz in soils is not entirely excluded. In connection with this it may be remarked that in the first instance silica-gel when ageing is not transformed into quartz, but into cristobalite. That the cristobalite lattice, although metastable, is very constant, can be made plausible by means of the following hypothesis. The decidedly hydrophile character of the silica-gel involves the supposition that the micelles are strongly hydrated. The possibility of a high content of water should therefore be considered as a condition of the building schema of the growing particles. The structure of quartz is too compact to have room for water-molecules; this structure is essentially „dry". The cristobalite pattern, however, leaves enough space for taking up water-molecules, so that it is conceivable that the simple cristobalite-lattice, filled up and enveloped by water-molecules forms the basis of the silicic gel. The lattice, which is itself metastable (i.e. in a dry state), is, as it were, supported by the water-molecules (see also BUERGER, 1935).

The weakly acid character of silicic acid, as well as the fact that *it has no fixed formula*, can also be explained with the aid of the cristobalite-lattice. The surface of an arbitrary fragment of a cristobalite-lattice is formed by a number of oxygen tetrahedra with a silicon in the centre, but in which necessarily 1 or 2 oxygens are lacking. It is probable that this form of surface does not exist in particles of strongly hydrophile material. It may be expected that the incomplete tetrahedra lying on the surface are completed by hydroxyls; this is possible when one oxygen of the incomplete tetrahedron is considered to be combined with a water-molecule to two hydroxyls. A small part of these hydroxyls will be dissociated. In this way an idea can be formed of the particles of the silica gel, which apparently can explain all sorts of properties of the silica gel, or the silicic acid, e.g. the hydrophile character and the weakly acid character of undetermined "valency", which latter is also determined by the size and the form of the particles. The "meta-silicic acid" can be found back as a structural element in the cristobalite-lattice, also the "di-silicic acid" and other "silicic acids". It is, however, easy to understand that none of these structural elements can form independent lattices, in accordance with the fact that independent hydrates of SiO_2 do not exist. The so-called silicic acids can only occur as particles with a definite form and a limited size. The leaf-shaped di-silicic acid is especially striking.

The general formula of the particles of a silica gel becomes:
$SiO_{2-p} (OH)_{2p} nH_2O$.

In soils of Java amorphous silica was found microscopically by Miss NEEB (1935). In the Netherlands in many clays silica appears as diatoms and remains of other siliceous organisms, perhaps also in other forms; as from this non-crystallized silicic acid (KAHANE and ANTOINE, 1936) cristobalite can be formed by ageing, the possibility of the occurrence of lines of cristobalite on X-ray photographs of clays should be taken into account.

b. Feldspars and other important rock-forming minerals.

The occurrence of appreciable quantities of important rockforming minerals (with the exception of quartz) in clay fractions is à priori not very probable. For the minerals concerned, such as feldspars, amphiboles, pyroxenes, biotite, olivine, leucite, and nephelite (and volcanic glass), are subject to hydrolysis, which acts very strongly upon very small particles. Especially in the soil, therefore, these very small particles have only a limited term of life. They can only be expected, therefore, if the clay fractions consist of still slightly weathered rock-powder, which itself is a product of extreme mechanical forces. Glacial deposits, and also fresh volcanic ashes can give rise to these special conditions.

The possibilities of finding appreciable quantities of rock-forming minerals in clay fractions are therefore limited to special cases, although these special cases are very important from the point of view of soil science and geochemistry. The chance of finding smaller quantities of rockforming minerals in clay fractions is naturally greater, but this also seems to be limited.

In accordance with the above, only few clay fractions have been described in the composition of which rock-forming minerals have to some extent an important share (for some examples see CORRENS, 1935–1937).

For the sake of completeness it must be remarked that the chief rock-forming minerals often play a great part in the coarser fractions of soils and clays, and also in the so-called intermediate fractions. As such they are of great importance for soil science, both fors oil systematics and for evaluating the mineral reserve. Microscopical examination is particularly suitable for the study of these fractions.

c. Muscovite and related minerals.

The geochemical position of muscovite is such that the occurrence of the mineral in clay fractions need not be wondered at. In eruptive rocks muscovite occurs rarely, in metamorphic rocks, however, it is very frequent, especially in those which have been formed at low temperature.

The composition of muscovite is relatively variable. If one takes as a theoretical composition the formula $K\,Al_2\,(Al\,Si_3)\,O_{10}\,(OH)_2$ and if one tries to form an idea of the variations possible, one should remember the following:

1. The number of potassiums is equal to the number of aluminiums within the brackets.

2. The potassiums may, as far as they occur at the surface of the particles, have been substituted by other bases or by hydrogen. This possibility comes more to the front, the smaller the particles are, and

can, indeed, be of importance in clay fractions.

3. The aluminium outside the brackets may have been substituted by magnesium and (or) iron.

So the general formula becomes:

$$(K,H)_{1-p}Al_{2-q}(Mg,Fe)_{\frac{3}{2}q}(Al_{1-p}Si_{3+p})O_{10}(OH)_2.$$

Now it seems that in the forms of muscovite more or less constant at low temperature (Grim, Bray and Bradley, 1937; Maegdefrau and Hofmann, 1937*a*) the factor p is considerable and may by first approximation be put at 0.5. The factor q is of less importance and amounts to 0.5–1.

So a probable formula for muscovites occurring in clays is:

$$(K,H)_2\,Al_6\,(Mg,Fe)_3\,Al_2Si_{14}O_{40}(OH)_8.$$

Grim, Bray and Bradley (1937) suggested the name of illite for this variety of muscovite relatively poor in potassium and rich in silicon, which is reminiscent of the phengite of the older mineralogical literature. Before, however, it has been decided by means of chemical analysis of pure preparations whether muscovite from Dutch clays corresponds with the above described variety, it would be premature to speak of illite in our case, so that we consider it desirable for the time being to adhere to the term muscovite.

Until lately there was a great confusion in the literature as regards the presence, if any, of muscovite in clay fractions. On the one hand a number of West-European investigators, Goldschmidt (1926) and his collaborators, Correns (1933) and his collaborators, Nagelschmidt (1934), further Clausen (1932) and van Baren (1934), believed that they had established the presence of the mineral in clay fractions. For a time this was contradicted, also for Dutch clays, by another group of investigators (e.g. Hofmann, Endell and Wilm, 1934; Jakob, Hofmann, Loofmann and Maegdefrau, 1935; Jakob, 1938). Later, these investigators wrote about „Tonmineral X" and still later about „Glimmerton"; a recent examination from this quarter (Maegdefrau and Hofmann 1937*a*), however, admitted the importance of the micas for the clays (see further Grim, Bray and Bradley, 1937).

Undoubtedly, many clays which lack muscovite, occur in our earth, but extensive areas have soils with clay fractions of which muscovite is an important constituent, and to these areas the Netherlands belong.

The X-ray identification of muscovite is possible by comparison with standard photographs (see Table II, p. 29), some of which have already been mentioned in the literature. For the mutual distinction of the different micas a publication by Nagelschmidt (1937) is of importance.

An important question is the significance of muscovite with regard to the adsorption phenomena in clay soils. Most investigators, who have occupied themselves with this question, have come to the conclusion that muscovite actually contributes to the adsorptive properties of clay fractions. Here the particle size of muscovite naturally plays an important part. As GRIM *et al.* were able to isolate pure very fine-grained muscovite (illite) from their samples with the aid of the ultracentrifuge, the possible presence of extremely fine-grained muscovite (therefore with a considerable total surface) should be taken into consideration.

Besides X-ray examination, also the dehydration curve is of importance for identifying muscovite. Characteristic is the dehydration between 400° and 600°, at which temperatures the other clay minerals have already lost their bound water.

The great significance of the presence of muscovite in clay fractions naturally lies in the bound potassium. First of all the occurrence of potassium in this manner is of great and fundamentally geochemical importance. In the earth's crust potassium and sodium occur in quantities of the same order. Sodium however can find no place in the lattices of the weathering minerals (with the exception of the unimportant zeolites) and is therefore washed out in order to accumulate in seawater, as is generally known.

Potassium, however, owing to the relative stability of the mica-lattice can remain part of the solid earths' crust, or, if it is considerably displaced in the dissolved state, it can, possibly from the seawater, be built into growing mica-lattices (see also CORRENS, 1938*b*). So the fact that at any rate certain forms of mica are stable at low temperatures involves a great difference in geochemical conduct between potassium and sodium. The mica in clays and other sediments therefore forms the counterpart of the sodium-content of the oceans.

From the point of view of soil science muscovite is of course of great importance in connection with the rôle potassium plays in plant nutrition. Owing to hydrolysis, potassium can be removed from the lattice of muscovite and used for vegetation. Thus SCHACHTSCHABEL (1937*a*) found a correlation between available potassium according to Neubauer and the muscovite content of some soils, at least if he took into consideration the particle size of muscovite. In other circumstances the growth of the muscovite-lattice is perhaps possible, which means fixation of potassium in the soil. On the phenomenon that some soils fix potassium in such a way that plants can hardly take it up, there is an extensive literature, among which several recent publications: CHAMINADE and DROUINEAU (1936), JOFFE and KOLODNY (1936), GORBUNOV (1936), SCHACHTSCHABEL (1937*a*), VOLK (1938). It has been attempted in these publications to connect this fixation of potassium with the development of muscovite (VOLK, 1933, 1934).

d. Kaolinite and related minerals.

Under this heading will be discussed:

kaolinite (and anauxite).
dickite and nakrite.
halloysite and metahalloysite.

Kaolinite, formerly considered as the typical clay mineral, has the formula $Al_2Si_2O_5(OH)_4$ or $Al_2O_3.2\ SiO_2.2\ H_2O$. It seems that the isomorphous variation of this composition is not very important. There are clays which contain more SiO_2 than is indicated by the formula of kaolinite, which, however, cannot be distinguished by X-rays from kaolinite. They are called anauxite and have the composition $Al_2O_3.2$–$3\ SiO_2.2\ H_2O$. The explanation of this curious deviation is not simple on the basis of their structure. GRUNER (1932*a*) was originally of the opinion that probably a number of silicon ions replaced aluminium and so were surrounded by four hydroxyls and two oxygens, which meant an absolute novelty in the crystal chemistry of the silicates (MACHATSKI, 1938). Later GRUNER (1937) changed his opinion in so far that he supposed that groups $Al_2O_2(OH)_4$ might be replaced by groups $SiO_4(H_2)$. A different explanation is that of HENDRICKS (1936) who hit upon the extremely interesting idea that the anauxites might be kaolinites with incomplete lattices marked by a deficiency in aluminium. Although HENDRICKS's hypothesis may not be considered as proved, we will dwell on it, because it gives a very suggestive idea of a complication which clay mineralogy has to take into account. Clay particles can be so small that *superficial lattice-distortion of the particles* can lead to an actual composition of the material, which can considerably deviate from the ideal composition according to the formula. HENDRICKS's hypothesis must be considered as such. If kaolinite particles have a diameter of about 55 Å, each aluminium layer contains about 150 aluminiums, of which about 50 are in superficial position. These 50 superficial aluminiums (together with a suitable quantity of hydroxyls) can be lacking without seriously disturbing the coherence of the lattice. With the above diameter of the particles, therefore, a third part of the aluminium may be lacking, which gives the extreme case of an anauxite with 3 SiO_2. With larger particles the percentage of superficial aluminiums is naturally smaller and then, in the extreme case, aluminiums which are farther removed from the surface should also be lacking. There are however many anauxites with less than 3 SiO_2.

As a possible cause of the lack of superficial aluminiums acid hydrolysis may be considered. Kaolinite is isoelectric at $pH = 4$, so that, according to the theory of the isoelectric weathering, at $pH > 4$ silica and at $pH < 4$ alumina must go into solution. In this train of thought alkaline hydrolysis may be made responsible for kaolinites with a deficiency in SiO_2. Such kaolinites are frequent.

As has already been remarked the exact explanation of the formula of the anauxites is far from simple. Both HENDRICKS and GRUNER look for the proof of their idea to a careful examination of the lattice-water. With such small particles, however, the distinction between adsorbed water and lattice-water is difficult to make. But we thought it right to point out that HENDRICKS's hypothesis, in spite of the as yet not quite convincing experimental basis, is characteristic of a difficulty which may be considered as inherent in clay mineralogy, and that the total composition of material consisting of very small particles cannot easily be interpreted.

The X-ray photograph of kaolinite is very characteristic and the interference, corresponding with a spacing of 7.1 Å, forms the chief distinguishing mark (Table III, p. 30).

The colloid chemical properties of kaolinite have repeatedly been studied, but it has appeared that the mineral is not very reactive, at least in normal concentrations of hydrogen ions. One of the present writers (EDELMAN, 1935, 1937) believed that this could be inferred from the crystal structure. In normal cases and with normal methods adsorption capacities of 1–10 milli equivalents per 100 grams of material smaller than 2 μ are found. There are two possibilities by which higher values may be found, viz. by carrying out the determination with high pH, e.g. with the Hissink method (HISSINK, HOOGHOUDT and v. D. SPEK, 1936), or by examining extremely fine-grained material. KELLEY (1935*b*) crushed kaolinite to such an extent that it no more yielded a good X-ray photograph and the lattice-water largely escaped at a low temperature; he then found a considerable adsorption capacity. It is, however, not known, whether such extremely fine-grained kaolinite occurs in nature.

Many studies (e.g. PIETERS, 1928) have been made of the dehydration of kaolinite, which is to be considered as a mineral which is the chief material of ceramic industry. The theory of the processes taking place in heating kaolinite will not be discussed here. The dehydration curve of kaolinite may be considered as characteristic.

Kaolinite originates in nature in very different ways, both hydrothermally and by surface weathering. Many deposits used for ceramic purposes consist of alluvial material.

Finally, it may be remembered (see also p. 5) that by kaolin one usually means a clay useful for ceramic purposes. Most of these clays contain kaolinite, but as a rule other minerals besides, such as quartz and (or) muscovite. The "standard" kaolin of Zettlitz, too, which plays a rather important part in the literature, is not a mineralogically pure kaolinite.

Mineralogy knows two other indisputable minerals with the same formula as kaolinite, but with different optical properties and a slightly different crystal structure, viz. *dickite* and *nacrite* (Ross and Kerr, 1931). Dickite is not particularly rare, but nacrite must be considered as a mineralogical curiosity. In examining ceramic clays the possibility of dickite being found should be taken into consideration. Hitherto however dickite has not been found with certainty in clay fractions of soils. Only Antipov—Karataev and Brunovskii (1936) suppose that they have shown dickite in a number of soils. A further confirmation of these finds is necessary, before the point of view accepted in Western Europe and America, that dickite is not a result of surface weathering but of a hydrothermal process, can be given up.

The X-ray photograph of dickite (Gruner, 1932*b*; Ksanda and Barth, 1935) and that of nacrite (Gruner, 1933) differ sufficiently from that of kaolinite to allow of an unambiguous identification of the minerals themselves.

Halloysite is a clay mineral in a narrower sense, which in contrast to the other clay minerals has a very limited stability. Above 50°, and in vacuo already at room temperature, it loses two molecules of water and passes into an isomere of kaolinite, called meta-halloysite (Hofmann, Endell, Wilm, 1934). Even in water by heating at 100° the transition takes place (Mehmel, 1937). The occurrence of this phenomenon has a great influence on the possibility of identifying the mineral in clay fractions. Nearly all clay fractions have been dried in the course of the preparation, often at 105°; in this way halloysite, if present, is transformed into the metahalloysite which resembles kaolinite.

It must be remarked that, before the above-mentioned discovery, by halloysite was meant an isotropic gel-like kaolinite (Ross and Kerr, 1934). After the application of X-ray analysis such a rough definition has no longer any sense and the name of halloysite is reserved by most authors for the mineral with the properties found by the German investigators. It is however to be understood that in the literature there is a great confusion on this score, because some of the properties attributed to halloysite have been determined on true halloysite, some on metahalloysite (dried preparations) and some on fine-grained, seemingly amorphous kaolinite. The optical properties of halloysite and metahalloysite have been discussed by Correns and Mehmel (1936).

According to the structure analysis of Mehmel (1935) true halloysite has the formula $Al_2O_3.2\ SiO_2.4\ H_2O$, or $Al_2\ (OH)_6.Si_2O_3\ (OH)_2$, therefore an ordered mixed gel.

Hendricks (1938*a*) suggested a different structure for halloysite. In his opinion sheets $Al_2Si_2O_5(OH)_4$ are separated by waterlayers. Further he calls halloysite what Mehmel calls metahalloysite and he uses the term "hydrated halloysite" for Mehmel's halloysite. This exchange of names must inevitably lead to further confusion.

The X-ray photograph shows a diffraction line at 10 Å, which, after drying of the material, has disappeared; a new line appears at 7.4 Å, belonging to the photograph of metahalloysite. For the other differences in the photographs of halloysite and metahalloysite we refer to MEHMEL (1935, 1938) and to HENDRICKS (1938*a*).

Most of the halloysites occurring in nature have already been partly dehydrated, owing to which both the interferences of halloysite and those of metahalloysite occur on the X-ray photograph.

The colloid-chemical properties of halloysite are still little known, partly because here too the confusion halloysite — metahalloysite has played a part.

The course of the dehydration of halloysite is characterized by the loss of lattice-water at low temperature.

e. *The montmorillonite-group.*

This is the most important group of the clay minerals in a narrower sense, owing to the frequent occurrence of the minerals belonging to this group as well as to their significant colloid-chemical behaviour.

To this group are usually reckoned montmorillonite, beidellite and nontronite. There is not yet any complete certainty as regards their composition. Most investigators write the formule in this form: $Al_2Si_4O_{10}(OH)_2.nH_2O$, in which part of the aluminium can be replaced by magnesium and according to some authors (e.g. MARSHALL, 1935*b*) part of the silicon by aluminium. Others (e.g. KERR, 1932) think that the formula should run: $Al_2O_3.MgO.5SiO_2.H_2O.nH_2O$, which however cannot be written as a "mica" with the structural group Si_2O_5. Further a number of analyses also show calcium and alkali, usually also represented as replacers of aluminium, which however seems improbable.

The difficulties connected with the formula can be reduced to different causes:

1. Many of the preparations used were not pure.
2. The exchangeable bases have not always been taken into account as such.
3. Montmorillonite always consists of very small particles, of which the real composition, as has been said on p. 11, may deviate considerably from the ideal composition.

One would have to know the import of these three possibilities, before being able to judge how far the composition can vary by isomorphous substitution, so that for the present the knowledge of the composition of montmorillonite must be considered as still insufficient.

Beidellite is taken to be a mineral with the composition $Al_2O_3.3\,SiO_2.H_2O.nH_2O$, and nontronite is the corresponding ferric compound. These two minerals, as some say, form a complete isomorphous series of mixed crystals. The composition of these substances, too, is still little known.

In view of HENDRICKS's hypothesis (p. 20) as to the relation kaolinite — anauxite one is tempted to consider beidellite as an alkaline hydrolized montmorillonite, but this is only a suggestion.

The most striking property of the minerals of the montmorillonite group is their linear swelling, i.e. the dimension of the unit cell in the direction of their c-axis varies with the water content. Strongly dried montmorillonite gives X-ray photographs with an inner interference corresponding with a (001)-spacing of about 10 Å; of air-dry montmorillonite it amounts to 15 Å, and to 20 Å when montmorillonite is saturated with water.

This *linear* swelling, first described by HOFMANN, ENDELL and WILM (1933), has of late years frequently formed a subject of research. HOFMANN and BILKE (1936), further MAEGDEFRAU and HOFMANN (1937*b*) adhered to their original view, that the swelling takes place continuously with the water content, whereas according to BRADLEY, GRIM and CLARK (1937) the swelling seemed to be discontinuous (see also NAGELSCHMIDT, 1936), which means that the distance between two successive sheets of montmorillonite corresponds with one, two or more layers of water-molecules, and that intermediate distances do not occur. On the strength of this these authors think it desirable to speak of different hydrates of montmorillonite. It does not seem easy to bridge the differences of opinion between the American and the German authors.

It is clear that the continuous or discontinuous swelling of montmorillonite is of very great importance for explaining the conduct towards water of clays containing montmorillonite.

The crystal structure suggested by HOFMANN, ENDELL and WILM (1933) has repeatedly been exposed to criticism. MAEGDEFRAU and HOFMANN (1937*b*) as well as BRADLEY, GRIM and CLARK (1937) tried to defend the structure, but for this purpose they had to introduce all sorts of auxiliary hypotheses which would seem hardly probable (see also NAGELSCHMIDT, 1938*a*). DE LAPPARENT (1938) suggested an alteration in the structure which, however, found little approval from the other investigators. HOLZNER (1935), too, suggested a more complicated structure. Apart from the difficulties in indexing, the structure suggested by HOFMANN *et al.* has the drawback, that it cannot make plausible either the swelling or the base exchange (EDELMAN, 1935, 1937). It may be assumed that the last word about this structure has not yet been said.

The nature of the X-ray photographs may appear from Table IV, p. 31.

The special behaviour of the minerals of the montmorillonite group with regard to water has already been dealt with; they may be considered as extremely hydrophile.

The base exchange of montmorillonite also has a special character, namely because it is not proportional to the total external surface of the particles (e.g. MARSHALL, 1935*b*; WHITT and BAVER, 1937). This property can only be explained by supposing that the bases have their places on the (001)-planes, to which they have access owing to the relatively great distance between successive sheets of the lattice. For the adsorption capacity of montmorillonite values are usually found of 80–100 milli equivalents per 100 grams of substance.

The *distribution of the minerals of the montmorillonite group* is very considerable. They form the chief element of most of the clays indicated by the names "vollersaarde", "bleekaarde", "fuller's earth", "Walkerde" and "bentonite", but they have also already been shown to occur in the clay fractions of many soils. By their high specific adsorption-capacity they can play a very important rôle in the adsorption-phenomena of clay fractions.

f. Of the other clay minerals talc and pyrophyllite must in the first place be mentioned, respectively $Mg_3Si_4O_{10}(OH)_2$ and $Al_2Si_4O_{10}(OH)_2$, (GRUNER, 1934), which, owing to their occurrence in nature, give rather the impression of hydrothermal products; they have accordingly not yet been found in soils.

Sepiolite $2\,MgO.3SiO_2.4H_2O$ (MIGEON, 1936), whose crystal structure is not yet known, may still appear to be of local importance, as likewise the isomorphous mixtures with the corresponding aluminium compound, the palygorskites (LONGCHAMBON, 1936, 1937). As regards the position of these not yet sufficiently known minerals there is as yet no certainty. The same holds good for the attapulgites (see DE LAPPARENT, 1936, 1938; KERR, 1937).

Glauconite (GRUNER, 1935; MAEGDEFRAU and HOFMANN, 1937*a*) can also be reckoned with the clay minerals, as also some chlorites (McMURCHY, 1934) and vermiculites (GRUNER, 1934), but it is as yet quite uncertain whether these minerals occur in clay fractions.

Besides the minerals mentioned here, carbonates can also occur in the clay fractions (CORRENS, 1938*a*) and in some clays the various hydrates of Al_2O_3 and Fe_2O_3 play a part.

The older mineralogical literature knows several names of minerals to be reckoned in the more comprehensive idea „clay". X-ray analysis has shown that these badly defined minerals often proved to be mixtures or could be identified as known minerals, e.g. as montmorillonite and sometimes as halloysite. With regard to this we may refer to the summary by NOLL (1938).

Finally some remarks may be made on the name allophane. This term was formerly used for the amorphous aluminium silicates of varying composition containing water, which according to later conceptions should be reckoned with the mixed gels (Ross and KERR, 1934). This group has lost much of its importance. There can no longer be question of allophanoid clays as an important group. As we already remarked above (p. 7) we do not think it justifiable to deny the presence of amorphous substances in clay fractions. So it seems to us that the name allophane should be maintained as the mineralogical conception of the mixed gels consisting of the hydrates of SiO_2 and Al_2O_3 in varying amounts.

Summarizing, we may remark that the chief minerals occurring in clay are quartz, muscovite, kaolinite and montmorillonite, to which in special cases halloysite and some others may perhaps be added.

g. Of late years an extensive literature has already arisen dealing with the occurrence of the above minerals in clay colloids both of industrial clays and of soils. MAEGDEFRAU and HOFMANN (1937*a*) give a table with data as regards the composition of 207 clay fractions examined by them. In 82 cases kaolinite was the chief mineral, in 78 montmorillonite, in 42 muscovite, in 1 halloysite, while 4 clay fractions had other minerals (among which the palygorskites) as chief elements. It is not impossible that later on the distribution of the clay minerals in nature will appear to deviate from these figures, but at any rate they give a first approximation. The following publications, which have not been mentioned in the preceding sections, are of importance for the knowledge of the distribution of the clay minerals in nature (the list does not claim to be complete): ENDELL, HOFMANN and WILM (1934), BRAY, GRIM and KERR (1935), KAWAMURA and FUNABIKI (1936), GRIM and BRAY (1936), DE LAPPARENT (1936), FREY, YOVANOVITCH and BURGHELLE (1936), KELLEY and DORE (1937), NOLL (1937), BRAY (1937), JUNG (1937), CLARK, RIECKEN and REYNOLDS (1937), AARNIO (1938), PRALOW (1938).

4. QUALITATIVE X-RAY INVESTIGATIONS OF THE MINERALOGICAL COMPOSITION OF SOME DUTCH CLAYS.

The first X-ray photographs of Dutch clays were made at the request of the late Professor J. VAN BAREN (1933) of Wageningen by Prof. Dr W. KEESOM in Leyden. These photographs could at the time not be identified, but they were sufficient to show that the clay fractions of Dutch clays were crystalline. One of the present writers (F. A. VAN BAREN, 1934) later examined three Dutch clays microscopically and also by means of X-rays, applying the method used in Rostock; in the fraction $< 1\ \mu$ the presence of quartz, muscovite and calcite could be shown. From the microscopical examination of the intermediate fraction it appeared that two of the clays contained feldspar; in one sample biotite was also present, another contained kaolinite.

Jacob, Hofmann and Loofmann (1935) found montmorillonite in some Dutch soils, among which the marine clay of the „Wieringermeer", and at the time they argued against the presence of muscovite in our soils.

In 1935 in the Geological Laboratory at Wageningen it was possible to make a beginning with the more systematic examination of the Dutch clays, owing to the fact that the Jubilee stipend of the Society „Het Nederlandsche Natuur- en Geneeskundig Congres" was awarded to F. A. van Baren. We express our gratitude to the Board of this Society for their aid, without which our investigations could not have been started. In 1936 the Dutch Government allowed a special assistantship to be instituted for the mineralogical examination of clay, and this place was occupied by F. A. van Baren up to May 1937 and after his departure to the Dutch East Indies by J. Ch. L. Favejee.

Part of the work done by F. A. van Baren was devoted to the microscopical examination of the intermediate fractions of the clays; this investigation has been continued, but, as has already been remarked on p. 8, it is not yet finished; the work done by J. Ch. L. Favejee was entirely concerned with the X-ray examination.

As the Geological Laboratory at Wageningen did not until 1937 get the partial use of an X-ray apparatus for structure investigation, the photographs necessary for the examination were for a large part made with the aid of the apparatus of the Van 't Hoff Laboratory of the University of Utrecht. The measurements of the photographs were also made there. We wish to express our gratitude to Professor Dr E. Cohen, Director of the Van 't Hoff Laboratory in Utrecht, for offering us an opportunity of making the photographs in his Laboratory and to Dr N. H. Kolkmeyer, Head of the X-ray Department of this Laboratory, for his very much appreciated collaboration.

The following clays were chosen in order to get a first impression with regard to the occurrence of the clay minerals in the Dutch soils:

a. Marine clays. „Kwelder"silt outside Negenboerenpolder (Groningen).
Negenboerenpolder (Groningen).
Panserpolder (Groningen).
Bellingwolde (Groningen).
Wieringermeer (acid clay).
Bijleveldpolder (Zeeland).
Poppendamme (Zeeland).

b. Maas-clays. Echt (Limburg).
Hedel (Noord-Brabant).
Biesbosch (Noord-Brabant).
c. Miscellaneous. Loess (Limburg).
„Kleefaarde" (residual soil on limestone).
Fuller's earth (cretaceous) (Limburg).

As material for comparison we used: quartz (Kahlbaum), muscovite (Miask, Ural), kaolinite (McNamee Mine, near Langley, South Carolina), montmorillonite (Algeria) 1)). Also of the minerals the fractions $< 2\ \mu$ were used (only of quartz $< 1.5\ \mu$). Tables I–IV (copied from: FAVEJEE, 1939*a*) show their spacings and the numbers of an intensity scale. For comparison also the data of some other authors are mentioned (Key: ss = very strong; s = strong; m = medium; w = weak; ww = very weak; br = broad).

TABLE I α-QUARTZ

Number of the intensity scale	d measured	d 1) calculated	hkl	Number of the intensity scale	d measured	d 1) calculated	hkl
	–	5,39	001	9–10	1,285	1,285	104
22–23	4,25	4,25	100	12	1,253	1,253	302
8	3,71	(β)	101	6–7	1,226	1,226	220
28	3,34	3,34	101	12	1,196	1,197	213
	–	2,70	002			1,195	221
17	2,454	2,452	110		–	1,181	114
18	2,279	2,276	102	15	1,179	1,178	310
9	2,234	2,232	111	9	1,151	1,151	311
13	2,124	2,123	200		–	1,138	204
10–11	1,979	1,976	201		–	1,116	222
21	1,813	1,814	112		–	1,112	303
	–	1,798	003	11–12	1,079	1,079	312
15	1,668	1,668	202		–	1,079	005
	–	1,655	103		–	1,062	400
	–	1,605	210	9–10	1,044	1,045	105
20	1,537	1,538	211		–	1,041	401
7	1,448	1,450	113	8	1,033	1,032	214
3–4	1,415	1,415	300	8	1,013	1,013	223
	–	1,379	212		–	0,990	402
22	1,371	1,372	203	10	0,986	0,987	115
		1,369	301			0,985	313
	–	1,348	004				

1) $a = 4{,}903, \quad c = 5{,}393.$

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1) We wish to express our thanks to Prof. J. DE LAPPARENT for furnishing this sample.

TABLE II MUSCOVITE

Number of the intensity scale	d	Nagelschmidt (1937)		Grim (1937)	
		Intensity	d	Intensity	d
17	10,0	s	9,98	s	9,99
7	5,0	s	5,00	m	4,98
19	4,46	s	4,49	ss	4,47
				w	4,29
3	4,21				
				w	4,11
				ww	3,95
8	3,87	w	3,91	m	3,87
7	3,72	w	3,73	m	3,72
				ww	3,55
10	3,48	m	3,50	m	3,475
12	3,34	ss	3,33	ss	3,32
10	3,20	m	3,20	m-s	3,20
				ww	3,1
9–10	3,00	m	3,00	s	2,98
9	2,86	m	2,88	m	2,86
7	2,79	m	2,80	m	2,78
3	2,71				
				w	2,585
21	2,56	ss	2,57	ss	2,560
				w	2,49
7	2,464	w br	2,475	w	2,46
8	2,378	m	2,385	m	2,390 2,376
3	2,322				
7	2,231	w	2,28 1) 2,19	w br	2,245
4	2,196			w	2,185
11	2,127	s	2,134	m	2,14 2,13
3	2,068			ww	2,05
10	1,999	ss	1,995	s	1,991
6	1,961			w	1,95
2	1,839			ww	1,83
3	1,731	ww	1,730	w	1,76
2	1,685			w	1,654
12	1,643	s br	1,651	m	1,64
3	1,597			w	1,60
3	1,557	ww	1,546	w	1,55
2	1,524	ww	1,523	w	1,52
17	1,497	s	1,500	s	1,504
		ww	1,450		
		ww	1,421		
9	1,350	m	1,356 1) 1,337	m	1,354
5	1,335			w	1,335
11	1,294	m	1,296	w	1,295
3	1,270				
7	1,241	m	1,247	w	1,245
3	1,219				

1) Edges of broad line.

TABLE III

KAOLINITE

Number of the intensity scale	d	Nagelschmidt (1934)		Mehmel (1935)	
		Intensity	d	Intensity	d
23–24	7,1	ss	7,15	s	7,16
22	4,44	ss	4,46	m-s	4,39
19	4,17	s	4,17	m	4,17
8	3,84	m	3,86		
22	3,58	ss	3,61	s	3,56
4	3,39	w	3,36	w	3,36
		ww	3,09		
		ww	2,782		
18	2,55	s	2,570	m-s	2,55
17	2,50	s	2,502	m-s	2,48
21	2,337	ss	2,355	s	2,33
9	2,291	s	2,297	m-s	2,27
4	2,188	ww	2,205		
10	1,986	m	1,996	m-s	1,97
2	1,943	w	1,953		
2–3	1,891				
2–3	1,842	w	1,848	w	1,83
3	1,784	w	1,794	w	1,78
5	1,692				
16–17	1,660	ss	1,670 1)	s	1,65
6	1,619	m	1,623	m	1,61
2–3	1,580	ww	1,591		
5	1,537	w	1,547	m	1,53
18	1,486	s	1,493	s	1,48
4–5	1,452	ww	1,455		
		ww	1,396		
		ww	1,375		
4	1,336	m	1,344	w	1,34
5	1,304	m	1,311	m	1,30
6–7	1,282	m	1,287		
2–3	1,262				
9	1,234	m	1,243 1)		

1) Centre of broad line.

Of a number of other mineral species, X-ray photographs were made, but their data are not mentioned here, as these minerals were not present in the examined Dutch clay fractions.

As an example of the examined soil fractions the spacings of a riverclay (Maas-clay Hedel) are given (Table V) (qu = quartz, mu = = muscovite, ka = kaolinite, mo = montmorillonite).

TABLE IV MONTMORILLONITE

Number of the intensity scale	d	Nagelschmidt (1934)		Gruner (1935a)	
		Intensity	d	Intensity	d
28	15,3			8	15,0
11	5,1	s	5,05		
23–24	4,45	ss	4,45	3	4,45
8	4,26	ww	4,26		
		ww	3,74		
14–15	3,07	ss	3,03		
2–3	2,75			?	2,81
20–21	2,552	ss	2,534	2	2,535
12	2,497			?	2,43
		ww	2,341		
7	2,231	ww	2,24	0,5	2,228
		ww	2,16		
				0,5	1,851
13–14	1,691	m	1,689 1)	1	1,688
			1,652	1	1,643
19–20	1,492	ss	1,489	3	1,494
				0,5	1,415
13–14	1,288	m	1,288	1	1,285
9	1,244	m	1,239	0,5	1,241
		w	0,974		

1) Edges of broad line.

TABLE V MAAS-CLAY (HEDEL)

Number of the intensity scale	d	Mineral	Number of the intensity scale	d	Mineral
6	± 15 1)	mo	8	2,457	qu (mu)
9	10,0	mu	7	2,380	mu (ka)
5	7,2	ka	6	2,241	qu
4	5,9	Ca-oxal.	6–7	2,137	qu (mu)
4	5,2	mu	8–9	1,978	qu (mu)
	5,0		9	1,815	qu
18	4,47	mu(ka, mo)	8	1,672 2)	qu (mu)
12	4,23	qu	7	1,539	qu
4	3,73	qu (mu)	11–12	1,501	mu
5	3,60	ka	4	1,448	qu
20–21	3,35	qu (mu)	4	1,412	qu
5	3,20	mu	10	1,375	qu
5	2,96	mu	3	1,353	mu
5	2,83	mu	8–9	1,283	qu
17	2,57	mu			

1) Too indistinct for exact measuring.
2) Centre of broad line.

Although the method according to which the powder-photographs are obtained (the Debije-Scherrer-Hull method) is in principle very simple, it appeared clearly that in examining clay fractions a very accurate method should be followed and moreover all sorts of special precautions should be taken. This appeared among other things from the following. From the beginning we found in the X-ray photographs lines which could not be identified with those of one of the known minerals. It turned out that these lines belonged to the X-ray photograph of calcium oxalate, which occurred in the clays in consequence of the fact that we had dispersed the clays with sodium oxalate. The drawbacks of this admixture are not, it is true, unsurmountable, yet sufficient not to advise the sodium oxalate dispersion for clays in the X-ray analysis of soil.

Another difficulty was to identify montmorillonite. This mineral is characterized by the (001) interference, which has a very high spacing (about 15 Å). Owing to the presence of central blackening on the powder photographs this interference is hard to observe, so that montmorillonite in quantities smaller than 15% can in general not be detected with certainty. With the method at present applied in our Laboratory, worked out and described by one of the present writers (FAVEJEE, 1939*a*), with which the central blackening is avoided, it is possible to show 2–3% of montmorillonite.

From the examination of the above mentioned Dutch soils it has appeared that:

1. All the examined clay fractions contain quartz.
2. All the examined clay fractions contain muscovite as an important factor, with the exception of residual soil on limestone from South-Limburg.

It may be added, that the striking difference between loess and residual soil on limestone, which occur side by side in South-Limburg, may be considered as a new argument for the essential contrast consisting between the two formations.

The residual soil on limestone is geologically closely related to the clay with flints (argile à silex), well-known in England, Belgium and France and often chosen as material for studies in soil science (e.g. by MARSHALL). The lack of muscovite in the examined sample may be considered as a bridge between the opinions of foreign investigators who have often paid little or no attention to muscovite, and the Dutch and some German investigators, who have defended the importance of muscovite as a constituent of clays.

For it has now appeared that both groups are right as regards the material examined by them.

In our opinion the occurrence of muscovite in the Dutch clays has now been proved and we consider the discussion on this point as finished.

3. Nearly all the clay fractions examined contain montmorillonite in noticeable quantities. The old, almost forgotten occurrence of fuller's earth in the Cretaceous of South-Limburg is particularly rich in montmorillonite.
4. A slight content of kaolinite is characteristic of all the examined samples.
5. From the third publication in this series (HARDON and FAVEJEE, 1939) it will appear that a somewhat important content of metahalloysite could easily be established by means of the at present usual method, so that it is now certain that the Dutch clays examined by us do not contain the mineral halloysite (metahalloysite) in noticeable quantities.

These results show that, apart from the residual soil on limestone already dealt with, the examined Dutch clays are mixtures of the same four constituents. So the possible contrasts in composition between the Dutch clays can only be established by means of quantitative examination (FAVEJEE, 1939*b* and *c*).

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