Studies on the zeolites.

Part I.   General review.

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THE zeolites form a group of minerals of considerable interest by reason of their peculiar properties.   In particular, their remarkable continuous dehydration curves, in part reversible, and the ready base-exchange of some members have attracted attention.   But in spite of much work, many important characters remain quite uncertain.   Many of the zeolites show variations in composition which are not recognized or are incorrectly interpreted by the accepted formulae.   Optical investigation has all too rarely been made on analysed material, and little is known of the variation of the optical properties of most members with their composition, and practically nothing of the variations consequent on artificial base-exchange reactions.   In spite of much work, conflicting views are still held as to the interpretation of the dehydration results.   In some instances even the crystal-system is still uncertain.

In these circumstances the extensive series of zeolites in the British Museum collection, recently greatly augmented by Mr. F. N. Ashcroft, invites detailed study, and it is the author's purpose to take the various species one by one, making thorough optical and physical studies of analysed material and endeavouring to trace regularities in the variation in composition.   In many cases the material studied will be the same as that used by Prof. W. L. Bragg and his co-workers in their studies of crystal-structure.

Before coming to the detailed examination of the various species, it seems desirable to review shortly the general characteristics of the zeolites, and their relations to other groups of minerals and to certain artificial products.

The zeolites form a well-defined group, generally regarded as hydrated silicates of aluminium and the alkalis or alkaline earths, with the notable characteristic that the molecular ratio Al_2O_3: $(Ca,Sr,Ba,Na_2,K_2)O$ is always equal to unity. (Some authors include hydrated silicates such as apophyllite, which contains little or no alumina, and laubanite, in which the above ratio is not equal to unity, but these lack some of the characteristic properties of the zeolites proper, and are best regarded as a separate group.) It follows from this characteristic that $O/(Al + Si) = 2$; indeed the two ratios are only different ways of expressing the same thing. The former relation has been most generally recognized, but the latter has the advantage of being more related to the crystal-structure.

As Prof. W. L. Bragg has pointed out in a lecture before this Society (March, 1930), the silicates are in general built up of kations of the stronger bases, together with anions composed of silicon and oxygen, or of silicon, aluminium, and oxygen (boron and trivalent iron, chromium, and vanadium may probably also take part in the anion), and hydroxyl groups or water molecules. The anion is a non-polar bonded structure, in which silicon (or aluminium) and oxygen alternate, and may be a small, finite group, or may be infinitely extended in one, two, or three dimensions (strings, sheets, or blocks).

The last case is characterized by the ratio $O/(Al + Si) = 2$. It is exemplified by the various forms of silica; but kations cannot enter into such a structure unless alumina or other trivalent atoms replace part of the silicon, when kations enter to balance the electrovalence.

Mr. W. H. Taylor (1930) has shown that analcime does indeed exemplify such a structure. It consists of an infinite tridimensional anion in which silicon or aluminium and oxygen alternate, forming an open framework within which sodium ions and water molecules are arranged. The meshes of the anion framework are large enough to permit the passage of the water molecules and sodium ions, thus allowing of dehydration and base-exchange, while the strong non-polar bonds of the framework permit these reactions to take place without destruction of the structure.

A similar type of structure is probable for the other zeolites. On this basis, the zeolites may be defined as hydrated aluminosilicates of the alkalis and alkaline earths, having an indefinitely extended tri-, dimensional anion, in consequence of which the atomic ratio $O/(Al + Si) = 2$. In most of them the composition varies considerably,

and in many the ratio Si/Al is variable, a fact not brought out by the usually accepted formulae, but the best analyses always show a close agreement with the above condition.

If such a view of the constitution of the zeolites be accepted, then apart from variations of the water-content two main variations are possible. On the one hand, the kations may vary, Ca being replaced by Sr or Ba, Na_2 or K_2, or vice versa. Until recently, this has been recognized as the principal variation in composition. But since Si and Al are structurally equivalent to a marked degree (see, for example, W. L. Bragg, 1930), variations in the Si/Al ratio are equally possible, provided the electrovalence is kept balanced by corresponding kationic variation.

This variation has commonly been overlooked altogether, or attributed to the presence of a few trisilicate (Si_3O_8) or disilicate (Si_2O_5) groups in place of orthosilicate (SiO_4) or metasilicate (SiO_3) groups—finite groupings of a kind which Prof. Bragg has shown to exist in a small minority of silicates only. G. Friedel (1896) suggested that a part at least of the silica in zeolites was present as adsorbed SiO_2 molecules, having no more essential function than he assigned to the water. He supported his view by experiments in which the silica content of a zeolite was changed by treatment with alkali silicate solutions. These experiments are probably to be explained by deposition of silica gel in cleavage and other fissures of the crystal. They may have a significance in the interpretation of the natural zeolites, but it is impossible to say how much, without very full studies of the variation in optical and other physical properties with the composition.

Recently, in 1925, A. N. Winchell has recognized the variation in the Si/Al ratio in some zeolites, and has pointed out that to a marked degree the increase of this ratio is accompanied by a replacement of alkaline earths (Ca,Sr,Ba) bv alkalis (Na,K), thus constituting an isomorphic replacement of the type familiar in the felspars, $CaAl \gtrless NaSi$. In the author's opinion, however, Winchell has underestimated the extent of the replacement $Ca \gtrless Na_2$, partly, perhaps, because in his care to exclude all doubtful analyses, he has restricted himself to a very small number of good analyses. If the replacement were strictly of the felspathic type, the number of kationic atoms in the unit cell would be constant. It will be the author's task to show that in many instances this is far from being the case, with material of unquestionable purity.

The author's theory is that the Si/Al ratio in a zeolite is governed principally by the Si/Al ratio in the magmatic solution from which it was deposited. The ratio of alkaline earths to alkalis (contracted for convenience to Ca/Na) is also, naturally, governed to some extent by the corresponding ratio for the solution, but it is markedly affected by a tendency for the number of kationic atoms in the unit cell to attain a characteristic integral value. As a rule, these two factors will clash more or less, and it is possible that the Si/Al ratio may be slightly modified in consequence.

But the actual Ca/Na ratio found in any specimen will not necessarily be that for the material as originally deposited, since the subsequent action of solutions may result in a replacement of Ca by Na_2 or vice versa. And not only may subsequently penetrating solutions alter the ratio, but so may the mother-liquor which laid down the zeolite, for the Ca/Na ratios in the solution and the crystal in equilibrium are not necessarily the same, so that Ca or Na may accumulate in the mother-liquor.

It is a possible explanation of the more markedly constant number of kations per unit cell found by Winchell that his carefully selected analyses included few of material that had been exposed to this subsequent action. For the action would probably also tend to render the material impure, and so exclude it from Winchell's consideration. If this is true, Winchell's curves enable us to eliminate the effect of subsequent action to a considerable degree, and offer us an indication of the great influence of the tendency to a constant number of kations.

Zeolites that do contain (within the limits of experimental error) the number of kations per unit cell characteristic for their species will be referred to as *Normal* zeolites.

It is to be emphasized that in consequence of their anion extending through the crystal, and its very strong, non-polar bonded structure, the zeolites cannot be expected to show the same behaviour as the great majority of inorganic salt hydrates. It is to the stability of this anion and its open structure that the remarkable dehydration phenomena are due, the one maintaining the structure after removal of the water, the other permitting the removal without disturbance of the structure. The same structural characteristics are also responsible for the notable hardness of the zeolites.

The dehydration relations are probably really fairly simple, as has been increasingly brought out by recent work. In some zeolites the

water may probably be all removed without any discontinuity at all; as dehydration proceeds, there is a tendency for the whole structure to shrink somewhat, provided the temperature is maintained high enough for a long enough period, and after such shrinkage, the re-absorption of water is prevented, or at least slowed. If, however, the dehydration is carried out at a low temperature in vacuo, the lattice-shrinkage ('Gitterreaktion') of Rinne (1920) and Scheumann (1921) is largely or entirely avoided, and the rehydration is rapid.

The dependence of the reversibility on the thermal history has been one of the most puzzling things about the dehydration phenomena of the zeolites, but there can be little doubt that Rinne's idea of a lattice-shrinkage, the reaction-velocity of which is, at least for moderate temperatures, lower than the velocity of dehydration under the usual experimental conditions, offers the correct explanation. The structure remains fundamentally the same during both dehydration and lattice-shrinkage, but this does not exclude quite appreciable continuous migrations of the various atoms in so far as they have variable parameters.

Apart from the lattice-shrinkage, such a continuous dehydration is simply an instance of the possible but uncommon case where a hydrate and the corresponding anhydrous salt form mixed crystals.[1] That the water molecules probably have definite positions in the unit cell is shown by W. H. Taylor's X-ray study (1930) of analcime and dehydrated analcime.

While such a theory probably represents all the behaviour in some cases, there are others (e.g. natrolite, scolecite, and mesolite) in which the most recent work, mainly that of A. Cavinato (1927), has

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[1] An instance of a hydrate which forms mixed crystals with a lower hydrate was first noted by H. Buxhoevden and G. Tammann (1897) in magnesium platinocyanide ($MgPtCy_4.7-6H_2O$), and its dehydration studied by G. Tammann (1897). G. Wyrouboff (1900) added two examples, sodium ammonium ferri- and alumino-oxalates, $Na_3Am_3Fe_2(C_2O_4)_6.7-5H_2O$ and $Na_3Am_3Al_2(C_2O_4)_6.7-5H_2O$. E. Löwenstein (1909) added further instances, oxalates of some of the rare-earths, a basic oxalate of zirconium, and strychnine sulphate ($6-0H_2O$). This list includes, in strychnine sulphate and the rare-earth oxalates, definite cases where the hydrate is miscible with the anhydrous salt. The basic zirconium oxalate (a definite crystalline compound) is especially remarkable because its crystals, when immersed in water or suspended in water vapour at a sufficient pressure, can swell to some eight times their original bulk without losing their sharpness of outline or birefringence. In this they resemble the crystallized proteins studied by A. F. W. Schimper (1881). These 'swelling' crystals are deserving of much more detailed study, and perhaps constitute an extreme (and readily reversible) case of the 'Gitterreaktion' or lattice-shrinkage.

indicated that there is a discontinuity. Here it is probable that we have relations corresponding to an interrupted series of mixed crystals. Up to a certain point the dehydration proceeds continuously, a mixed crystal of hydrate and anhydrous salt (or lower hydrate) forming. But when a certain temperature is reached, this mixed crystal becomes unstable with respect to another, in which the anion has practically the same atomic positions, but the positions of the kations and the number and positions of the water molecules have altered, often considerably. Water is lost suddenly, there is a sharp break in the dehydration curve and optical properties, and the crystal-system may change. But because of the bonded structure of the anion, its constituent atoms may shift their positions slightly to fit in with a different symmetry, without the crystal disintegrating; α- and β-quartz exemplify such a change. This new mineral then exhibits the same continuous dehydration as the original material, proceeding to form mixed crystals with its anhydrous salt. It is also possible that a transformation might occur without change in the water content, and this may yet be met with in the less-studied zeolites.

While this theory seems to the author to be the only one that satisfactorily outlines all the relations of the zeolites and their dehydration products, other views have been and are held. The property of continuous dehydration and reabsorption, discovered and further studied by A. Damour (1857, 1858) was at first merely regarded as a curious fact and no explanation attempted. But when the constancy of the vapour-pressure of hydrated salts had been demonstrated, and the phase rule came to be generally applied in physico-chemical studies, the peculiar position of the zeolites was realized.

The continuity of the dehydration was emphasized by the continuity of the concomitant optical changes, and E. Mallard (1882) compared the zeolites to a sponge which merely imbibed water in its pores. This view was also adopted by G. Friedel (1896) when he found that dehydrated zeolites will absorb other vapours in place of water—carbon dioxide, hydrogen, alcohol, hydrogen sulphide, silicon fluoride, and even air. In various forms it has been adhered to by G. Bodländer (1898), E. Sommerfeldt (1902), C. Doelter (1905), F. Zambonini (1905, 1906, 1908), and others.

Sommerfeldt believed he had proved that analcime was an adsorption product and not a true hydrate or mixed crystal when he

found a lower experimental value for the heat of rehydration than he had calculated; but Zambonini (1906) showed that the material had probably rehydrated little or not at all, so that the basis of his argument vanishes.   Zambonini himself (1905, 1906) bases his conclusions largely on the fact that the reversibility is not perfect, time and temperature of dehydration affecting it.   This effect is probably due simply to the lattice-shrinkage.   The contraction on dehydration had already been noted for analcime by G. Friedel (1896).   The possibility of a dehydrated zeolite absorbing more water than it set out with, when initial conditions are restored, is simply due to adsorption on the walls of the fissures invariably present in large numbers when dehydration has been carried to any extent.   These eventually fill with liquid water.[1]

Following on his discovery of the continuous dehydration of $MgPtCy_4.7–6H_2O$, G. Tammann (1897) formulated the view above adopted, that zeolites are essentially mixed crystals of hydrate and anhydrous salt.   He pointed out a distinction between the behaviour of zeolites and of silica gels, to which many observers have compared them.   The former show irreversibility only after considerable dehydration, whereas the gels only show reversibility at small degrees of hydration.   F. Rinne (1899, 1913, 1920) agreed with Tammann, and E. Löwenstein (1909) adduced further evidence for this view.

Löwenstein pointed out that if a percentage-of-water : vapour-pressure curve is drawn for any temperature for one of the crystallized hydrates of zeolitic behaviour (zeolites, oxalates of the rare-earths, &c.) the curve is concave to the pressure axis (d^2p/dc^2 is positive), whereas for the colloids such as silica gel, clays, or the ferrocyanides of zinc and copper, it is convex (d^2p/dc^2 is negative).   More strictly, the curve is S-shaped, and this criterion applies to the more advanced stages of the dehydration. $MgPtCy_4.7–6H_2O$ forms an apparent exception, the curve being convex to the pressure axis, but this is probably because only the first half of the S, so to speak, can be

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[1] Thus if 2 grams natrolite (volume 1 c.c. approx.) have absorbed 3 % extra water, this corresponds to fissures of volume 0·06 c.c.   To cause opacity, the fissures must have been about $100\mu\mu$ wide at least.   (An absorption of any appreciable amount of extra water will not occur unless dehydration has been carried well beyond the point at which it produces opacity.)   If this is taken as the width of the fissures, they will divide the crystal into fragments of about 0·1 mm. size; study shows that fissures of such number and dimensions may quite reasonably be assumed.

observed, breakdown to the pentahydrate preventing observation of the point of inflexion.

F. Grandjean (1910) extended the list of substances which dehydrated zeolites will absorb to include iodine, mercury, sulphur, and cinnabar, and noted that the products are often pleochroic, which led him to adopt the solid solution theory. It is not every vapour or liquid, however, that can be absorbed. Thus O. Weigel and E. Steinhoff (1925) found that while chabazite will absorb ethyl and methyl alcohols and formic acid, it does not absorb ether, benzene, or acetone, the molecules of which are probably too large to pass through the meshes of the anionic net. Oils, too, merely fill all crevices and fissures, but are not taken up into the crystal-structure. Further, some vapours and gases are much more readily absorbed than others ; thus R. Seeliger (1921) found that nitric oxide and ammonia were absorbed far more readily than other gases of comparable boiling-points. R. Nacken and W. Wolff (1921) have also studied the absorption of gases by dehydrated chabazite.

O. Weigel (1924) has put forward a formula enabling him to calculate the absorption to be expected for any molecule which will pass the meshes of the silicate net, but it requires much more testing ; and it may be remarked that although he develops it on the assumption that the water and other molecules have not definite positions in the crystal-structure, this assumption is not strictly necessary. The fact that other vapours than water can be absorbed is, of course, simply due to the residual affinity of the anhydrous structure ; if the latter has undergone shrinkage, this largely satisfies the affinities within the structure itself, and neither other vapours nor water can be absorbed. The absorption will also be affected by the polarity of the molecules offered for absorption, the more polar ones, with greater free affinity, being more absorbed, provided, of course, that they can pass the meshes of the silicate net.

An entirely different view of the condition of the water in zeolites has been put forward by A. Beutell and his co-workers (A. Beutell and K. Blaschke, 1915 ; G. Stoklossa, 1918; A. Beutell, 1921). These observers consider that the continuous dehydration curve does not correspond to equilibria, but is influenced by ' cohesion' effects. Rehydration curves are not so invalidated, and by a study of these, it is concluded that the zeolites are simply hydrates of the normal type, the rehydration proceeding step-wise. For each species a large number of hydrates are established. Other workers (O. Weigel,

1919, 1921; K. H. Scheumann, 1921) have shown that it is these rehydration curves that do not correspond to true equilibria, and have succeeded in attaining the equilibrium curve from both sides (within the reversible range). The rehydration curves of false equilibrium are not, however, without their significance, for they show a marked fall in the velocity of rehydration at points corresponding to integral numbers of water molecules, probably indicating a slightly enhanced stability of such compositions due to their more perfect homogeneity.

The other most characteristic property, distinguishing zeolites from most other minerals and most other hydrates, is their capacity for base-exchange. Like the dehydration phenomena, this property is consequent on their peculiar structure, the strong, stable anion with its open build permitting a mobility of the kations, which is demonstrated by their high electrical conductivity as compared with most other solid salts, as well as by the base-exchange.

The electrical conductivity of a number of zeolites has been measured by O. Weigel (1923). He interprets his observations as indicating that the kations play no part in the conduction, which he attributes to the water. But the matter requires much further investigation, for his values are not of the same order as those of Günther-Schulze (1914), who confirmed his measurement of the electrical conductivity of natrolite by measurements of the velocity of base-exchange.

Weigel found that the resistance is greatly increased by slight dehydration, and bases his conclusion largely on this. ·Günther-Schulze found the same effect for permutite, an artificial product closely allied to the zeolites. But he demonstrated conclusively that in this case the kations are responsible for the conduction, since on electrolysis of dry sodium-permutite between copper electrodes, a layer of blue copper-permutite was formed at the anode. The present author has attempted to repeat this experiment with zeolites (heulandite, natrolite) but without success, owing probably to the much lower conductivity of the zeolites.

The increase of resistance on slight dehydration is probably due to a decreased mobility of the kations, the attraction of the anionic complex being increased by the removal of the highly polar water. And the increase in the resistance with time, when the zeolite is electrolysed between dry electrodes, is probably due to the formation of a thin layer of electrolysis products at each electrode, imposing

a high film resistance. That removal of the water does decrease the mobility of the kations is shown by the observation of A. Beutell and K. Blaschke (1915), that after dehydration to the irreversible stage, zeolites almost lose the property of base-exchange. Lattice-shrinkage may also account for part of the loss.

The phenomenon of base-exchange was first discovered by J. T. Way (1850, 1852, 1854) as a property of soils. H. Eichhorn (1858) found that it is shared by zeolites, and satisfied himself that when a zeolite is treated with a salt solution, there is simply an inter-change of kations in equivalent amounts; the anion remains unabsorbed ; and, provided the salt is either neutral or alkaline in reaction, the zeolite is not decomposed, losing neither silica nor alumina.

H. Schneiderhöhn (1915) has summarized and criticized the extensive studies of J. Lemberg (1876, 1877, 1883, 1885) and S. J. Thugutt (1892, 1895) and concludes that they are of little value, since most of the products were amorphous, and it is often quite uncertain how far any of them were homogeneous.

E. Löwenstein (1909) showed that a number of potassium-zeolites had higher vapour-pressures for the same temperature and water-content than had the corresponding natural calcium salts ; and that on re-converting the potassium salts to the calcium salts, the original vapour-pressures were restored.

I. Zoch (1915) made a thorough study of the base-exchange of stilbite, and demonstrated that the reaction is not complete, but leads to a definite equilibrium between the kations involved in the solution and in the crystal. His studies are the first to show defi-nitely that the anion really remains unaffected by the base-exchange, the material retaining its crystalline nature, while the optical properties change in a continuous manner, the original optical properties returning in all respects when the original composition is restored. This important point the work of F. W. Clarke and G. Steiger (1899, 1900, 1902, 1905) lacks, though they showed many of their products to be homogeneous and crystalline. They studied the action of fused silver and thallium nitrates and of dry ammonium chloride, and obtained many interesting products, but an optical study of these silver-, thallium-, and ammonium-zeolites is very desirable. That ferrous and silver salts will partake in base-exchange with zeolites was shown by K. Dalmer (1878) and A. H. Church (1899) respectively.

The action of solutions of acid-reacting salts was studied by H. Kappen and B. Fischer (1928), who found that $FeCl_3$, $AlCl_3$, and $ZnCl_2$ give no base-exchange, their activity leading to complete decomposition of the zeolite. Ferrous and copper salts, on the other hand, gave a true base-exchange, at least with the less acid-sensitive zeolites. These workers were mainly interested in the exchange-acidity, that is the acidity, titratable by alkali, communicated to a neutral salt solution when it is digested with a zeolite that has been treated with acid or an acid-reacting salt. This phenomenon, discovered by G. Daikuhara (1914), has not yet been properly explained. At first sight, one would imagine hydrogen is participating in the base-exchange and giving a hydrogen-zeolite, which reacts with the neutral salt solution with liberation of free acid. But Daikuhara showed that the salt solution after digestion contains alumina; and Kappen and Fischer found the amount of the latter such that its precipitation accounts for almost or quite the whole of the alkali used in titration. Moreover, analyses by Kappen and Fischer of zeolites before and after acid-treatment show a considerable loss of alumina, but curiously enough, only a small loss of alkalis or alkaline earths when small quantities of dilute acid are used.

With stronger acid,[1] the alumina and bases are totally removed, and a silica gel remains. F. Rinne (1896, 1897, 1902) found that with certain of the more siliceous zeolites (heulandite, stilbite, brewsterite, harmotome, and chabazite) this silica remains coherent and has distinct birefringence, and quite definite optical properties which remain even after ignition. G. Tschermak and his pupils (1903, 1905, 1906, 1908, 1909, 1912) also studied these silica gels, and found that when desiccated at the ordinary temperature, there is a fairly sharp break in the velocity of dehydration. They analysed the material at this point, and took it to represent the particular silicic acid of the zeolite studied. Their results were adversely criticized, with some justice, by O. Mügge (1908) and J. van Bemmelen (1908), and especially by M. Theile (1913). It is, however, probable that they are not without significance in those cases where the silica gel has definite optical properties.

If all the alumina and kations are eliminated, the product will not be coherent unless the Si/Al ratio is high enough. A simple consideration shows that if the ratio is 1 or less, each silicon will be

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[1] Strong sulphuric acid, however, only effects a partial dehydration, without decomposition, at least in many cases (F. Rinne, 1896, 1897).

isolated, and the gel cannot be coherent—indeed a sol rather than a gel is likely to be formed. With a Si/Al ratio of 3 or more, on the other hand, the elimination of the alumina will leave a network of silicon and oxygen, which is likely to be sufficiently rigid to retain definite crystalline and optical characters. And it is precisely the zeolites with this ratio which yield such stable skeletons.

While there is no evidence for the existence of hydrogen-zeolites, the free acids may be prepared in one series which in some respects is related to the zeolites. The clays[1] are also aluminosilicates, and they exhibit the phenomena of base-exchange in an even more striking degree than do the zeolites. On the whole, very little is known about them, but they appear to be of a micaceous structure, and are perhaps based on infinite two-dimensional anions. In the property in which they are most comparable to the zeolites—the base-exchange—they show two important differences, the capacity to form free acids, and the ability to take up large kations, such as the methylene blue ion, a property which the zeolites lack. Genetically, they are derived from the breakdown under weathering of felspars, and perhaps also of micas, whereas the zeolites form one of the last deposits from magmatic solutions. The dehydration of the clays has been less studied. E. Löwenstein (1909) studied some of the clay-minerals, and came to the conclusion that they contain no water of zeolitic behaviour, but only adsorbed water and firmly combined water. The latter is presumably present as hydroxyl groups, and constitutes the acidic water of these acids. Löwenstein's conclusions, however, have not been accepted generally. Practically no study of the soil-clays in this respect has been made.

More closely related to the zeolites are the ultramarines, the permutites, and the artificial ' zeolites ' first prepared by J. T. Way (1850, 1852). The ultramarines, including not only the wide group of artificial products, but also the natural minerals lazurite, nosean,

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[1] Mineralogists in the past have tended to confine the clays to a group composed of silica, alumina, and water only, abandoning the study of the wider group of soil-clays to agriculturalists. Recent developments (see, for example, S. B. Hendricks and W. H. Fry (1930); C. E. Marshall (1930)) have shown that the soil-clays are mixtures containing definite salts of isolable acids, and that the acids are probably, in part at least, to be identified with the clay-minerals. Collaboration of mineralogists and colloid chemists in this field is particularly desirable, for there can be little doubt that the clays with their ready base-exchange play an appreciable part in maintaining conditions favourable to plant-life in the portion of the earth's crust of greatest importance to mankind —the soil.

haüyne, and sodalite, have a structure very similar to that of the zeolites; but in place of mobile water, they have mobile anions $(Cl',SO_4'',S_3'', \&c.)$ and the concomitant kations $(Na',K',Ag',Ca'',Ba'', \&c.)$. They show a ready exchange of both anions and kations (F. M. Jaeger, H. G. K. Westerbrink, and F. A. van Melle, 1927; F. M. Jaeger and F. A. van Melle, 1927, 1929; F. M. Jaeger, 1929).

The permutites, discovered by R. Gans (1905, 1906) have been very widely studied, but with very little result from the mineralogical point of view. Prepared by the fusion of kaolin with sodium carbonate and leaching the product with water, they have similar compositions to the zeolites, having the ratio $Al_2/(Na_2,Ca) = 1$ (whence $O/(Al,Si) = 2$), and a variable Si/Al ratio[1] in the neighbourhood of $1\frac{1}{2}$–2. In base-exchange they resemble the zeolites, except that the velocity of reaction is far greater, in accordance with the greater velocity of kationic diffusion and greater electrical conductivity, as observed by Günther-Schulze (1914). As with the zeolites, and unlike the clays, large ions (e. g. methylene blue, or the tetramethylammonium ion) and hydrogen cannot partake in the exchange. Their dehydration does not appear to have been studied. No crystalline structure has been detected, but the grains are coherent, and appear as a rule very free from fine fissures or pores, though of a coarsely porous structure. For methylene blue only stains a very thin skin on the surface, without penetrating the grains (G. Weigner and K. Müller, 1929). This rather suggests that they are perhaps 'amorphous' zeolites, not devoid of structure, but devoid of symmetrical arrangement, consisting of an infinite tridimensional anion of Al, Si, and O, together with kations and water molecules, precisely like the zeolites, but without the regular arrangement of the Al atoms and kations which gives the latter their crystalline character.

Lastly, the 'artificial zeolites' prepared by J. T. Way (1850, 1852), H. Deville (1862), and B. von Ammon (1862), by the interaction of solutions of sodium aluminate and sodium silicate, sodium aluminate and silica gel, or sodium silicate and alumina or aluminium salts, are also related to the zeolites in many ways. They have been little studied (cf. R. Gans (1906), and F. Singer (1910)), but some work has recently been done by P. S. Burgess and W. T. McGeorge

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[1] F. Singer (1910) prepared permutites with Si/Al ratios up to 10, and also replaced Al by B,V,Mn,Fe, and Co, and Si by Ti and Pb, while for Na he substituted K,Am,Mn,Ni,Ca,Cu,Ba, and Ag.

(1927), who rediscovered them, and by O. C. Magistad, (1928, 1929). They also have the ratio $O/(Al,Si) = 2$, but the Si/Al ratio varies over a much smaller range than in the permutites, for a large variation in the Si/Al ratio for the solution. Their base-exchange relations closely resemble those of the zeolites and permutites. Structurally nothing appears to be known about them. They may perhaps be identical with the permutites, or they may be a colloidal mixture of zeolites. In either case, they will undoubtedly repay further study.

Bibliography.

1850   J. T. WAY, Journ. Roy. Agric. Soc., vol. 11, p. 313.
1852   J. T. WAY, Journ. Roy. Agric. Soc., vol. 13, p. 123.
1854   J. T. WAY, Journ. Roy. Agric. Soc., vol. 15, p. 491.
1857   A. DAMOUR, Compt. Rend. Acad. Sci. Paris, vol. 44, p. 975.
1858   A. DAMOUR, Ann. Chim. Phys., ser. 3, vol. 53, p. 454.
—   H. EICHHORN, Ann. Phys. Chem. (Poggendorff), vol. 105, p. 130.
1862   B. VON AMMON, [Inaug.-Diss., Köln, 1862], Jahresber. Chem. (Kopp and Will), 1862, p. 138.
—   H. SAINTE-CLAIRE DEVILLE, Compt. Rend. Acad. Sci. Paris, vol. 54, p. 324.
1876   J. LEMBERG, Zeits. Deutsch. Geol. Gesell., vol. 28, p. 519.
1877   J. LEMBERG, Zeits. Deutsch. Geol. Gesell., vol. 29, p. 457.
1878   K. DALMER, Neues Jahrb. Min., p. 257.
1879   W. FRESENIUS, Zeits. Kryst. Min., vol. 3, p. 25.
1881   A. F. W. SCHIMPER, Zeits. Kryst. Min., vol. 5, p. 131.
1882   E. MALLARD, Bull. Soc. Min. France, vol. 5, p. 255.
1883   J. LEMBERG, Zeits. Deutsch. Geol. Gesell., vol. 35, p. 557.
1885   J. LEMBERG, Zeits. Deutsch. Geol. Gesell., vol. 37, p. 959.
1892   S. J. THUGUTT, Zeits. Anorg. Chem., vol. 2, p. 65.
1894   F. W. CLARKE, Amer. Journ. Sci., ser. 3, vol. 48, p. 187.
1895   S. J. THUGUTT, Neues Jahrb. Min., Beil.-Bd. 9, p. 554.
1896   G. FRIEDEL, Compt. Rend. Acad. Sci. Paris, vol. 122, p. 1006; Bull. Soc. Franç. Min., vol. 19, p. 94.
—   F. RINNE, Neues Jahrb. Min., vol. 1, p. 24,
1897   H. BUXHOEVDEN and G. TAMMANN, Zeits. Anorg. Chem., vol. 15, p. 319.
—   F. RINNE, Neues Jahrb. Min., vol. 1, p. 40.
—   F. RINNE, Neues Jahrb. Min., vol. 2, p. 28.
—   G. TAMMANN, Ann. Phys. Chem. (Wiedemann), vol. 63, p. 16.
—   G. TAMMANN, Zeits. Physik. Chem., vol. 27, p. 325.
1898   G. BODLÄNDER, Neues Jahrb. Min., Beil.-Bd. 12, p. 52.
1899   A. H. CHURCH, Min. Mag., vol. 12, p. ix.
—   F. W. CLARKE and G. STEIGER, Amer. Journ. Sci., ser. 4, vol. 8, p. 245; Zeits. Anorg. Chem., vol. 23, p. 135.
—   F. RINNE, Neues Jahrb. Min., vol. 1, p. 1.
1900   F. W. CLARKE and G. STEIGER, Amer. Journ. Sci., ser. 4, vol. 9, pp. 117, 345; Zeits. Anorg. Chem., vol. 24, pp. 135, 139.

1900 G. Wyrouboff, Bull. Soc. Franç. Min., vol. 23, p. 65.

1902 F. W. Clarke and G. Steiger, Amer. Journ. Sci., ser. 4, vol. 13, p. 27; Zeits. Anorg. Chem., vol. 29, p. 338; Bull. U.S. Geol. Survey, no. 207.

— F. Rinne, Centr. Min., p. 594.

— E. Sommerfeldt, [Habilitationsschrift, Tübingen, 1902]. Quoted by F. Zambonini, 1906 (see below).

— G. Steiger, Amer. Journ. Sci., ser. 4, vol. 14, p. 31.

1903 A. Johnsen, Neues Jahrb. Min., vol. 2, p. 130.

— G. Tschermak, Sitzungsber. Akad. Wiss. Wien, Math.-naturwiss. Kl., Abt. I, vol. 112, p. 355.

1905 F. W. Clarke, Zeits. Anorg. Chem., vol. 46, p. 197.

— C. Doelter, Physikalisch-Chemische Mineralogie (Leipzig, 1905), p. 179.

— R. Gans, Jahrb. Preuss. Geol. Landesanst., vol. 26, p. 179.

— G. Steiger, Bull. U.S. Geol. Survey, no. 262, p. 75.

— G. Tschermak, Sitzungsber. Akad. Wiss. Wien, Math.-naturwiss. Kl., Abt. I, vol. 114, p. 455; Zeits. Physik. Chem., vol. 53, p. 349.

— F. Zambonini, Atti (Mem.) Accad. Lincei, Cl. Sci. fis. mat. nat. Roma, ser. 5, vol. 5, p. 344.

1906 R. Gans, Jahrb. Preuss. Geol. Landesanst., vol. 27, p. 63.

— G. Tschermak, Sitzungsber. Akad. Wiss. Wien, Math.-naturwiss. Kl., Abt. I, vol. 115. p. 217.

— F. Zambonini, Atti (Mem.) Accad. Lincei, Cl. Sci. fis. mat. nat. Roma, ser. 5, vol. 6, p. 102.

1908 J. van Bemmelen, Zeits. Anorg. Chem., vol. 59, p. 225.

— O. Mügge, Centr. Min., pp. 129, 325.

— G. Tschermak, Centr. Min., p. 225.

— F. Zambonini, Atti Accad. Sci. Fis. Mat. Napoli. ser. 2, vol. 14, pp. 88, 116, 297.

1909 F. Löwenstein, Zeits. Anorg. Chem., vol. 63, p. 69.

— G. Tschermak, Zeits. Anorg. Chem., vol. 63, p. 230.

1910 F. Grandjean, Bull. Soc. Franç. Min., vol. 33, p. 5.

— F. Singer, Dissertation, Berlin. 1910. 'Ueber künstliche Zeolithe.'

1912 G. Tschermak, Sitzungsber. Akad. Wiss. Wien, Math.-naturwiss. Kl., Abt. II b, vol. 121, p. 1087.

1913 F. Rinne, Fortschr. Min. Krist. Petr., vol. 3, p. 159.

— M. Theile, [Inaug.-Diss., Leipzig, 1913], Neues Jahrb. Min., 1915, vol. 1, Ref. p. 16.

1914 G. Daikuhara, Bull. Imp. Centr. Agric. Exp. Stat. Japan, vol. 2, p. 1.

— A. Günther-Schulze, Zeits. Physik. Chem., vol. 89, p. 168.

1915 A. Beutell and K. Blaschke, Centr. Min., pp. 4, 142, 195. [Min. Abstr., vol. 1, p. 153.]

— H. Schneiderhöhn, Neues Jahrb. Min., Beil.-Bd., 40, p. 163. [M.A. 1–234.]

— I. Zoch, Chemie der Erde, vol. 1, p. 219. [M.A. 4–371.]

1917 G. Tschermak, Sitzungsber. Akad. Wiss. Wien, Math.-naturwiss. Kl., Abt. I, vol. 126, p. 541. [M.A. 2–302.]

1918 G. Stoklossa, Neues Jahrb. Min., Beil.-Bd. 42, p. 1. [M.A. 1–153.]

— G. Tschermak, Sitzungsber. Akad. Wiss. Wien, Math.-naturwiss. Kl., Abt. I, vol. 127, p. 177. [M.A. 2–302.]

1919 O. Weigel, Sitzungsber. Gesell. Naturwiss. Marburg, p. 48. [M.A. 2–57.]

1920   F. Rinne, Ber. Sächs. Akad. Wiss. Leipzig, Math.-phys. Kl., vol. 72, p. 12. [M.A. 4–372.]

1921   A. Beutell, Centr. Min., pp. 694, 721. [M.A. 2–57.]

—   R. Nacken and W. Wolff, Centr. Min., pp. 364, 388. [M.A. 2–56.]

—   K. H. Scheumann, Ber. Sächs. Akad. Wiss. Leipzig, Math.-phys. Kl., vol. 73, p. 3. [M.A. 4–372.]

—   R. Seeliger, Physikal. Zeits., vol. 22, p. 563. [M.A. 4–373.]

1922   O. Weigel, Centr. Min., pp. 164, 201. [M.A. 2–57.]

1923   O. Weigel, Zeits. Krist., vol. 58, p. 183. [M.A. 2–300.]

1924   O. Weigel, Sitzungsber. Gesell. Naturwiss. Marburg, p. 107. [M.A. 4–373.]

1925   O. Weigel and E. Steinhoff, Zeits. Krist., vol. 61, p. 125. [M.A. 2–528.]

—   V. Rothmund, Rec. Trav. Chim. Pays-Bas, vol. 44, p. 329.

—   A. N. Winchell, Amer. Min., vol. 10, pp. 88, 112, 145, 166. [M.A. 3–13.]

1926   V. Rothmund, Zeits. Elektrochem., vol. 32, p. 367.

1927   P. S. Burgess and W. T. McGeorge, Univ. Arizona, Coll. Agric. Techn. Bull., no. 15.

—   A. Cavinato, Atti (Mem.) R. Accad. Lincei, Cl. Sci. fis. mat. nat. Roma, ser. 6, vol. 2, p. 320. [M.A. 4–320.]

—   F. M. Jaeger, H. G. K. Westerbrink, and F. A. van Melle, Proc. Sect. Sci. Akad. Wiss. Amsterdam, vol. 30, p. 249.

—   F. M. Jaeger and F. A. van Melle, Proc. Sect. Sci. Akad. Wiss. Amsterdam, vol. 30, pp. 479, 885.

1928   H. Kappen and B. Fischer, Zeits. Pflanzenernährung, Düngung und Bodenkunde, Teil A, vol. 12, p. 8. [M.A. 4–317.]

—   O. C. Magistad, Univ. Arizona, Coll. Agric. Techn. Bull., no. 22.

1929   F. M. Jaeger, Proc. Sect. Sci. Akad. Wiss. Amsterdam, vol. 32, p. 156.

—   F. M. Jaeger and F. A. van Melle, Proc. Sect. Sci. Akad. Wiss. Amsterdam, vol. 32, p. 167.

—   O. C. Magistad, Journ. Amer. Soc. Agronomy, vol. 21, p. 1045.

—   G. Weigner and K. Müller, Zeits. Pflanzenernährung, Düngung und Bodenkunde, Teil A, vol. 14, p. 321. [M.A. 4–317.]

1930   W. L. Bragg, lecture to Min. Soc., March 3, 1930; the same subject-matter appears in Zeits. Krist., vol. 74, p. 237. [M.A. 4–354.]

—   S. B. Hendricks and W. H. Fry, Soil Science, vol. 29, p. 457.

—   C. E. Marshall, Trans. Faraday Soc., vol. 26, p. 173.

—   W. H. Taylor, Zeits. Krist., vol. 74, p. 1. [M.A. 4–369.]