DEPARTMENT OF THE INTERIOR.

BULLETIN

OF THE

UNITED STATES GEOLOGICAL SURVEY

No. 125

WASHINGTON
GOVERNMENT PRINTING OFFICE
1895

UNITED STATES GEOLOGICAL SURVEY
CHARLES D. WALCOTT, DIRECTOR

THE

CONSTITUTION OF THE SILICATES

BY

FRANK WIGGLESWORTH CLARKE
CHIEF CHEMIST

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THE CONSTITUTION OF THE SILICATES.

By F. W. Clarke.

CHAPTER I.

INTRODUCTION.

In the solid crust of the earth the silicates are by far the most important constituents. They form at least nine-tenths of the entire known mass, and comprise practically all of the rocks except the sandstones, quartzites, and carbonates; even these exceptions are commonly derivatives of the silicates, which break up under various conditions, yielding simpler bodies of their own class, together with free silica and limestone. From a geological point of view, therefore, the silicates are of fundamental importance, and a study of their inner constitution may be reasonably expected to shed light upon many serious problems. For example, every primitive rock or eruptive mass contains an aggregation of silicates, each one of which is capable of undergoing chemical change in accordance with limitations imposed by the structure of its molecules. When these changes take place, secondary compounds, alteration products, are formed, and in time the rock becomes transformed into new substances, quite unlike those which originally existed. A knowledge of the processes which thus occur should be applicable to the study of the rocks, and should ultimately render it possible so to investigate a metamorphosed mass as to clearly indicate its origin. These processes are dependent upon chemical structure, and the study of this with regard to the silicates is the purpose of the present memoir.

From the standpoint of the chemist the problem under consideration is one of great importance, but also of great difficulty. Some of the difficulty is real, some only apparent. At first sight the natural silicates appear to be compounds of great complexity; but this difficulty becomes much less serious after careful examination. Few of the natural silicates exist in even an approximately pure condition; many that seem fresh have undergone traces of alteration; isomorphous mixtures are exceedingly common; and much confusion is due to defective analyses. By multiplied observations these difficulties can be eliminated from the problem, but others yet remain to be disposed of. The organic chemist, to whom most of our knowledge of chemical structure is due, deals mainly with bodies of known molecular weight, which can be measured by the density of a vapor or by cryoscopic methods. To the mineral chemist such knowledge is not available, for the compounds which interest him are neither volatile nor soluble, and their molecular weights can only be inferred. The simplest empirical formula of a silicate is not necessarily its true formula; the latter may be a multiple or polymer of the former; and here we find a difficulty which is at present almost insuperable. Strong evidence can be brought to bear upon this side of the question, but it is only partial evidence and not finally conclusive. The case, however, is by no means hopeless, for even the partial solution of a problem is better than no solution at all. An approximation is some gain, and it is possible so to investigate the constitution of the silicates as to bring many relations to light, developing formulæ which express those relations and indicate profitable lines for future research.

The problem is open to attack from several points of view, and various methods of investigation can be brought to bear upon it. First, of course, the empirical formula of each silicate must be definitely ascertained, which involves the discussion of sufficiently numerous analyses and the elimination of possible errors due to impurity, alteration, and isomorphous admixtures. In this work the microscope renders important service to the analyst, and makes his results much more certain. By the aid of the microscope many supposed mineral species have been proved to be mixtures, and the problem of the silicates has been thereby simplified. Indeed, the final outcome of such investigation generally indicates, for any given natural silicate, simplicity of composition; and this is what should be expected. These compounds are, as a rule, exceedingly stable salts, while complex substances are commonly characterized by instability. The mineral silicates are formed in nature under conditions of high temperature or are deposited from solutions in which many reactions are simultaneously possible, and these circumstances are strongly opposed to any great complications of structure. Furthermore, they are quite limited in number, only a few hundred at most being known; whereas, if complexity were the rule among them, slight variations in origin should produce corresponding variations in character, and millions of different minerals would be generated. That few variations exist is presumptive evidence that only few are possible, and hence simplicity of constitution is reasonably to be inferred. In fact, we find the same small range of mineral species occurring under the same associations in thousands of widely separated localities; a few typical forms containing a few of the commonest metals being almost universally distributed. The longer the evidence is considered, the stronger the argument in favor of simple silicate structures becomes.

Having established the empirical formula of a silicate, its physical properties may next be considered; and of these the crystalline form and the specific gravity are the most important. From identity of form, or complete isomorphism between two species, we infer similarity of chemical structure, and the inferences thus drawn are often of the highest value. On the other hand, dissimilarity of form and identity of composition indicate isomerism, as for example in the cases of andalusite and kyanite; and here again we secure evidence which bears directly upon the study of chemical constitution. From the specific gravity the so-called molecular volume of a species may be computed, and that datum gives suggestions as to the relative condensation of a molecule in comparison with others of similar empirical composition. For instance, leucite and jadeite are empirically of similar type; but the latter has by far the greater density, together with superior hardness. It is, therefore, presumably more complex than leucite, and this supposition must be taken into account in considering its ultimate formula.

From what may be called the natural history of a mineral, still another group of data can be drawn, relating to its genesis, its constant associations, and its alterability. In this connection pseudomorphs become of the utmost interest, and, properly studied, shed much light upon otherwise obscure problems. An alteration product is the record of a chemical change, and as such has weighty significance. The decomposition of spodumene into eucryptite and albite, the transformation of topaz into mica, and many like occurrences in nature, are full of meaning with reference to the problem now under consideration. Just here, however, great caution is necessary. Mineralogical literature is full of faulty records regarding alterations, and many diagnoses need to be revised. Pseudomorphs have been named by guesses, based upon their external appearance, and often a compact mica has been called steatite or serpentine. In every case an alteration product should be identified with extreme care, both by chemical and by microscopical methods; for without such precautions there is serious danger of error. In each instance the supposed fact must be scrupulously verified.

Closely allied to the study of natural alterations is their artificial production in the laboratory. The transformation of leucite into analcite, and of analcite back into leucite, is a case in point, and the admirable researches of Lemberg furnish many other examples. Work of this character is much less difficult than was formerly supposed, and its analogy to the methods of organic chemistry renders its results highly significant. Atoms, or groups of atoms, may be split off from a molecule and replaced by others, and the information so gained bears directly upon the question of chemical structure. With evidence of this sort relations appear which could not otherwise be recognized, and these relations may be closely correlated with observations of natural occurrences.

Evidence of the same or similar character is also furnished by the thermal decomposition of silicates, a line of investigation which has been successfully followed by several investigators. Thus garnet, when fused, yields anorthite and an olivine; natrolite gives nepheline; talc, upon ignition, liberates silica; and the prolonged heating of ripidolite produces an insoluble residue having the empirical composition of spinel. All of these facts have relevancy to the problem of chemical constitution, and their number could easily be enlarged by experiment. As yet the field has been barely scratched upon the surface; upon deeper cultivation a goodly crop may be secured.

The artificial synthesis of mineral species, with the allied study of crystalline slags and furnace products, furnishes still more evidence of pertinent utility. But, here again, caution is needed in the interpretation of results. A compound may be produced in various ways, and it does not follow that the first method which is successful in the laboratory is the method pursued by nature in the depths of the earth. The data yielded by synthesis are undoubtedly helpful in the determination of chemical constitution, but they furnish only a small part of the proof needed for complete demonstration, and their applicability to geological questions is limited in the extreme. For the latter purpose they are only suggestive, not final.

Suppose now that the empirical formula of a silicate has been accurately fixed, and that a mass of data such as I have indicated are available for combination with it. Suppose the physical properties to be determined, the natural relations known, the alteration products observed, its chemical reactions and the results of fusion ascertained; what then? It still remains to combine these varied data into one expression which shall symbolize them all, and that expression will be a constitutional formula. To develop this, the established principles of chemistry must be intelligently applied, with due regard to recognized analogies. The grouping of the atoms must be in accord with other chemical knowledge; they must represent known or probable silicic acids; and any scheme which fails to take the latter consideration into account is inadmissible. Not merely composition, but function also is to be represented, and the atomic linking which leaves that disregarded may be beautiful to see, but is scientifically worthless. A good formula indicates the convergence of knowledge; if it fulfills that purpose it is useful, even though it may be supplanted at some later day by an expression of still greater generality. Every formula should be a means toward this end, and the question whether it is assuredly final is of minor import. Indeed, there is no formula in chemistry to-day of which we can be sure that the last word has been spoken.

In the development of constitutional formulæ for the silicates it sometimes happens that alternatives offer between which it is difficult to decide. Two or more distinct expressions may be possible, with the evidence for each so strong that neither can be accepted or abandoned. In such cases nothing can be done but to state the facts and await the discovery of new data, to which, however, the formulæ themselves may give clews. This sort of uncertainty is peculiarly common among the hydrous silicates, and often arises from the difficulty of discriminating between water of crystallization, so called, and constitutional hydroxyl. If in every silicate analysis the state of hydration were carefully examined, the conditions of dehydration being observed at different temperatures, much of this obscurity would be avoided.

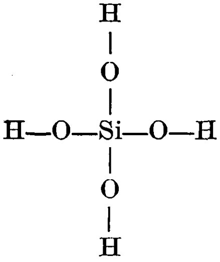
In discriminating between rival formulæ, one rule is provisionally admissible. Other things being equal, a symmetrical formula is more probable than one which is unsymmetrical. Symmetry in a molecule conduces to stability; most of the silicates are exceedingly stable; and hence symmetry is to be expected. This rule has presumptive value only, as an aid to judgment, and can not be held rigidly. It expresses a probability, but gives no proof. In a problem like that of the silicates, however, even a suggestion of this kind may render legitimate assistance.

CHAPTER II.

THE THEORY OF THE SILICATES.

If all of the silicates were salts of a single silicic acid, the problem of their constitution would be relatively simple; but this is not the case. Many silicic acids are theoretically possible, and several of them have representatives in the mineral kingdom, although the acids themselves, as such, are not known. Their nature must be inferred from their salts, and especially from their ethers, and this side of the problem is the first to be considered.

Since silicon is quadrivalent, its ortho acid is necessarily represented by one atom of the element united with four hydroxyl groups, thus—$Si(OH)_4$, or, structurally:



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{O} \\ | \\ \mathrm{H{-}O{-}Si{-}O{-}H} \\ | \\ \mathrm{O} \\ | \\ \mathrm{H} \end{array}$$

To this acid, orthosilicic acid, the normal silicic ethers and many common minerals correspond. Its normal salts, reduced to their simplest expressions, may be typically represented as follows:

Types.	*Examples.*
$R^{i}_4SiO_4$	$(C_2H_5)_4SiO_4$
$R^{ii}_2SiO_4$	Mg_2SiO_4
$R^{iii}_4(SiO_4)_3$	$Al_4(SiO_4)_3$
$R^{iv}SiO_4$	$ZrSiO_4$

Any silicate in which the oxygen atoms outnumber the silicon atoms by more than four to one, as for example the compound Al_2SiO_5, must be regarded as a basic salt.

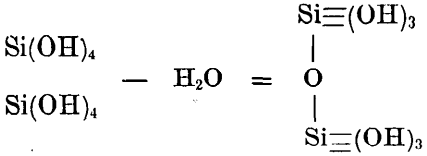
By elimination of water orthosilicic acid may be conceived as yielding, first, metasilicic acid, H_2SiO_3, and, secondly, the anhydride, SiO_2, thus:

$$Si(OH)_4 \qquad O{=}Si{=}(OH)_2 \qquad O{=}Si{=}O$$

Corresponding to metasilicic acid many salts are known, but as yet no ethers have been certainly obtained. The ethers first described by Ebelmen were supposed to be metasilicates, but all recent investigations have shown them to be ortho compounds, possibly more or less impure. Troost and Hautefeuille, however, have described an ether having the formula, $(C_2H_5)_8Si_4O_{12}$, which is a polymer of a metasilicate; but its true nature has not been determined. The simplest formulæ for typical metasilicates are as follows:

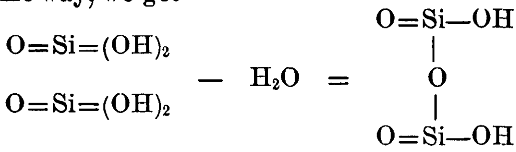
Types.	*Examples.*
$R^{i}_2SiO_3$	Na_2SiO_3
$R^{ii}SiO_3$	$MgSiO_3$
$R^{iii}_2(SiO_3)_3$	$Al_2(SiO_3)_3$*
$R^{iv}(SiO_3)_2$	$Zr(SiO_3)_2$*

By eliminating a molecule of water from two molecules of orthosilicic or metasilicic acid, a disilicic acid may be produced. From orthosilicic acid we have



$$\begin{matrix}Si(OH)_4\\ \\Si(OH)_4\end{matrix} \quad - \quad H_2O \quad = \quad \begin{matrix}Si{\equiv}(OH)_3\\ |\\ O\\ |\\ Si{\equiv}(OH)_3\end{matrix}$$

or, $H_6\,Si_2\,O_7$; a sexbasic acid of which several ethers have been obtained. It is, therefore, a well-established acid, and a number of silicates appear to be salts of it. It may be called diorthosilicic acid. From metasilicic acid, in the same way, we get



$$\begin{matrix}O{=}Si{=}(OH)_2\\ \\O{=}Si{=}(OH)_2\end{matrix} \quad - \quad H_2O \quad = \quad \begin{matrix}O{=}Si{-}OH\\ |\\ O\\ |\\ O{=}Si{-}OH\end{matrix}$$

or dimetasilicic acid, $H_2Si_2O_5$. No ethers of this acid are known, but among its salts are the minerals petalite, milarite, ptilolite, and mordenite.

By a similar process, that is, the elimination of water from three or four molecules of orthosilicic acid, a series of tri- and tetrasilicic acids may be theoretically developed. These higher acids would present many possibilities for isomerism, and with their long chains of atoms would presumably be unstable. At all events, with a single exception, it is unnecessary to consider them in order to account for the natural silicates. The one exception is the tetrabasic acid $H_4Si_3O_8$, which appears most notably in eudidymite, the feldspars, the micas, and the scapolite group. The feldspars of this type, however, albite and orthoclase, are represented by Groth as mixed salts of two other silicic acids, when $Si_2O_5+SiO_3=Si_3O_8$; so that the trisilicic acid in question can be left out of consideration. But a general view of the whole field seems to point to its existence; at least greater simplicity is secured by retaining it in the scheme of silicic acids; and that policy

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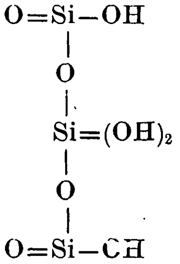
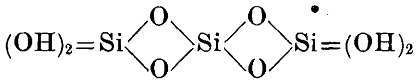
* Salts not actually known, but theoretically possible.

will be followed throughout this memoir. As opposed to Groth's view, we have also to consider the theory of Becker* that metasilicates may be really mixtures or compounds of ortho- and trisilicates, with $H_4SiO_4 + H_4Si_3O_8 = 4H_2SiO_3$. This theory may easily be pushed to an extreme, for the weight of evidence shows that true metasilicates exist; but in many cases it has real significance; that is, mixed salts are known having pseudometasilicate ratios, and these are most simply explained by Becker's theory, which, in the case of the micas, had been independently developed by myself. As to the constitution of trisilicic acid, we have no positive evidence, and at least two independent structures are conceivable, thus:



and



The first of these formulæ has the closer analogy with the formulæ of the other silicic acids, and is, therefore, in default of evidence, to be preferred. Furthermore, it indicates possibilities of isomerism, such as we find in the case of orthoclase and microcline, a consideration which is well worth bearing in mind.

So far, then, there are five silicic acids whose salts occur in the crust of the earth. They are:

Orthosilicic acid	H_4SiO_4
Metasilicic acid	H_2SiO_3
Diorthosilicic acid	$H_6Si_2O_7$
Dimetasilicic acid	$H_2Si_2O_5$
Trisilicic acid	$H_4Si_3O_8$

and unless we admit the possible polymerization of metasilicic acid, as suggested by Troost and Hautefeuille's ether, no others need be invoked in order to account for the facts which are now available. The possibility of other silicic acids is an entirely distinct question.

If the natural silicates were simple normal salts of the five silicic acids the problem of their constitution would not be difficult. But relatively few of the known species are of this description; the greater number are double salts, and even triple replacements are not uncommon. Furthermore, there are acid and basic salts to be interpreted,

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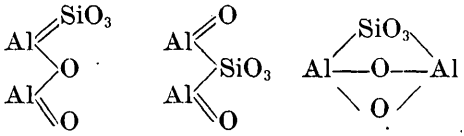
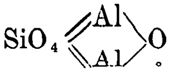
*Am. Jour. Sci., (3) XXXVIII, p. 154, 1889.

and the latter class offers the most serious difficulties. A basic metasilicate, for example, may have the same empirical composition as an orthosilicate; so that its ratios, studied apart from other evidence, tell nothing as to the class in which it belongs. Take for instance the formula Al_2SiO_5, which represents the composition of three distinct minerals, andalusite, sillimanite, and kyanite, and it admits of several different structural expressions. As a basic metasilicate it may be written



and as an orthosilicate it becomes either

$O=Al-SiO_4\equiv Al$, or 

If its molecular weight is a multiple of that indicated by the formula Al_2SiO_5, then the possibilities of isomeric structure become still more complicated. Its composition alone does not give its molecular structure, and other evidence, as shown in the introduction to this memoir, must be brought to bear before the problem can be even approximately solved. This evidence is sometimes available, sometimes not, as will be seen in the systematic discussion of the individual species later.

A hasty glance over the entire field of the natural silicates will show, first, that many of them are most easily interpreted as orthosilicates, and, secondly, that by far the greater number are salts of aluminum. As regards both abundance and variety the aluminous silicates outrank all the others, and from the wide range of composition which they exhibit we can obtain clews to their constitution. In other words, they furnish the most evidence, and some of it is of the highest import. Their relations to one another are oftentimes clear and unmistakable, so that the constitution of one salt is the key to that of a second; and thus generalization becomes possible.

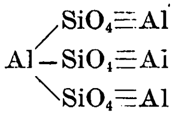
If we consider first the orthosilicates of aluminum, one general relation is easily made apparent. By a general relation I do not mean a universal relation, for exceptions are possible; but only that many of the salts are connected by a simple regularity, or even a law. To make this apparent it is necessary to recognize the fact that aluminum is now properly regarded as a trivalent metal, its formerly supposed quadrivalency being no longer admissible. Formulæ in which aluminum appears as a tetrad are not valid; and ferric iron, which replaces aluminum, follows the same rule. This point has been made clear by the vapor density and cryoscopic investigations of recent years, and is sustained also by the position of aluminum in the periodic classification of the elements.

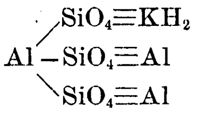
This much admitted, the general relation of which I have spoken is as follows: Many, perhaps all, of the orthosilicates of aluminum are most simply represented as substitution derivatives of the normal salt $Al_4(SiO_4)_3$. To illustrate this rule for present purposes, the following examples will suffice:

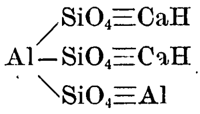
Aluminum orthosilicate	$Al_4(SiO_4)_3$
Eucryptite	$Al_3(SiO_4)_3Li_3$
Nephelite	$Al_3(SiO_4)_3Na_3$
Kaliophilite	$Al_3(SiO_4)_3K_3$
Muscovite	$Al_3(SiO_4)_3KH_2$
Paragonite	$Al_3(SiO_4)_3NaH_2$
Andalusite	$Al_3(SiO_4)_3(AlO)_3$
Topaz	$Al_3(SiO_4)_3(AlF_2)_3$
Natrolite	$Al_2(SiO_4)_3Na_2H_4$
Biotite	$Al_2(SiO_4)_3MgKH$
Grossularite	$Al_2(SiO_4)_3Ca_3$
Prehnite	$Al_2(SiO_4)_3Ca_2H_2$
Phlogopite	$Al(SiO_4)_3Mg_3KH_2$

These formulæ express not only the composition of the minerals, but also many facts concerning their relations, such as their association, their alteration one into another, and so on. Thus, topaz and andalusite are crystallographically akin; both minerals, as well as others in the series, alter easily into muscovite, and these facts become intelligible in the light of the formulæ given. In the use of the formulæ, however, one possible misconception must be avoided. They express a relationship of constitution, but do not imply that Nature first generated the normal salt and then actually developed the other compounds from it. To emphasize this point an analogy may be drawn from organic chemistry. Alizarin, derived constitutionally from anthracene, was originally obtained from a glucoside contained in madder root. But nobody supposes that the madder plant took anthracene as a starting point from which to produce the dye. The constitutional or structural derivation is one thing; the natural origin is quite another.

Whether aluminum orthosilicate as such exists in nature is still a matter of doubt. The rare mineral xenolite has the composition $Al_4(SiO_4)_3$, but it needs further study before its integrity as a species can be fully recognized. At present the weight of evidence seems to be in its favor, but its occurrence is that of a secondary mineral. Among the products of primitive magmas it has not been observed. As regards its ultimate constitution or chemical structure, that question must also be left open. It can be written structurally in several ways; either with each aluminum atom linked with all the SiO_4 groups or with only one atom so connected. In a sense this problem is analogous to that offered by the benzene ring, prism, or nucleus, a conception of which the utility is fully recognized, in spite of outstanding uncertainties. For practical purposes, that is, for the coordination of known facts, expressions like the following are sufficient:







These expressions indicate the observed replaceability of aluminum atoms by other atoms or groups, and have no ulterior significance. So long as their limitations are kept in mind they are useful, but beyond this it would be unreasonable to go. With prolonged discussion and more evidence we may get a deeper insight into the nature of the fundamental molecule; at present, speculation concerning it would be premature. The relations expressed are clear, no matter what others may be revealed in the future. As a working hypothesis, the conception of substitution from a normal salt may be applied to many nonaluminous silicates, as in the magnesian series, the silicates of quadrivalent metals, and so on. These points will be developed in subsequent chapters. In the systematic discussion I shall begin with the orthosilicates, starting with those of aluminum, for the reason that they show most clearly the evidence relative to structure. In a classification of the silicates the starting point would be different, but this is not a classification. The trisilicates will be considered with the orthosilicates, for reasons which are obvious. In the feldspar, zeolite, and mica groups the ortho- and trisilicates can not well be separated.

CHAPTER III.

THE ORTHOSILICATES OF ALUMINUM.

I. THE NEPHELITE TYPE.

If, in accordance with the ideas developed in the preceding chapter, we start out from the normal salt $Al_4(SiO_4)_3$, the first and simplest replacement possible is that of a single aluminum atom by three monads, giving a compound of the general formula $Al_3(SiO_4)_3R'_3$. This formula represents several well-known minerals, and I propose to designate it as the *nephelite type.* At first sight it seems to be reducible to the simpler expression $R'AlSiO_4$, but that expression, as will be seen later, does not indicate all the known relations of the group.

The first three representatives of this type are as follows:

Eucryptite	$Al_3(SiO_4)_3Li_3$
Nephelite	$Al_3(SiO_4)_3Na_3$
Kaliophilite	$Al_3(SiO_4)_3K_3$

These species are all hexagonal, are nearly equal in density, and all gelatinize with hydrochloric acid. The second and typical member of the series has been made synthetically, and is then found to have the composition indicated by the formula. The natural nephelite, however, has a composition which is more exactly represented by the complex formula $R'_8Al_8Si_9O_{34}$, in which a little potassium appears among the components of R′, while there is an excess of silica over the amount required by theory. The potassium is doubtless due to an isomorphous admixture of kaliophilite, and the excess of silica can be explained by the presence of a salt isomeric with albite and having the composition $Al_3(Si_3O_8)_3Na_3$. This replacement of SiO_4 by Si_3O_8 appears to be common among the silicates, and its recognition clears up many discrepancies. In this case one molecule of the trisilicate commingled with fifteen of the ortho-salt will produce the divergence from normal composition shown in the analyses of natural nephelite.

By direct alteration nephelite passes easily into two zeolitic minerals, having the subjoined formulæ:

Hydronephelite	$Al_3(SiO_4)_3Na_2H.3H_2O$
Natrolite	$Al_2(SiO_4)_3Na_2H_4$

In natrolite, two atoms of aluminum have been replaced by $R'_6 = Na_2H_4$, and this species, with others of like origin, falls therefore into another group. Still it is desirable now to call attention to the fact, observed by Doelter,[*] that natrolite on fusion yields nephelite. The connection between the two species is unmistakable.

Eucryptite and nephelite both alter with great ease into muscovite, a potassium salt of which paragonite is the sodium equivalent. Furthermore, C. and G. Friedel,[†] by heating finely divided muscovite to 500° in a solution of alkali, obtained nephelite in crystals. From this evidence the formulæ of muscovite and paragonite become directly related to those of the nephelite series, thus:

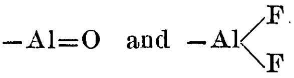
Nephelite	$Al_3(SiO_4)_3Na_3$
Muscovite	$Al_3(SiO_4)_3KH_2$
Paragonite	$Al_3(SiO_4)_3NaH_2$

Physically, the two micas have no resemblance to nephelite, being different in form, slightly denser, and refractory toward acids. The relationship is purely one of chemical type, and is established by the fact of alteration from one into another.

Through muscovite a connection is recognizable between the foregoing species and the two minerals andalusite and topaz, whose simplest formulæ, tripled, may be written as follows:

Topaz	$Al_3(SiO_4)_3(AlF_2)_3$
Andalusite	$Al_3(SiO_4)_3(AlO)_3$

Here we encounter the evidently univalent atomic groups

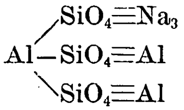


$$-Al{=}O \quad \text{and} \quad -Al\begin{matrix}\diagup F\\ \diagdown F\end{matrix}$$

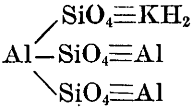
both of which play an important part in various other minerals. The two species, topaz and andalusite, are closely allied crystallographically. They have sensibly identical molecular volumes, and both undergo alteration into muscovite mica. In topaz, as shown by the investigations of Penfield and of Jannasch, hydroxyl commonly replaces a part of the fluorine; hydroxyl and fluorine being clearly isomorphous. The formula given is that of normal topaz, entirely free from alteration.

To sum up, we have now eight definite species represented by the fundamental type $Al_3(SiO_4)_3R'_3$, the first substitution from the normal orthosilicate of aluminum. Leaving hydronephelite on one side, because of its water of crystallization, the remaining seven species fall into three subtypes, as follows:

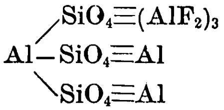
Nephelite.



Muscovite.



Topaz.



symbols which clearly indicate the known chemical relations between the several minerals. In five of the eight examples the simplest pos-

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[*] Allgem. Chem. Mineralogie, p. 183.

[†] Bull. Soc. Min., XIII, p. 129, 1890.

sible formulæ have been tripled, for otherwise the relationships which exist could not be structurally shown. The correctness of this procedure will appear still more definitely in the consideration of the groups which follow.

The species sillimanite is isomeric with andalusite, but the structural character of the isomerism is not clear. The minerals kornerupine and kryptotile, which will be considered later, are possibly also representatives of the nephelite type.

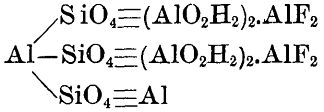
II. THE GARNET-BIOTITE TYPE.

By this title I propose to designate the second series of derivatives from the normal salt $Al_4(SiO_4)_3$, in which two atoms of aluminum have been replaced. The general formula of the type, obviously, is $Al_2(SiO_4)_3R'_6$, and in this series bivalent elements or radicles frequently appear. In natrolite, $R'_6=Na_2H_4$; in biotite, $R'_6=R''_2R'_2$; and in garnet R'_6 are entirely replaced by R''_3. There are, therefore, three subtypes to consider; one in which all the replacing atoms are univalent, one in which all are bivalent, and one intermediate between the other two.

Under the first subtype three species seem definitely to occur, viz:

Natrolite	$Al_2(SiO_4)_3Na_2H_4$
Dumortierite	$Al_2(SiO_4)_3(AlO)_6$
Zunyite	$Al_2(SiO_4)_3R'_6$*

Natrolite, as we have already seen, may be directly derived from nephelite by alteration. Dumortierite is analogous to andalusite, and, like the latter, is orthorhombic. In zunyite R'_6 is composed of the groups $-Al=F_2$, $-Al=Cl_2$, and $-Al=(OH)_2$, with possibly a little $-Al=O$, and the mineral thus seems to be chemically related to dumortierite in the same way that topaz is related to andalusite. But topaz and andalusite have crystallographic analogy, while zunyite, being isometric, is quite unlike its chemical congeners. The species evidently needs further study, but at present, if we unite the chlorine in it with the fluorine, it may be provisionally represented by the expression



$$\begin{array}{l} \quad\diagup SiO_4\equiv(AlO_2H_2)_2.AlF_2 \\ Al-SiO_4\equiv(AlO_2H_2)_2.AlF_2 \\ \quad\diagdown SiO_4\equiv Al \end{array}$$

This formula expresses the facts which are now available, but is not conclusive. Its isometric character, however, helps to connect zunyite with the garnet and sodalite groups, as has been shown by Brögger.†

In the second subtype, when R'_6 is partly composed of bivalent and partly of univalent atoms, two species may be placed, thus:

Prehnite	$Al_2(SiO_4)_3Ca_2H_2$
Biotite	$Al_2(SiO_4)_3Mg_2HK$

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* Groth's formula, generalized.

† Zeit. Kryst. Min., XVIII, p. 209.

Possibly the tetragonal sarcolite, which has the general formula of a garnet with the lime partly replaced by soda, may fall here also; but the analyses of this mineral are unsatisfactory, and its relations are still uncertain. Biotite will be more fully considered in the special chapter devoted to the mica group. Prehnite, according to Doelter,* decomposes on fusion, yielding the same products as garnet.

Under the third subtype of this series we find the garnet group itself, together with epidote and several related species. The sodalite group is also akin to garnet and to the second subtype, and will be considered in this connection a little later. Under the generic term garnet several species are included, all being isometric and strictly isomorphous, in which magnesium, calcium, and ferrous iron replace one another, while chromium, aluminum, and ferric iron are also equivalent terms. Thus we have:

Grossularite	$Al_2(SiO_4)_3Ca_3$
Pyrope	$Al_2(SiO_4)_3Mg_3$
Almandite	$Al_2(SiO_4)_3Fe''_3$
Spessartite	$Al_2(SiO_4)_3Mn_3$
Andradite	$Fe_2(SiO_4)_3Ca_3$
Ouvarovite	$Cr_2(SiO_4)_3Ca_3$

To these may be added schorlomite, a garnet in which titanium occurs both as part of the acid, that is, with TiO_4 replacing SiO_4, and also as Ti''' among the triad bases, equivalent to aluminum. The monoclinic partschinite, isomeric with spessartite, also falls into this group.

In the epidote group, at least four species appear, one, zoisite, being orthorhombic, while the other three are monoclinic. These species are characterized by the bivalent group of atoms $=\dot{Al}-OH$, thus:

Zoisite	$Al_2(SiO_4)_3Ca_2(AlOH)$
Epidote, *a*	$Al_2(SiO_4)_3Ca_2(AlOH)$
Epidote, *b*	$Fe_2(SiO_4)_3Ca_2(FeOH)$
Piedmontite	$(AlMn)_2(SiO_4)_3Ca_2(AlOH)$
Allanite	$(AlCeFe)_2(SiO_4)_3(CaFe)_2(AlOH)$

or, in general, as compared with garnet,

Garnet	$R'''_2(SiO_4)_3R''_3$
Epidote	$R'''_2(SiO_4)_3R''_2(R'''OH)$

The facts that garnet alters into epidote and that the two minerals are often associated give emphasis to the formulæ. For epidote, however, an alternative formula is possible, in which the hydroxyl is supposed to be united with calcium rather than with aluminum. But epidote is a peculiarly stable mineral, while the group $\dot{-}Ca-OH$ would imply instability and easy alteration. The alternative formula, therefore, is improbable, although it would ally epidote more easily with anorthite, which is a product of its fusion.

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* Allgem. Chem. Mineralogie, p. 183.

Although garnet, as a rule, is unattacked by acids, and epidote is only in part decomposable, both species are so broken up by strong ignition as to be readily acted upon by hydrochloric acid, with separation of gelatinous silica. According to Doelter and Hussak,[*] garnet yields upon fusion sometimes anorthite and an olivine; or meionite, augite, and olivine; or melilite and anorthite; and occasionally spinel. Epidote, says Doelter,[†] yields lime-augite and anorthite, and prehnite behaves like garnet. These facts indicate analogies between the several species named, but are not easy of complete interpretation. The different products observed may be due in part to a direct splitting up of the original insoluble mineral into soluble species like anorthite and a lime-olivine, and in part to secondary reactions taking place during the prolonged fusion and cooling of the resultant magma. In other words, two sets of phenomena are probably involved in the observations, and it is impossible at present to distinguish between them. The first set alone is immediately relevant to the constitutional question now before us.

In the four species sodalite, haüynite, nosite, and lazurite we have a group of minerals which Brögger has classified as alkali garnets.[‡] Like garnet, they are all isometric, and they are characterized by the presence of the bivalent groups $=Al-Cl$, $=Al-SO_4-Na$, and $=Al-S-S-S-Na$. There are also artificial products, ultramarines, in which the groups $=Al-S-S-Na$ and $=Al-S-Na$ appear. Adopting Brögger's formulæ, which are preferable to those formerly proposed by myself,[§] these species may be written as follows:

Sodalite	$Al_2(SiO_4)_3Na_4(AlCl)$
Haüynite	$Al_2(SiO_4)_3Na_2Ca(AlSO_4Na)$
Nosite	$Al_2(SiO_4)_3Na_4(AlSO_4Na)$
Lazurite	$Al_2(SiO_4)_3Na_4(AlS_3Na)$

They fall, therefore, properly under the second subtype, but are considered at this point on account of their analogies with garnet.

Through these species, and especially through sodalite, a connection with several other minerals is established. Sodalite occurs in elæolite syenytes, and is evidently derived from nephelite, and like the latter it yields natrolite, hydronephelite, and muscovite by alteration. Furthermore, C. and G. Friedel,[||] on heating powdered muscovite with soda solution and sodium chloride at a temperature of 500°, obtained sodalite artificially, although nephelite was probably first formed as an intermediary, and the two species were commingled in the product.

The two hexagonal species, cancrinite and microsommite, are also, like sodalite, undoubtedly derivatives of nephelite, but their formulæ are rather uncertain. Cancrinite approximates to the composition

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[*] Allgem. Chem. Mineralogie, p. 182.

[†] Allgem. Chem. Mineralogie, p. 183.

[‡] Brögger and Bäckström, Zeit. Kryst. Min., XVIII, p. 209.

[§] Bull. U. S. Geol. Survey No. 42, p. 38.

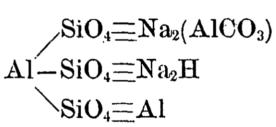
[||] Bull. Soc. Min., XIII, p. 183.

$Al_2(SiO_4)_3Na_4H(AlCO_3)$, in which a little soda is replaced by lime, and the univalent group $-Al{=}CO_3$ may be partly substituted by $-Al{=}SiO_3$. Microsommite, according to the published analyses, varies in composition widely, containing always potassium, and having a notable proportion of chlorine and sulphuric acid among its constituents. If, however, we assume in it the univalent radicles $-Al{=}Cl_2$ and $-Al{=}SO_4$, its composition reduces easily to the form $Al_2(SiO_4)_3(NaK)_3Ca(Al(SO_4.Cl_2))$, like cancrinite, both species having then the composition of the general type $Al_2(SiO_4)_3R'_6$. The theory as proposed, then, assumes univalent complex radicles for cancrinite and microsommite, and bivalent radicles for the sodalite group, thus:

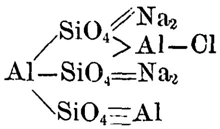
In cancrinite group.	*In sodalite group.*
$-Al{=}Cl_2$	$=Al-Cl$
$-Al{=}SO_4$	$=Al-SO_4-Na$
$-Al{=}CO_3$	$=Al-S_3-Na$
$-Al{=}SiO_3$	

and the typical structures are as follows:

Cancrinite.



Sodalite.



Concerning these formulæ and the peculiar uni- and bivalent radicles assumed in them, there are arguments both for and against. The assumption of a group $-Al{=}SiO_3$, equivalent to and replacing $-Al{=}CO_3$, is clearly suggested by the experiments of Lemberg,* who, by the action of sodium silicate solution upon elæolite, obtained a compound which he designates as a cancrinite containing Na_2SiO_3 in place of Na_2CO_3. By similar reactions with sodium carbonate he produced a substance having the composition of true cancrinite. Hence, whatever the ultimate molecular structure of cancrinite may be, we are amply justified in assuming in it the replaceability of CO_3 by SiO_3.

These experiments fairly represent a large number of like kind which are due to Lemberg, and which may be found recorded in his various papers. Some of these will be cited later, but a reference to the work of his colaborer Thugutt† is in place at this point. Starting from a hydrated nephelite, artificially prepared from kaolin, Thugutt succeeded in producing a large series of compounds analogous to sodalite, in which the original silicate had taken up, at moderately high degrees of heat and pressure, various other salts of sodium, such as the chlorate, selenate, formate, oxalate, and so on. These compounds, however, are all hydrated, and so differ from the natural minerals of the sodalite group, and they are regarded by Thugutt as formed by molecular

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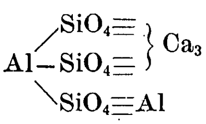
* Zeitsch. Deutsch. Geolog. Gesell., 1885, p. 962. †Mineralchemische Studien, Dorpat, 1891.

union. Following Lemberg, he regards sodalite as a molecular compound of nephelite with sodium chloride, and taking his series of compounds throughout, he looks upon the sodium salts which have been added to the fundamental silicate as equivalent in function to water of crystallization. In favor of this view he cites many arguments, some of which are entitled to considerable weight. Thus, when sodalite is ignited NaCl is driven off, whereas if the chlorine were united with aluminum $AlCl_3$ should be expelled. Similarly, by the action of water alone, sodium chloride can be split off from the sodalite molecule, thus indicating a looser form of union than the proposed structural formulæ show.

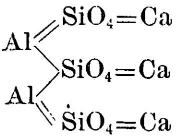
But what is molecular union? To this question there is no satisfactory answer, and even in the case of water of crystallization the term is only a confession of ignorance. Unless we assume the existence of two kinds of chemical union, it means merely that the structural linking is unknown, and that the problem is laid on one side, conveniently labeled for future reference. The constitutional formulæ here adopted for sodalite and cancrinite are intended to give a provisional solution of the problem in their particular cases, and to express the genetic relationships with nephelite on the one hand and the crystallographic analogy with garnet on the other. The objections to them raised by Thugutt are serious, but not absolutely conclusive. When sodium chloride is split off from sodalite the mechanism of the reaction is quite unknown, and the relative affinities in the molecule are quite unstudied. Until these are understood the objections raised by Lemberg, Thugutt, and others are not fatal. Furthermore, the presence of a group $=Al-Cl$ does not imply, as Thugutt supposes, the splitting off of $AlCl_3$ by heat. To effect such a decomposition three molecules of sodalite would have to be broken up, and there is no probability that such a disintegration could occur. At all events the formulæ proposed fulfill a definite purpose, even though they are not finally established. They express known relations, but not necessarily all the relations which the future may reveal. The facts that the sodalite-cancrinite minerals are derivable from nephelite, and that nephelite is again derivable from them, are unquestionable.

Taking now the formula of a typical garnet, $Al_2(SiO_4)_3Ca_3$, the question of its molecular structure remains to be considered. Regarding it as a derivative of the normal salt $Al_4(SiO_4)_3$, it may be written in at least two ways, thus:

1.



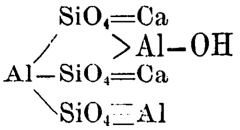
2.

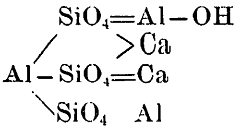


That is, isomerism is possible; and of the two species partschinite and spessartite, one may belong to one type and the other to the other.

In the first expression there is still a replaceable atom of aluminum, in the second expression none; in the first, at least, one calcium atom must link two SiO_4 groups, while in the other no such linkage occurs; and these facts may be connected with others. For example, garnet alters into mica; and the mica group, as will be seen later, contains members in which the third aluminum atom is replaced. This points at once to the first type of formula as preferable, and the alterability of garnet into epidote brings the latter mineral into the same category.

Zunyite and sodalite, being isometric, should also follow garnet; but derivatives of the second type are theoretically possible and may exist. Even under the first type alone, isomerism is conceivable, and the orthorhombic zoisite may be contrasted with the monoclinic lime epidote as follows:

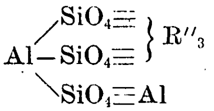




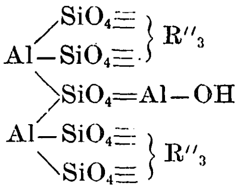
even though we can not assign either species to either formula definitely. My object here is merely to show that the formulæ have properties by virtue of which they are able to express known differences.

Additional evidence for the formula assigned to garnet is furnished by the composition of vesuvianite, which is most simply represented as formed by the coalescence of two garnet molecules, with elimination of silica. The following formulæ express this relation, and also a relation to epidote, quite perfectly:

Garnet.



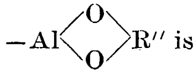
Vesuvianite.



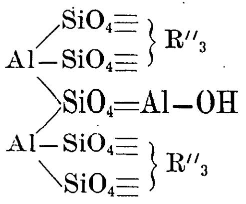
If in vesuvianite $R''_6=Ca_5Mg$, this formula gives for the composition of the typical mineral:

SiO_2	38.38
Al_2O_3	19.55
CaO	35.81
MgO	5.12
H_2O	1.14
	100.00

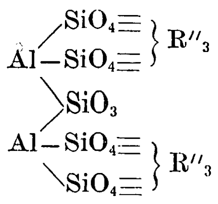
This agrees well with the published analyses, if we remember that ferric iron may partly replace aluminum, and that fluorine sometimes replaces hydroxyl. It is also sustained by the facts that garnet and vesuvianite often occur in contact limestones under similar conditions of genesis; that vesuvianite alters into garnet, and also, like garnet, into micas and chlorites; and that both species, as shown by Doelter,* yield essentially the same products upon fusion. The analogies connecting them are remarkably suggestive and complete, and the formulæ here proposed render those analogies intelligible. In the Swedish "mangan-idocrase" a salt occurs which is doubtless the vesuvianite equivalent of spessartite, but the compound in a pure state is unknown.

Two additional species, melilite and gehlenite, which, like vesuvianite, are also tetragonal, may perhaps be best considered at this stage of the discussion. For melilite, the analyses are somewhat discordant; but on the whole they agree best with Groth's formula $(CaMgNa_2)_6(AlFe)_2Si_5O_{19}$. This may be written so as to resemble the formula of vesuvianite, but with the linking SiO_4 group replaced by the bivalent SiO_3. For gehlenite, the empirical formula $Ca_3Al_2Si_2O_{10}$ is commonly assumed, but a careful comparison of the published analyses has convinced me that it is not entirely satisfactory. Most of the analyses show appreciable amounts of water, but this may be due to alteration; for the artificial gehlenite, prepared by the igneous method, is nonhydrated. A different formula, which relates gehlenite to melilite and vesuvianite, seems to be preferable; and such a formula is empirically $Ca_7MgAl_4Si_5O_{24}$. In this the univalent group  $-Al\langle{}^{O}_{O}\rangle R''$ is to be assumed, which occurs also among the clintonite micas, and which, in natural gehlenite, may be replaced in part by $-Al{=}(OH)_2$. On this basis the three species are comparable as follows:

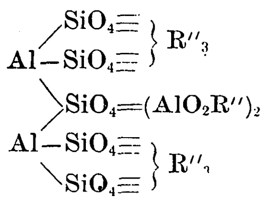
Vesuvianite.



Melilite.



Gehlenite.



These symbols are not absolutely unobjectionable, but they are useful for purposes of correlation. Gehlenite alters into garnet, melilite sometimes occurs among the products of fusion of garnet, and the formulæ suggest such relations. Furthermore, Lemberg† has shown that gehlenite, heated to 200° with a solution of potassium carbonate, gives calcium carbonate and a product having the composition of a potash mica; while similar treatment with sodium carbonate converts the mineral into cancrinite. Gehlenite, garnet, cancrinite, and muscovite are therefore related to one another, and this fact is expressed by the formulæ proposed. In melilite the calcium is partly replaced by sodium, and

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*Allgem. Chem. Mineralogie, p. 183.

† Zeitsch. Deutsch. Geolog. Gesell., 1892, p. 237.

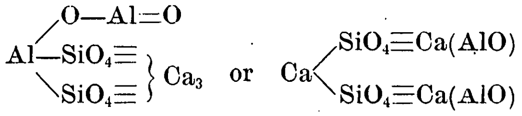
in some gehlenites obtained from furnace slags the same replacement has been observed.*

At the Orawitza locality, gehlenite occurs in rolled pebbles containing grains of vesuvianite. As this gehlenite contains little or no water, we may compare Janovsky's analysis of it† with the results obtained from calculation, both with the formula $Ca_3Al_2Si_2O_{10}$, and with the new formula $Al_2(SiO_4)_5R''_6(AlO_2R'')_2$, when $R''_8=Ca_7Mg$.

The results are as follows:

	Janovsky.	Old formula.	New formula.
SiO_2	32.39	30.77	32.05
Al_2O_3	18.53	26.15	21.80
Fe_2O_3	1.25		
FeO	3.61	43.08	
CaO	37.65		41.88
MgO	6.69		4.27
Ign	.51	....	....
	100.63	100.00	100.00

Neither formula compares perfectly with the analysis, but the new is rather better than the old. With some other analyses this advantage is reversed. We need new data, based upon purer and more definite material than seems to have been as yet collected. If the old formula should be sustained, then it might be written structurally in either of two ways, thus:



The first formula would serve to connect gehlenite with garnet and the micas, while the second represents a derivative of calcium orthosilicate and fails to indicate the various relationships of the mineral to other species of this group. Neither formula, however, is so suggestive as the one which is based upon the type of vesuvianite.

Another alternative is offered by the theory of Vogt,‡ who regards melilite and gehlenite as varying mixtures of two end products; one, the "gehlenite silicate," $R'''_2R''_3Si_2O_{10}$, and the other, åkermannite, $R''_4Si_3O_{10}$. The last compound is a basic silicate, found in slags, which needs further study. Vogt's theory is plausible, and, if established, will take the two species in question, gehlenite and melilite, out of the present category as related minerals to vesuvianite and garnet.

The little-known mineral arctolite is possibly another member of

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* See Hintze, Handbuch der Min., p. 310.

† Dana's System of Mineralogy, 6th ed., p. 476.

‡ Neues Jahrb., 1892, II, p. 73.

this group, with affinities toward prehnite. Its composition is fairly expressed by the formula

$$Al_2(SiO_4)_3CaMgH_2$$

which is that of prehnite with CaMg in place of Ca_2. The integrity of this species, however, is not yet fully established.

III. THE FELDSPARS AND SCAPOLITES.

Although orthosilicic and trisilicic acids are technically distinct, and from a chemical point of view should be studied separately, their salts containing aluminum occur in such a variety of mixtures that in several groups of minerals the two acids must be considered as mutually equivalent, and their compounds discussed together. Two such groups, closely allied, are the feldspars and the scapolites.

For each of these groups the theory developed by Tschermak has met with general acceptance. In the case of the feldspars, Tschermak was undoubtedly anticipated in great part by Hunt, Waltershausen, and others, but he gave to the theory its most precise statement, and to him its final establishment is due. According to this theory the triclinic plagioclase feldspars consist of albite, $AlNaSi_3O_8$, and anorthite, $Al_2Ca(SiO_4)_2$; which, commingled in various proportions, give the intermediate oligoclase, labradorite, andesite, and so on. There are also the triclinic microcline and its monoclinic equivalent, orthoclase, both represented by the formula $AlKSi_3O_8$, and the barium feldspars, such as hyalophane, which may be regarded as mixtures of orthoclase with a barium salt analogous to anorthite in composition. Microcline and orthoclase, from a chemical point of view, may be considered as isomers; and so also may albite and soda-orthoclase; but the nature of the isomerism is not clear. It may be due to the structure of the salt as such, or to the existence of two isomeric acids $H_4Si_3O_8$, and both possibilities are conceivable. For present purposes this problem may be left outstanding, and our attention can be confined to the two typical compounds, anorthite and albite. In the discussion, later, of the species eudidymite and epididymite, the question of isomeric trisilicates will come up.

For the scapolite series Tschermak has elaborated a theory which is closely parallel to that of the feldspars. These tetragonal minerals are shown to be most easily interpretable as mixtures of two end compounds, meionite, $Al_6Ca_4Si_6O_{25}$, and marialite, $Al_3Na_4Si_9O_{24}Cl$. Neither end compound has yet been found in nature quite free from the other; but the variations in composition, in optical character, etc., are all accounted for, and the theory, so far as it goes, is satisfactory. I have tentatively examined some possible alternative hypotheses, and none of them fulfills all necessary conditions so well as this scheme of Tschermak's.

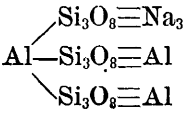
Upon studying the feldspars and scapolites more closely, certain analogies appear other than those indicated by the parallelism of the two series. Both groups of minerals are easily alterable, and both yield kaolin as a final product of the change. Furthermore, both alter into muscovite, or pinite, which is only an impure pseudomorphous mica; and kaolin, crystallographically, has close relations with the mica family. Feldspars, scapolites, muscovite, and kaolin are therefore presumably connected, and the structural formulæ of the minerals should render the relationship apparent.

The empirical formulæ to be considered are now as follows:

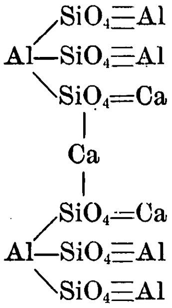
Albite	$AlNaSi_3O_8$
Anorthite	$Al_2CaSi_2O_8$
Meionite	$Al_6Ca_4Si_6O_{25}$
Marialite	$Al_3Na_4Si_9O_{24}Cl$
Muscovite	$Al_3KH_2Si_3O_{12}$
Kaolin	$Al_2H_4Si_2O_9$

For muscovite the constitution has already been indicated; and this clew, together with the general hypothesis of derivation from normal salts, enables us to correlate all six of the formulæ given. To do this it is necessary to triple the formulæ of albite and anorthite, and we have the following expressions:

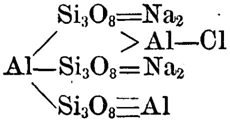
Albite.



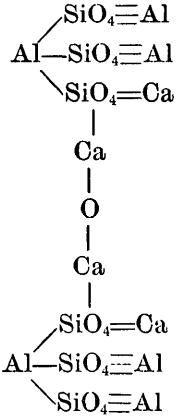
Anorthite.



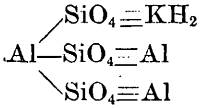
Marialite.



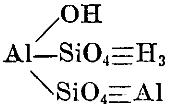
Meionite.



Muscovite.



Kaolin.

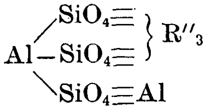


On this basis anorthite becomes the calcium equivalent of nephelite, which latter species is also alterable into kaolin. Again, garnets are known to alter into feldspars and scapolite; and, according to Brauns,* in the alteration of diabase, prehnite and epidote are sometimes derived from anorthite. These species, therefore, are all connected by numerous cross relations, all emphasizing one another and pointing to a community of molecular type. I have already called attention to the facts that anorthite and meionite occur among the products of fusion of garnet, and these data fit in well with the others. So far the formulæ are highly suggestive, but as yet they do not indicate the mechanism of the reaction by which a trisilicate feldspar breaks down into kaolin, and they need development in that direction.

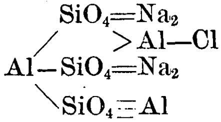
Closely allied to the feldspar in its petrographic relations is the isometric mineral leucite, $AlKSi_2O_6$. Empirically it seems to be a metasilicate, and is commonly so regarded, but it may easily be conceived as a mixed salt, containing ortho- and trisilicate molecules. By alteration it yields orthoclase, nephelite, muscovite, and kaolin, and the pseudo-leucite of Magnet Cove has been shown by J. F. Williams to consist of orthoclase and elæolite intimately commingled.† This case probably represents the typical breaking up of leucite, the formation of kaolin or of muscovite in other instances being due to secondary reactions. On the other hand, C. and G. Friedel‡ have obtained leucite synthetically from muscovite as a starting point, orthoclase and nephelite being produced at the same time; and Lemberg,§ in his experiments, has transformed leucite into sanidine, anorthite, and microsommite, and also into andesine. In a later paper|| Lemberg describes the action upon various silicates of the salt $Na_2SiO_3, 8H_2O$, at 200° under pressure, kaolin, albite, elæolite, leucite, and analcite all yielding a silicate-cancrinite containing SiO_3 in place of CO_3. These facts connect the several species together, but to their explanation the empirical expression $AlKSi_2O_6$ gives no clew. A formula for leucite, to be satisfactory, must be a multiple of this, and several such multiples fulfill the conditions of the problem.

The isometric form of leucite suggests at once a relation with garnet and the sodalite group, and this can be indicated by the quadrupled formula $Al_4K_4Si_8O_{24}$. We then have, as a distinct possibility, the following series of molecules:

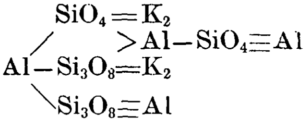
Garnet.



Sodalite.



Leucite.



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* Neues Jahrbuch, 1892, II, p. 1.

† Ann. Rept. Geol. Survey of Arkansas, 1890, II, p. 267 et seq.

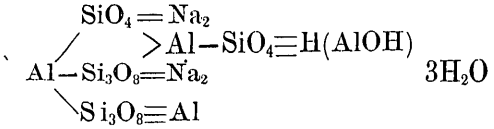
‡ Bull. Soc. Min., XIII, p. 134, 1890.

§ Zeitsch. Geol. Gesell., XXVIII, pp. 611-615, 1876.

|| Zeitsch. Geol. Gesell., pp. 961-2, 1885.

Upon this basis leucite is clearly reduced to the uniform type of the minerals to which it is related crystallographically, and also of those into which it alters; but the formula proposed can not be regarded as final. It is offered here only as a first approximation toward answering the questions which are suggested, and is therefore subject to modification in the future.

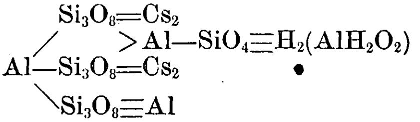
Closely allied to leucite is another isometric mineral, analcite, which, empirically, has the composition $AlNaSi_2O_6,H_2O$. This species alters, like leucite, into feldspar, and an alteration into prehnite is also recorded.* Furthermore, Lemberg has shown, in the papers already cited, that leucite, by the action of soda solutions, may be transformed into analcite, and that analcite, by similar treatment with potash, yields leucite again. With these facts in view, analcite may be written



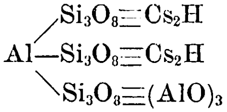
one-fourth of the water being regarded as constitutional. This last supposition, however, needs to be checked by careful experiments upon dehydration, for the data now on record are not absolutely conclusive.† A change in this detail would modify the formula given, but would not affect its general type.

Still another isometric mineral, pollucite, should possibly be considered here. Two empirical formulæ deserve to be regarded: one, based upon analyses of the Elba mineral, and given by Groth, $H_2Cs_2Al_2Si_5O_{15}$; the other, deduced by Wells‡ for the Maine pollucite, $H_2Cs_4Al_4Si_9O_{27}$. Both formulæ give metasilicate ratios, but both are reducible to the type of leucite and analcite, thus:

Elba.



Maine.



Neither formula can be regarded as conclusive, and their only value here is to show that pollucite is not necessarily a metasilicate, and that it can be represented as similar in constitution to the minerals with which it is morphologically allied. Wells's analyses are probably the better; but the formula drawn from the Elba pollucite indicates the closer analogy to leucite and analcite.

Although kaolin, mineralogically, is not a member of the feldspar group, it is properly discussable here as a derivative. The formula assigned to it in the foregoing pages is not unimpeachable, but it suggests its relations to the feldspars and micas, and also represents the

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* Dana's System of Mineralogy, 6th ed., p. 598.

† Compare Hersch, Der Wassergehalt der Zeolithe, Zürich, 1887.

‡ Am. Jour. Sci. (3) XLI, p. 213, 1891.

fact that the water in it is wholly constitutional. In fact, the mineral is stable far above the ordinary temperatures of dehydration, so that the water can be regarded only as an essential part of the molecule.

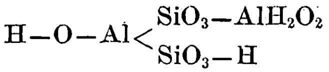
In addition to the formula proposed for kaolin, the following expressions are possible without assumption of any higher molecular weight:

(1) $$Si_2O_7.H_4(AlO)_2$$

(2) $$Si_2O_7.H_2(AlOH)_2.$$ Brauns's.

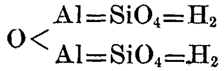
(3) $$Si_2O_5.(AlH_2O_2)_2.$$ Groth's.

(4)



$$H-O-Al<\begin{matrix}SiO_3-AlH_2O_2\\SiO_3-H\end{matrix}$$

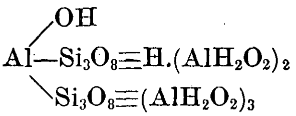
(5)



$$O<\begin{matrix}Al=SiO_4=H_2\\Al=SiO_4=H_2\end{matrix}$$

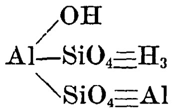
If the formula be tripled, then kaolin may be written as a basic trisilicate, thus:

(6)



$$Al\begin{matrix}\diagup OH\\-Si_3O_8\equiv H.(AlH_2O_2)_2\\\diagdown Si_3O_8\equiv(AlH_2O_2)_3\end{matrix}$$

Of all these symbols only the last and the one originally chosen indicate the relations between kaolin and its parent species. As for these two, the formula



$$Al\begin{matrix}\diagup OH\\-SiO_4\equiv H_3\\\diagdown SiO_4\equiv Al\end{matrix}$$

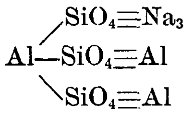
is the simpler, and would seem to represent the greater stability. Kaolin, under ordinary circumstances, is scarcely attacked by the strongest hydrochloric acid, a fact which seems to be most in harmony with the orthosilicate expression. That expression, therefore, is to be preferred; at least until more positive evidence is attainable. After dehydration at low redness, kaolin is completely decomposable by hydrochloric acid, but the ignited mass contains no silica soluble in sodium carbonate solution. These facts, developed by experiments made under my direction by Mr. George Steiger, seem to indicate the formation of a salt $Al_3Si_2O_7$ as the result of ignition, but other interpretations are possible. The data are given here simply as data, which may become available for a fuller discussion of the problem by and by. It will be seen later, when the other clays are considered, that their formulæ are in harmony with that chosen for kaolin.

IV. THE NORMAL ZEOLITES.

By this title is indicated a well-defined group of hydrous silicates, unmistakably related to nephelite and the feldspars, and for which the term *feldspathic zeolites* would be equally appropriate. A few zeolitic species, ptilolite, mordenite, laubanite, etc., are excluded from the present scheme, as being from a chemical point of view more properly placed elsewhere.

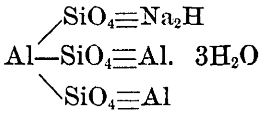
Three of the minerals in this group have already been mentioned, namely, hydronephelite, natrolite, and analcite. All of these occur as alteration products of elæolite or nephelite,[*] and natrolite yields nephelite again upon fusion. Natrolite and analcite are both derivable by natural processes from albite;[†] analcite, as shown in the preceding section, yields feldspathic pseudomorphs, and the relations of analcite to leucite are beyond controversy. From sodalite, both natrolite and hydronephelite may be generated, and from nephelite, by artificial means, Doelter has produced analcite and natrolite.[‡] All of these relations, with others, both morphological and genetic, are covered by the formulæ which have already been developed, but which, in part at least, may be advantageously repeated here. Thus we have:

Nephelite.



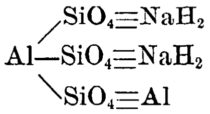
$$\mathrm{Al}\begin{array}{l}\diagup\mathrm{SiO_4{\equiv}Na_3}\\ -\mathrm{SiO_4{\equiv}Al}\\ \diagdown\mathrm{SiO_4{\equiv}Al}\end{array}$$

Hydronephelite.



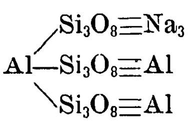
$$\mathrm{Al}\begin{array}{l}\diagup\mathrm{SiO_4{\equiv}Na_2H}\\ -\mathrm{SiO_4{\equiv}Al.\ 3H_2O}\\ \diagdown\mathrm{SiO_4{\equiv}Al}\end{array}$$

Natrolite.



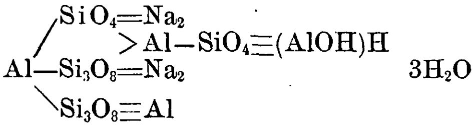
$$\mathrm{Al}\begin{array}{l}\diagup\mathrm{SiO_4{\equiv}NaH_2}\\ -\mathrm{SiO_4{\equiv}NaH_2}\\ \diagdown\mathrm{SiO_4{\equiv}Al}\end{array}$$

Albite.



$$\mathrm{Al}\begin{array}{l}\diagup\mathrm{Si_3O_8{\equiv}Na_3}\\ -\mathrm{Si_3O_8{\equiv}Al}\\ \diagdown\mathrm{Si_3O_8{\equiv}Al}\end{array}$$

Analcite.



$$\mathrm{Al}\begin{array}{l}\diagup\mathrm{SiO_4{=}Na_2}\\ \qquad\qquad{>}\mathrm{Al{-}SiO_4{\equiv}(AlOH)H}\\ -\mathrm{Si_3O_8{=}Na_2}\qquad\qquad\qquad\qquad\mathrm{3H_2O}\\ \diagdown\mathrm{Si_3O_8{\equiv}Al}\end{array}$$

For the full significance of these expressions the previous sections must be consulted; the analcite formula being correlated with the formulæ of garnet, leucite, and the minerals of the sodalite group.

In a similar way, but rather less completely, many zeolitic minerals may be connected with anorthite, the calcium end of the plagioclase feldspar series. For example, by heating anorthite with freshly precipitated silica and carbonic acid water at 200°, Doelter obtained heulandite.[§] The same investigator, after fusion of various zeolites and subsequent slow cooling, found anorthite among the substances produced by chabazite, heulandite, stilbite, scolecite, laumontite, and thomsonite.[||] In some cases anorthite was the chief product of fusion; in others it was subordinate to something else. Again, by various wet reactions, some of them unfortunately involving several stages, Lemberg has generated analcite[¶] from chabazite, gmelinite, laumontite, harmotome, phillipsite, stilbite, and heulandite, in some cases studying several varieties of the same species. It is clear, therefore, that the connection between the zeolites and the feldspars is unquestionable, and it

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[*] See Brögger, Zeit. Kryst. Min., XVI, p. 223 et seq.

[†] Neues Jahrb., 1892, II, p. 1; Brauns.

[‡] Neues Jahrb., 1890, I, p. 134.

[§] Neues Jahrb., 1890, I, p. 128, et seq.

[||] Neues Jahrb., 1890, I, p. 118, and Allgem. Chem. Mineralogie, p. 183.

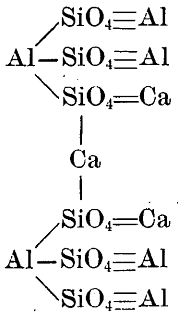
[¶] Zeitsch. Geolog. Gesell., 1885, p. 959 et seq.

only remains to work out the details for each individual mineral. The fundamental relations between the two groups have been recognized by many writers; but their interpretations have been diverse.

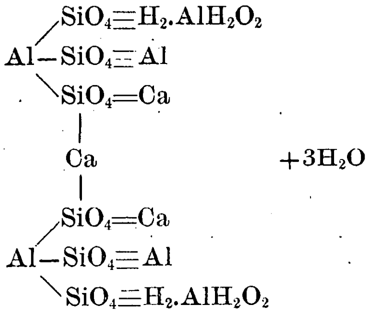
In the systematic treatment of the zeolites, the most serious difficulty is found in the hydration of the several species. To determine in any case what part of the water is constitutional and what crystalline is not easy, and no fixed criterion exists upon which judgment may be based. Water which is retained by a mineral above 300° of temperature is almost certainly constitutional; water lost at or below 100° is probably water of crystallization; but between the two there is a range of considerable vagueness. There is, however, one datum which has claims to high consideration. Certain zeolites, at various temperatures between the limits indicated, lose water which is regained without change of crystalline character upon subsequent exposure of the minerals to moist air, and this, as has been urged by several authorities, should be regarded as water of crystallization. By considerations of this kind we can be guided to some extent, but beyond them each zeolite must be studied independently, in the light of such collateral evidence as may be available. For some species the evidence is full, for others it is meager; but such as it is it will appear in the systematic discussion following.

In a recent publication* I have shown how all of the normal zeolites may be formulated as substitution derivatives of the feldspars, although in some cases alternative formulæ are readily conceivable. Thus, from anorthite several species are directly derivable, as follows:

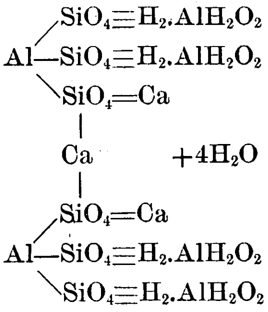
Anorthite.



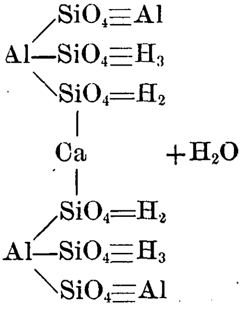
Thomsonite.



Gismondite.



Foresite.



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* Am. Jour. Sci. (3), XLVIII, p. 187, 1894.

Of these formulæ, the last one, that of foresite, is uncertain, on account of great variations in the published analyses. It is therefore to be regarded as approximate only, and as peculiarly subject to revision. For gismondite the composition is empirically that given by Dana, and the calcium is partly replaceable by potassium. Gismondite is said to give off one-third of its water at 100°, and in the formula that amount is represented as water of crystallization. For thomsonite the evidence is much fuller. Here four-sevenths of the water is regarded as constitutional, a proportion which is fairly in accord with the data by Damour and by Hersch, as cited in Dana.* In nature thomsonite often occurs as a derivative of elæolite, while, according to Doelter (loc. cit.), it yields anorthite upon fusion. In some cases thomsonite, variety mesole, carries an excess of silica, which may be attributed to an admixture of trisilicate groups; that is, to Si_3O_8 replacing SiO_4. In a thomsonite derived from a plagioclase feldspar this should be expected, and so also should the almost invariable replacement of a part of the calcium by sodium. Nonsodic thomsonite exists, but is probably rare. A thomsonite containing Ca_2Na_2 in place of Ca_3 would have the following theoretical composition:

SiO_2	37.27
Al_2O_3	31.68
CaO	11.59
Na_2O	6.42
H_2O	13.04
	100.00
$\frac{3}{7}H_2O$ (water of crystallization)	5.59

This agrees well with published analyses, so that the formula proposed satisfies all the conditions imposed by the evidence and also by the general substitution theory.

In scolecite, $Al_4Ca_2H_8(SiO_4)_6.2H_2O$, we find a zeolite with relations to natrolite on one side and to anorthite on the other. Approximately one-third of its water is given off at temperatures below 300°, to be taken up again in moist air, and on fusion, according to Doelter, it yields anorthite. By the slow action of soda solutions it is transformed into natrolite and mesolite, while natrolite, by means of calcium chloride, is convertible into scolecite.† Mesolite, which is intermediate between natrolite and scolecite, may be regarded as a mixture of the two, or it may be formulated as an independent compound. Written on the anorthite type, scolecite and mesolite become

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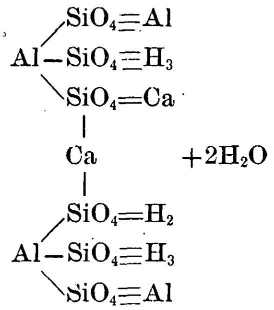
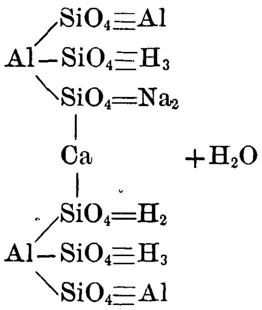
*Syst. Min., 6th ed., p. 608. Compare Hersch, Der Wassergehalt der Zeolithe, Zürich, 1887.

†Lemberg, Zeitsch. Geol. Gesell., XXVIII, p. 551, 1876.

Scolecite.

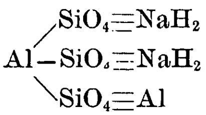


Mesolite.

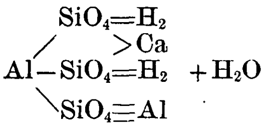


the two species being possibly miscible. On the other hand, the scolecite formula may be halved and correlated with that of natrolite, thus:

Natrolite.



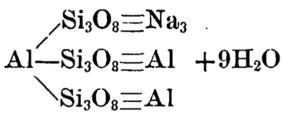
Scolecite.

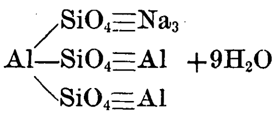


Both formulæ for scolecite satisfy the evidence, but between them it is difficult to decide. The existence of mesolite may perhaps turn the scale in favor of the anorthite structure.

By the action of barium chloride solution upon an artificial natrolite, Lemberg* obtained a barium compound which may be the equivalent of scolecite. It is also near the tetragonal edingtonite in composition. The evidence as to the constitution of edingtonite, however, is very imperfect, and dehydration data are entirely wanting. It may also be represented as the barium equivalent of the monoclinic gismondite, the difference in form being due to a difference of combination on the part of the water. At all events, it is highly probable that edingtonite is a derivative of a barium feldspar.

In the rhombohedral zeolites, gmelinite, levynite, and chabazite with its varieties, the ratios are approximately metasilicate, but somewhat variable. In this respect they resemble the feldspars, and the pseudometasilicate character is ascribable to mixtures of ortho- and trisilicates, with sometimes one and sometimes the other predominating. Gmelinite is essentially a sodium zeolite, with comparatively little or no lime in its composition, and when lime is present it can be attributed to a hydrous anorthite with 18 molecules of water. Apart from the lime, gmelinite is easily interpreted as a mixture of two silicates of precisely similar chemical type; one an albite, and the other its orthosilicic equivalent, thus:





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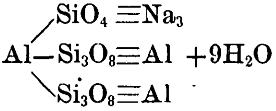
* Zeitsch. Geol. Gesell., XXVIII, p. 553, 1876.

Calculating for mixtures in the ratios of 1:1 and 2:1, we get from these formulæ the following composition of gmelinite, in comparison with analyses by Rammelsberg and by Pirsson:*

	Rammelsberg.	Pirsson.	1:1.	2:1.
SiO_2	46.48	50.67	46.89	50.89
Al_2O_3	20.64	18.50	19.92	18.21
Fe_2O_3		.15		
CaO	3.78	1.05	12.11	11.27
Na_2O	7.19	9.88		
K_2O	1.74	.16		
H_2O	20.41	20.15	21.08	19.63
	100.24	100.56	100.00	100.00

The water is probably all crystalline, thus distinguishing gmelinite from a sodium chabazite; but the evidence on this point is incomplete. Pirsson's analysis may also be represented by a mixed salt of this character:



$$Al\begin{cases} SiO_4\equiv Na_3 \\ Si_3O_8\equiv Al \\ Si_3O_8\equiv Al \end{cases} +9H_2O$$

indicating a relationship to analcite. Such a relation is suggested by the experiments of Lemberg,† who not only derived analcite from the zeolites of this group, but also, starting from fused analcite, obtained a compound approximating to gmelinite in composition.

For chabazite the fundamental ratios are essentially the same as with gmelinite, but the proportions between lime and soda vary greatly. Potassium is also present to a noteworthy extent in some cases, indicating a partial derivation of the mineral from leucite, orthoclase, or microcline. As regards hydration, a part of the water in chabazite appears to be constitutional, probably two molecules out of the nine shown in the gmelinite formula, but this point is not absolutely certain. The evidence in its favor is strong, but not conclusive.

The analyses of chabazite are numerous. Some of them reduce easily to mixtures of anorthite+18 aq. and albite+9 aq., and some, showing little lime, represent isomers of gmelinite. But many chabazites are very low in alkalies, while the ratio between Si_3O_8 and SiO_4 remains practically constant. In these cases it seems necessary to assume the existence of a trisilicate anorthite, or calcium albite, which, by itself, is not known in nature. According to Doelter,‡ chabazite yields upon fusion a mixture of anorthite and silica, a fact which is in harmony

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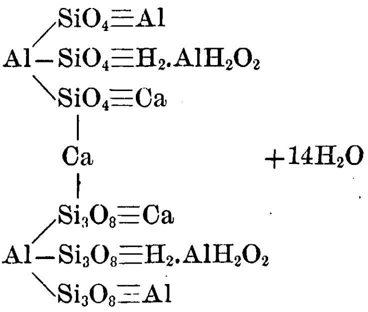
* Dana; 6th ed., p. 594.

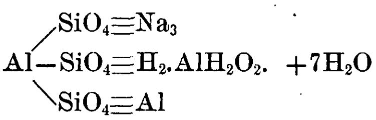
† Zeitsch. Geol. Gesell., 1885, p, 972.

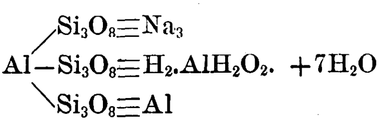
‡ Allgem. Chem. Mineralogie, p. 183.

with the foregoing conjecture. Taking all the data into account, chabazite may be formulated as a mixture of the compound



with the salts





the latter being isomeric with the gmelinite molecules. A sodium chabazite agrees in empirical composition with gmelinite, and the calcium salt by itself has the following composition, as compared with chabazite from Aussig, as analyzed by Lemberg:*

	Found.	Calculated.
SiO_2	47.50	47.43
Al_2O_3	20.00	20.15
CaO	10.20	11.07
Na_2O	.23	
K_2O	1.24	
H_2O	21.40	21.35
	100.57	100.00

It is perfectly evident that the calcium chabazite may also be written as an equimolecular mixture derived from anorthite and its trisilicate equivalent; and in levynite, the last member of the rhombohedral group, we have a mineral of the same type, although differing in hydration. Instead of 18 molecules of water, as in chabazite, levynite contains only 15; but in both cases 4 molecules are to be regarded as constitutional, in accordance with the observations made by Damour. Computing from Hillebrand's analyses,† levynite contains the ortho- and trisilicate molecules in the ratio of 3:2, giving the following empirical composition to the species:

$$3Al_6(SiO_4)_6Ca_3.\ 15H_2O + 2Al_6(Si_3O_8)_6Ca_3.\ 15H_2O,$$

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* Analysis No. 4 in Dana's table, Syst. Min., p. 591.

† Bull. U. S. Geol. Surv. No. 20, p. 38.

with the subjoined comparison between observation and theory:

	Found.	Calculated.
SiO_2	47.76	46.55
Al_2O_3	21.91	21.98
CaO	11.12	12.07
Na_2O	1.34	
K_2O	.21	
H_2O	18.65	19.40
	99.99	100.00

Here, as with the preceding minerals of this group, the accordance is quite satisfactory.

One more point with regard to chabazite remains to be noted. According to Kenngott,* a crystal of this mineral, heated to nearly the melting point of glass, retains its form and luster, but loses transparency. If, after cooling, such a dehydrated crystal be moistened with a drop of water, the latter is taken up with evolution of much heat. This observation may possibly imply that the constitutional hydroxyl of chabazite is united wholly or in part with calcium, in which case the formula as written by me should be correspondingly modified. CaOH would appear in it in place of AlH_2O_2, but the fundamental type need not be thereby changed. The question thus raised suggests profitable lines for experimental investigation, which ought to shed much light upon the constitution of this and other allied minerals.

The supposition that the minerals of the chabazite group may be partly derived from a trisilicate anorthite is strongly sustained by the composition of stilbite, which, most typically, is represented by the empirical formula $Ca_3Al_6(Si_3O_8)_6 + 18H_2O$. This requires

SiO_2	57.51
Al_2O_3	16.29
CaO	8.94
H_2O	17.26
	100.00

which agrees with many analyses. Some varieties of stilbite show less silica, which may be due to the presence of orthosilicate molecules, and in most cases a little soda or potash replaces lime. The latter fact represents the presence of albite, elæolite, or orthoclase among the parent minerals of the zeolite, and involves no change in the structure of the molecule. So far as can be determined from the observations of Hersch, about two-ninths of the water in stilbite is retained at moderately high

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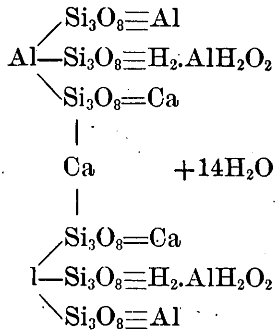
* Quoted by Hersch, p. 36.

temperatures, and may therefore be regarded as constitutional. On this basis the formula of the mineral becomes



which, in type, resembles that of chabazite, although the two species are crystallographically dissimilar.

To heulandite and epistilbite, two isomeric compounds, essentially the same formula belongs, but with less water of crystallization. Calculated with $Al_6(Si_3O_8)_6Ca_3.16H_2O$, we have for their composition

SiO_2	58.63
Al_2O_3	16.61
CaO	9.12
H_2O	15.64
	100.00

in close agreement with analysis. Hersch's work on heulandite shows about three-fourths of the water, or 12 molecules, to be easily expelled, leaving 4 molecules, as in stilbite, constitutional. Hence its structural formula may be written like that of stilbite, with 12 instead of 14 H_2O; or, $Al_4(Si_3O_8)_6Ca_3H_4(AlH_2O_2)_2.12H_2O$. Brewsterite appears to be like heulandite, but with barium and strontium replacing calcium.

According to Doelter, stilbite and heulandite, on fusion, yield a pyroxenic mineral with silica and an amorphous ground mass, and sometimes also anorthite. The same chemist* also effected the synthesis of heulandite from anorthite by digesting the latter with freshly precipitated silica and carbonated water at a temperature of 200°. These data are but partially interpreted by the constitutional formulæ here given, and for which alternative expressions are possible. A connection with anorthite is established, but the isomerism between heulandite and epistilbite, and the formation of a substance resembling pyroxene from stilbite and heulandite, remain to be accounted for. Possibly epistilbite

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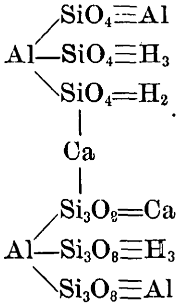
* Neues Jahrb., 1890, I, p. 128.

may have the formula already given for this group, while stilbite and heulandite may contain the molecule



plus $8H_2O$ in one species and $6H_2O$ in the other. This formula was adopted in my former paper on the zeolites, and its configuration, with eight atoms of acid hydrogen, would indicate a complex breaking up upon complete dehydration. Between the two forms of expression, further investigation must decide. Both are in harmony with the fundamental theory, so that the questions at issue are mainly questions of detail.

To stilbite, morphologically, the species harmotome and phillipsite are closely allied. To harmotome may be assigned the formula $Al_6(SiO_4)_2(Si_3O_8)_4Ba_3.14H_2O$, which requires

SiO_2	45.23
Al_2O_3	16.48
BaO	24.72
H_2O	13.57
	100.00

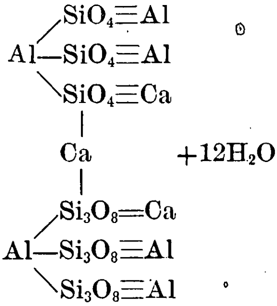
A little barium is commonly replaced by potassium or sodium, perhaps, or even probably as $Al_3(Si_3O_8)_3K_3.7H_2O$, the water being loosely combined and therefore all crystalline. In all probability harmotome is a derivative by hydration of the barium feldspar, hyalophane.

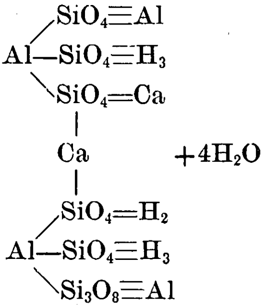
In phillipsite, which, since the investigations of Fresenius, has been generally recognized as the calcium equivalent of harmotome, we find a larger proportion of the bivalent metal replaced by potassium or sodium, and a more variable ratio between SiO_4 and Si_3O_8. A typical phillipsite approaches nearly to the formula $Al_6(SiO_4)_3(Si_3O_8)_3Ca_2K_2.14H_2O$, which requires

SiO_2	48.52
Al_2O_3	20.63
CaO	7.54
K_2O	6.33
H_2O	16.98
	100.00

Here again no water is constitutional. In my former paper I assigned to both phillipsite and harmotome a hydration of 15 molecules, but 14 agrees better with the published analyses. In some cases the calcium of phillipsite is lower and the alkaline metals higher than is shown by the ratio Ca_2K_2, but the ratio CaR'_4 does not appear to be reached, unless by the presence of H among the components of R'_4 The general formula for phillipsite and harmotome, as shown by all trustworthy analyses, is $Al_6X_6R''_3.14H_2O$, when X represents $SiO_4+Si_3O_8$ and R'' is made to include the equivalent of the alkalies. Fusion experiments upon the two species seem to be wanting.

To laumontite, $CaAl_2Si_4O_{12}.4H_2O$, two constitutional formulæ may be assigned, as follows:



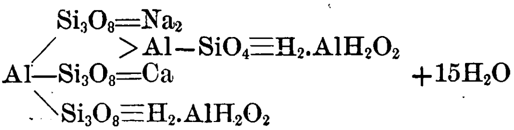


Both expressions give the same empirical composition, but the first is the more symmetrical. The second indicates a ratio between constitutional and crystalline water which agrees with the somewhat incomplete recorded data, but the first is adjustable in such a manner as to represent the same facts. According to Doelter,* laumontite upon fusion gives anorthite, together with a pyroxenic mineral and an amorphous ground mass, and this evidence may harmonize with either formula. A fuller experimental investigation of this species is evidently necessary.

For the isometric faujasite the formula may be written structurally in two ways. One is in uniformity with the expressions assigned to the previous species, and is

$$Al_4(SiO_4)_4(Si_3O_8)_2Na_2CaH_8.15H_2O$$

The other is based upon the analcite formula, as developed in the preceding chapter, thus:



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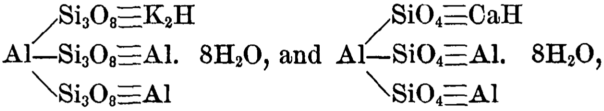
* Neues Jahrb., 1890, I, p. 130.

From these, which are empirically identical, we get the subjoined comparison between theory and the analysis by Damour:*

	Found.	Calculated.
SiO_2	46.12	47.46
Al_2O_3	16.81	16.14
CaO	4.79	4.43
Na_2O	5.09	4.91
H_2O	27.02	27.06
	99.83	100.00
$15H_2O=$		21.36

According to Jannasch,† faujasite loses 10.88 per cent of water at 105°–110°. At 150° it loses 16.83, about 12 molecules, which is regained in moist air. Between 250° and 260° it loses 22.67 per cent, and the remainder of the water is expelled upon ignition. Of the two formulæ given, the one corresponding to the leucite-analcite type is preferable, for it represents the morphological analogy between the species. Furthermore, faujasite on treatment with hydrochloric acid is decomposed, but does not gelatinize, a fact which may indicate a predominance of trisilicate over orthosilicate groups. This datum, however, is of questionable significance.

One more zeolite, the little-known species offretite, remains to be considered in this connection. This may be represented as a mixture of two molecules,



$$Al\begin{cases} Si_3O_8\equiv K_2H \\ Si_3O_8\equiv Al \\ Si_3O_8\equiv Al \end{cases} .\ 8H_2O,\ \text{and}\ Al\begin{cases} SiO_4\equiv CaH \\ SiO_4\equiv Al \\ SiO_4\equiv Al \end{cases} .\ 8H_2O,$$

in the ratio of 2:1. This gives, in comparison with Gonnard's analysis, the following composition:

	Found.‡	Calculated.
SiO_2	52.47	52.02
Al_2O_3	19.06	18.95
CaO	2.43	2.30
K_2O	7.72	7.77
H_2O	18.90	18.96
	100.58	100.00

This species is evidently a derivative of orthoclase and anorthite, and the calcium term in the foregoing formula may evidently be written on the anorthite type, namely, as $Al_6(SiO_4)_6Ca_2H_2.16H_2O$. The

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* Dana's System, 6th ed., p. 598.

† Neues Jahrb., 1887, II, p. 24.

‡ Dana's System, 6th ed., p. 1043.

character of its hydration, other than is shown in the formula as given, remains to be determined. The mineral is decomposable by acids with difficulty.

From the evidence given in the foregoing pages the constitutional and genetic connection between the normal zeolites and the feldspars seems to be perfectly clear, and it ought to be easily emphasized by investigations along petrographic lines. Data of this kind, in addition to those already cited, are even now available, and many alterations of the most pertinent kind have been observed. Thus laumontite, heulandite, stilbite, and analcite alter into albite or orthoclase; laumontite and stilbite into analcite; chabazite into natrolite; and gismondite into phillipsite. So also alterations into prehnite are recorded on the part of laumontite, scolecite, mesolite, natrolite, and analcite; and the identity of chemical type seems to be almost unquestionable. From the formulæ here developed all of these alterations become intelligible, and the theory of substitution from normal salts is very emphatically sustained. For the group of zeolites it only remains to summarize the expressions which have been adopted.

For starting points the following minerals are taken:

Nephelite	$Al_3(SiO_4)_3Na_3$
Albite and orthoclase	$Al_3(Si_3O_8)_3R'_3$
Anorthite	$Al_6(SiO_4)_6Ca_3$
Trisilicic anorthite	$Al_6(Si_3O_8)_6Ca_3$

The last compound is purely hypothetical. To these may be added leucite, from which analcite and faujasite are derivable, and the barium-strontium feldspars which give rise to brewsterite, edingtonite, and harmotome. Brewsterite, as the equivalent of heulandite, and harmotome, as a barium phillipsite, need not be considered further; and as for edingtonite, its constitution is very uncertain. The remaining zeolites are as follows, with the difference between water of constitution and water of crystallization disregarded, except in the few cases in which the distinction affects the integrity of the molecular type. The symbol X is used to express SiO_4 or Si_3O_8 indiscriminately:

Type $Al_3X_3R'_3$.

Hydronephelite	$Al_3(SiO_4)_3Na_2H, 3H_2O$
Offretite	$Al_3(SiO_4)(Si_3O_8)_2R'_3, 8H_2O$
Gmelinite	$Al_3(SiO_4)(Si_3O_8)_2Na_3, 9H_2O$

Type $Al_6X_6Ca_3$.

Thomsonite	$Al_6(SiO_4)_6Ca_3, 7H_2O$
Gismondite	$Al_6(SiO_4)_6Ca_3, 12H_2O$
Laumontite	$Al_6(SiO_4)_3(Si_3O_8)_3Ca_3, 12H_2O$
Phillipsite	$Al_6(SiO_4)_3(Si_3O_8)_3Ca_2K_2, 14H_2O$
Levynite	$Al_6X_6Ca_3, 15H_2O$
Heulandite, epistilbite	$Al_6(Si_3O_8)_6Ca_3, 16H_2O$
Stilbite	$Al_6(Si_3O_8)_6Ca_3, 18H_2O$
Chabazite	$Al_6(SiO_4)_3(Si_3O_8)_3Ca_3, 18H_2O$

Type $Al_2X_3R'_6$.

Natrolite	$Al_2(SiO_4)_3Na_2H_4$
Prehnite	$Al_2(SiO_4)_3Ca_2H_2$
Scolecite	$Al_2(SiO_4)_3CaH_4, H_2O$

Type $Al_4X_6Ca_6$.

Mesolite	$Al_4(SiO_4)_6CaNa_2H_8, H_2O$
Foresite	$Al_4(SiO_4)_6CaH_{10}, H_2O$

Some of these formulæ are conditioned by the replacements and alternatives cited in the previous pages and in my former paper upon the zeolites, and they are further modified by the character of the hydration. The expressions for analcite and faujasite, as based upon the leucite type, need not be repeated.

The morphological characteristics of the zeolites probably depend in great part upon their mode of hydration, but this point needs to be developed. So also does the relation between zeolites and kaolin, into which the minerals of this group sometimes alter. Furthermore, zeolitic substances of indeterminate nature are believed to exist in soils and clays, and it is conceivable that such bodies may be intermediately formed during the transition from feldspar into kaolin. In studying the mechanism of that change this possibility ought to be considered.

V. THE MICAS AND CHLORITES.

On account of their wide distribution, their variety of composition, and their genetic relations to other species, the micas and chlorites form one of the most instructive and interesting families of minerals. Two of the micas, muscovite and biotite, have already been noted among the members of the first and second of the preceding groups; and we have seen how frequently they arise from the alteration of other silicates, while these in some cases have been synthetically derived from micaceous material.

As regards the substitution theory, the minerals of this family are peculiarly suggestive, for the reason that they form a series of the most complete character. Thus, starting from the normal aluminum orthosilicate, we have

Normal orthosilicate	$Al_4(SiO_4)_3$
Muscovite	$Al_3(SiO_4)_3KH_2$
Normal biotite	$Al_2(SiO_4)_3Mg_2KH$
Normal phlogopite	$Al(SiO_4)_3Mg_3KH_2$

No further substitution of the same order is possible, for the reason that its formation would remove the linking atom of aluminum, and break up the fundamental molecule.

Muscovite, the first species in the foregoing series, occurs in nature as an independent mineral, and also as an alteration product of nephelite, eucryptite, topaz, andalusite, the feldspars, the scapolites, and various other natural silicates. All of these alterations become intelligible in the light of the formulæ adopted in this memoir. In its more typical occurrences muscovite agrees sharply with the formula given, but it varies in composition within well-defined limits. First, it ranges toward its sodium equivalent, paragonite, which has the corresponding formula $Al_3(SiO_4)_3NaH_2$. Secondly, in fuchsite, the chromic mica, a chromium salt partly replaces the aluminum compound, and similar ferric replacements are also known. In all of these variations, however, there is no change of ratios, and the typical formula remains undisturbed. In the barium mica, œllacherite, there is possibly a molecule of the type $Al_3(SiO_4)_3R''R'$, but this is uncertain. Other interpretations of the barium micas are admissible.

The most important variation in muscovite is in the direction of increased silica. Normal muscovite contains 45.3 per cent of SiO_2, but varieties exist in which the percentage rises to nearly 59. Muscovites of this class have been designated by Tschermak as phengites, and they are most easily explained upon the supposition of trisilicate admixtures. The molecule $Al_3(Si_3O_8)_3KH_2$ is identical in type with ordinary orthosilicate muscovite, and its presence completely accounts for all excesses of silica over the normal amount. In Sandberger's lepidomorphite, for instance, the orthosilicate and trisilicate molecules occur in nearly equal proportions. All known muscovite may be represented by the general formula $Al_3(SiO_4)_3R'_3+Al_3(Si_3O_8)_3R'_3$, in which the latter molecule varies from zero to fifty per cent, and with ferric iron or chromium sometimes replacing aluminum.

With the biotites and phlogopites the variability of composition is even greater than in the case of muscovite. For the typical molecules the composition would be

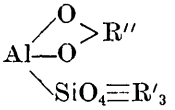
	$Al_2(SiO_4)_3Mg_2KH$.	$Al(SiO_4)_3Mg_3KH_2$.
SiO_2	43.06	43.27
Al_2O_3	24.40	12.26
MgO	19.14	28.85
K_2O	11.25	11.29
H_2O	2.15	4.33
	100.00	100.00

To these types but few natural micas actually correspond, although intermediate mixtures are very common. Furthermore, ferrous salts frequently replace the magnesium compounds, and ferric molecules replace those of aluminum. Manganese, also, sometimes occurs among the dyad bases, and occasionally trisilicates in small amount are commingled with the ortho-salts. Because of these complications, the reduction of a given analysis to a specific formula may be very difficult, and this difficulty is often increased by uncertainty in the determination of water, or of the state of oxidation of the iron. In spite of these difficulties, however, the reduction is generally possible, and the ferromagnesian micas, with some exceptions to be noted further on, are representable as mixtures of the two types shown in the formulæ as given. The iron mica siderophyllite agrees closely in composition with a normal ferrous biotite, $Al_2(SiO_4)_3Fe_2KH$. Aspidolite appears to be a sodium phlogopite, but needs reanalysis. In exceptional cases, muscovitic types seem to exist among these micas, and certain lepidomelanes approximate to the general formula $Al_3(SiO_4)_3Fe''K+Fe'''_3(SiO_4)_3Fe''K$. Another unusual mica is Breithaupt's alurgite, which, as analyzed by Penfield,* corresponds to a mixture of molecules

$$2.\ Al_3(Si_3O_8)_3KH_2$$
$$3.\ Al_2(SiO_4)_3K_2H_4$$
$$3.\ Al_2(SiO_4)_3Mg_2KH,$$

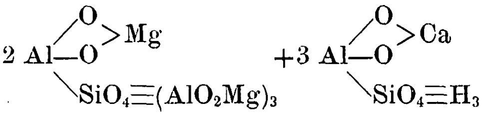
with a slight excess of H over K in the last compound. The second of these molecules, an alkaline biotite, is the characteristic feature of alurgite. Similar compounds, parallel to phlogopite, seem also to exist, having the general formula $Al(SiO_4)_3R'_9$; but all of these bodies conform sharply to the general theory of the micas, and are substitution derivatives of the normal aluminum salt.

In many of the magnesian micas fluorine is found, and the iron micas frequently contain oxygen in excess of the amount necessary to convert all of the silicon into the radicle SiO_4. When this excess is real, that is, not ascribable to defective analysis, it may be due either to alteration or to admixtures of micas belonging to the clintonite group. This group, the members of which resemble biotite morphologically, are extremely basic, and are representable by the general formula



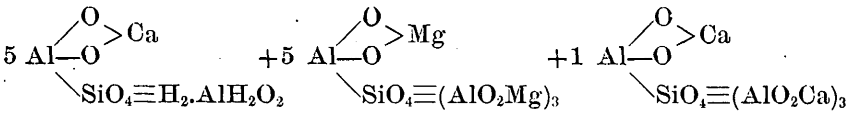
$$\mathrm{Al}\left\{\begin{array}{l}\left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right>\mathrm{R''}\\ \mathrm{SiO_4{\equiv}R'_3}\end{array}\right.$$

in which R'_3 may be replaced by Al, or by $R''R'$, R'' being magnesium, calcium, or ferrous iron. The univalent group AlO_2R'' may also appear in R', giving as the extreme end of the clintonite series the compound $(AlO_2R'')_4SiO_4$. In seybertite and brandisite we have nearly



$$2\ \mathrm{Al}\left\{\begin{array}{l}\left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right>\mathrm{Mg}\\ \mathrm{SiO_4{\equiv}(AlO_2Mg)_3}\end{array}\right. +3\ \mathrm{Al}\left\{\begin{array}{l}\left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right>\mathrm{Ca}\\ \mathrm{SiO_4{\equiv}H_3}\end{array}\right.$$

while xanthophyllite † is



$$5\ \mathrm{Al}\left\{\begin{array}{l}\left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right>\mathrm{Ca}\\ \mathrm{SiO_4{\equiv}H_2.AlH_2O_2}\end{array}\right. +5\ \mathrm{Al}\left\{\begin{array}{l}\left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right>\mathrm{Mg}\\ \mathrm{SiO_4{\equiv}(AlO_2Mg)_3}\end{array}\right. +1\ \mathrm{Al}\left\{\begin{array}{l}\left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right>\mathrm{Ca}\\ \mathrm{SiO_4{\equiv}(AlO_2Ca)_3}\end{array}\right.$$

The xanthophyllite, upon ignition, decomposes into a portion soluble and a portion insoluble in hydrochloric acid. The insoluble portion has the composition of spinel, a mineral which is generally found

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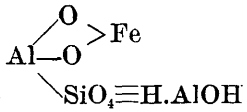
* Am. Jour. Sci., (3) XLVI, p. 289. 1893.

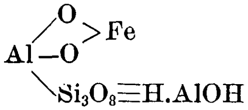
† See Clarke and Schneider, U. S. G. S. Bulletin No. 113, p. 27.

accompanying clintonite micas, and of which the formation is rendered intelligible by the formulæ. Whether chloritoid belongs here or not is doubtful, but if it does its formula may be written



$$\begin{array}{l}\quad\diagup\mathrm{O}\\ \mathrm{Al}-\mathrm{O}\end{array}\!>\!\mathrm{Fe}\qquad \mathrm{Al}\diagdown\mathrm{SiO_4{\equiv}H.AlOH}$$

Ottrelite may possibly be essentially the trisilicate equivalent of chloritoid,



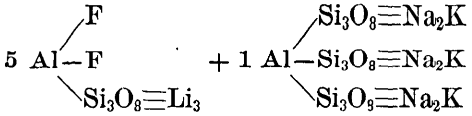
$$\begin{array}{l}\quad\diagup\mathrm{O}\\ \mathrm{Al}-\mathrm{O}\end{array}\!>\!\mathrm{Fe}\qquad \mathrm{Al}\diagdown\mathrm{Si_3O_8{\equiv}H.AlOH}$$

and Damour's venasquite approaches this composition. Variations in composition in ottrelite correspond to mixtures of this molecule with small quantities of chloritoid. Venasquite, however, is also reducible to the normal mica type, and agrees sharply with

$$\begin{array}{c}2\ \mathrm{Al_3(SiO_4)_3H_3}\ +\\ 3\ \mathrm{Al_2(SiO_4)_3Fe_2H_2}\end{array}$$

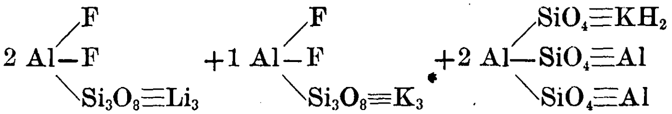
It may be that ottrelite and its varieties represent the first stage intermediate between micas and vermiculites; the alkalies of mica having been replaced by water, all R′ becoming H.

Although fluorine is found in micas of all classes, it is chiefly characteristic of lepidolite, zinnwaldite, and phlogopite, and is generally connected with a low oxygen ratio. Indeed, the extreme end of the lepidolite series, polylithionite, is entirely trisilicate in character, and its existence fully justifies the assumption that trisilicates occur in other micas. Furthermore, polylithionite furnishes a clew to the entire lepidolite or lithia mica series, and its formula is easily written



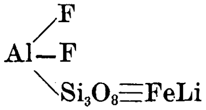
$$5\ \mathrm{Al}\begin{cases}\mathrm{F}\\ \mathrm{F}\\ \mathrm{Si_3O_8{\equiv}Li_3}\end{cases} + 1\ \mathrm{Al}\begin{cases}\mathrm{Si_3O_8{\equiv}Na_2K}\\ \mathrm{Si_3O_8{\equiv}Na_2K}\\ \mathrm{Si_3O_8{\equiv}Na_2K}\end{cases}$$

the dominant molecule being akin to clintonite in general constitution. Ordinary lepidolite contains the same molecule, mingled with molecules of the muscovite type, and an average example is represented by



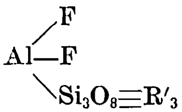
$$2\ \mathrm{Al}\begin{cases}\mathrm{F}\\ \mathrm{F}\\ \mathrm{Si_3O_8{\equiv}Li_3}\end{cases} +1\ \mathrm{Al}\begin{cases}\mathrm{F}\\ \mathrm{F}\\ \mathrm{Si_3O_8{\equiv}K_3}\end{cases} +2\ \mathrm{Al}\begin{cases}\mathrm{SiO_4{\equiv}KH_2}\\ \mathrm{SiO_4{\equiv}Al}\\ \mathrm{SiO_4{\equiv}Al}\end{cases}$$

In cryophyllite we have similar molecules, plus molecules of an iron biotite, $\mathrm{Al_2(SiO_4)_3Fe_2H_2}$. Cryophyllite is associated most intimately with an iron mica of that general character, and lepidolite, similarly, is always accompanied by muscovite. In zinnwaldite the molecule



$$\mathrm{Al}\begin{cases}\mathrm{F}\\ \mathrm{F}\\ \mathrm{Si_3O_8{\equiv}FeLi}\end{cases}$$

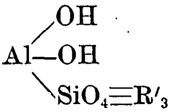
probably occurs, commingled with others of the ordinary lepidolite and muscovite types. In short, all the lithia micas contain compounds of the type



$$\mathrm{Al}\begin{cases}\mathrm{F}\\ \mathrm{F}\\ \mathrm{Si_3O_8}\equiv\mathrm{R'_3}\end{cases}$$

with members of the normal mica series.* The fluoriferous phlogopites may contain molecules of the same character, especially $\mathrm{AlF_2.Si_3O_8.MgK}$, or they may be of the normal type with univalent $-\mathrm{Mg}-\mathrm{F}$ among the monad bases. Between these alternatives it is difficult to decide, and more evidence is necessary.

By alteration lepidolite passes into cookeite, a mineral which well illustrates the equivalent character of hydroxyl and fluorine. Penfield's analysis gives for cookeite a general formula,



$$\mathrm{Al}\begin{cases}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{SiO_4}\equiv\mathrm{R'_3}\end{cases}$$

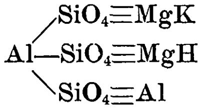
and in detail a mixture of molecules,

$$\begin{aligned}&10\mathrm{Al(OH)_2SiO_4.Li_3}\\ +&14\mathrm{Al(OH)_2SiO_4.H_3}\\ +&33\mathrm{Al(OH)_2SiO_4.Al}\end{aligned}$$

The identity of type between cookeite and lepidolite is perfectly clear, and the analogy with the clintonite micas is still more apparent.

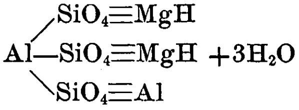
In a similar way the other micas alter by hydration, yielding a great variety of products which are known in general as vermiculites. This is especially true as regards the ferromagnesian micas, which lose alkalies and take up water with the greatest ease, in accordance with what seems to be a well-defined law. Thus we have

Biotite.



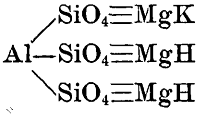
$$\mathrm{Al}\begin{cases}\mathrm{SiO_4}\equiv\mathrm{MgK}\\ \mathrm{SiO_4}\equiv\mathrm{MgH}\\ \mathrm{SiO_4}\equiv\mathrm{Al}\end{cases}$$

Hydrobiotite.



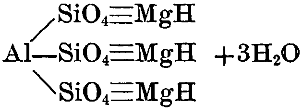
$$\mathrm{Al}\begin{cases}\mathrm{SiO_4}\equiv\mathrm{MgH}\\ \mathrm{SiO_4}\equiv\mathrm{MgH}\\ \mathrm{SiO_4}\equiv\mathrm{Al}\end{cases}+3\mathrm{H_2O}$$

Phlogopite.



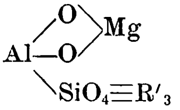
$$\mathrm{Al}\begin{cases}\mathrm{SiO_4}\equiv\mathrm{MgK}\\ \mathrm{SiO_4}\equiv\mathrm{MgH}\\ \mathrm{SiO_4}\equiv\mathrm{MgH}\end{cases}$$

Hydrophlogopite.



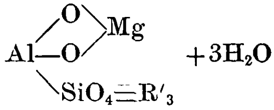
$$\mathrm{Al}\begin{cases}\mathrm{SiO_4}\equiv\mathrm{MgH}\\ \mathrm{SiO_4}\equiv\mathrm{MgH}\\ \mathrm{SiO_4}\equiv\mathrm{MgH}\end{cases}+3\mathrm{H_2O}$$

Clintonite.



$$\mathrm{Al}\begin{cases}\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\Big\rangle\mathrm{Mg}\\ \mathrm{SiO_4}\equiv\mathrm{R'_3}\end{cases}$$

Hydroclintonite.



$$\mathrm{Al}\begin{cases}\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\Big\rangle\mathrm{Mg}\\ \mathrm{SiO_4}\equiv\mathrm{R'_3}\end{cases}+3\mathrm{H_2O}$$

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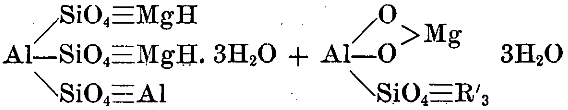
* For fuller discussion, see Bulletin U. S. G. S. No. 113, p. 22.

The micas in question occur in nature in great variety of admixture, and the corresponding vermiculites show a parallel complexity. In every case, however, the alteration of the one series into the other follows the line indicated by the formulæ, and the vermiculite is simply the mica with H in place of K or Na, plus 3 molecules of loosely combined water. Two of these molecules are, as a rule, given off at 100°, and regained in moist air, suggesting an analogy between the vermiculites and the zeolites. Some vermiculites, however, are only monohydrated, and many of the so-called species which have received names are mere mixtures of altered and unaltered micas, representing stages of transition between the original mineral and the final product. Among the more characteristic vermiculites, kerrite, protovermiculite, hallite, and lennilite appear to be essentially trihydrated mixtures of the hydrophlogopite and hydroclintonite types, commingled in ratios nearly as follows:

	Hydrophlog.		*Hydroclint.*
Kerrite	5	:	1
Protovermiculite	1	:	1
Hallite	7	:	18

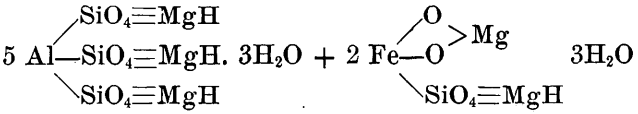
Lennilite is near hallite, and both may contain small admixtures of chloritic material. The kerrite is quite near the typical hydrophlogopite alone.

Jefferisite resembles protovermiculite in ratios, but with a hydrobiotite in place of the hydrophlogopite; that is,



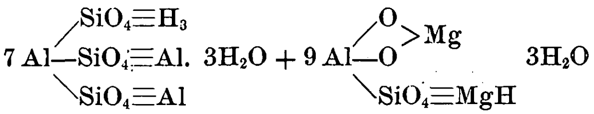
$$\mathrm{Al}\begin{array}{l}\diagup\mathrm{SiO_4{\equiv}MgH}\\ -\mathrm{SiO_4{\equiv}MgH}\\ \diagdown\mathrm{SiO_4{\equiv}Al}\end{array}.\ 3H_2O+\mathrm{Al}\begin{array}{l}\diagup\mathrm{O}\\ -\mathrm{O}\\ \diagdown\mathrm{SiO_4{\equiv}R'_3}\end{array}\!\!>\mathrm{Mg}\quad 3H_2O$$

and vaalite is very nearly



$$5\,\mathrm{Al}\begin{array}{l}\diagup\mathrm{SiO_4{\equiv}MgH}\\ -\mathrm{SiO_4{\equiv}MgH}\\ \diagdown\mathrm{SiO_4{\equiv}MgH}\end{array}.\ 3H_2O+2\,\mathrm{Fe}\begin{array}{l}\diagup\mathrm{O}\\ -\mathrm{O}\\ \diagdown\mathrm{SiO_4{\equiv}MgH}\end{array}\!\!>\mathrm{Mg}\quad 3H_2O$$

Maconite and lucasite are probably micas which have been partly vermiculitized, and an essential portion of the first-named mineral appears to be a derivative of muscovite. Roseite is very near a mixture of partially muscovitic character, viz:

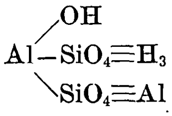


$$7\,\mathrm{Al}\begin{array}{l}\diagup\mathrm{SiO_4{\equiv}H_3}\\ -\mathrm{SiO_4{\equiv}Al}\\ \diagdown\mathrm{SiO_4{\equiv}Al}\end{array}.\ 3H_2O+9\,\mathrm{Al}\begin{array}{l}\diagup\mathrm{O}\\ -\mathrm{O}\\ \diagdown\mathrm{SiO_4{\equiv}MgH}\end{array}\!\!>\mathrm{Mg}\quad 3H_2O$$

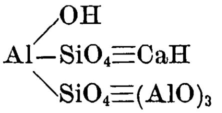
Each of these expressions gives the composition of its respective mineral very closely, and so strengthens the general mica theory. The character of the alteration from a mica is simple, and is what is most reasonably to be expected.

From some points of view, and especially with reference to its crystalline form, kaolin may be regarded as a member of the mica group. As such it would form a connecting link between the micas proper and the clintonite group, and with it the calcium mica, margarite, can be correlated. Furthermore, margarite yields an alteration product, dudleyite, which falls into line with the other two species, thus:

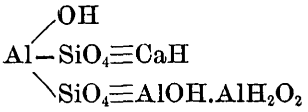
Kaolin.



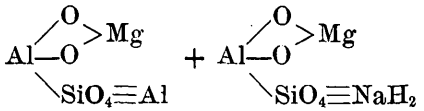
Margarite.



Dudleyite.



These expressions are suggestive, but not altogether conclusive. They represent the known facts fairly well, however, and can serve their purpose for the time being. Several other micaceous minerals are altogether doubtful in character, and need only passing mention. Thus helvetan may be a trisilicate of the biotite type. Caswellite,* an alteration product of a manganesian biotite, may be written as a member of the clintonite group. Willcoxite seems to be an alkaline clintonite, and corresponds very closely to



There are also several vermiculitic minerals which probably belong in the chlorite group. All of these supposed species need further investigation.

In roscoelite, which is a vanadium mica, the ratios are quite uncertain. According to Genth, the mineral contains V_2O_3, while Roscoe gives the vanadium as V_2O_5; and in other respects the analyses are discordant. If Genth's analysis is accepted, roscoelite has essentially the ratios of a phengitic muscovite, with half of the aluminum replaced by vanadium. This seems to be probable, but the species needs reanalysis.

Ganophyllite, described by Hamberg in 1890,† and regarded by the discoverer as a manganese zeolite, should probably be classed with the micas. Like the micas, it is monoclinic, highly cleaveable, and gives a percussion figure consisting of a six-rayed star. In all its physical characteristics it resembles the micas, with one of which, manganophyll, it is associated. It loses water, however, in vacuo, regaining the amount lost on exposure to moist air, and on this account it may be compared either with the zeolites or with the vermiculite group.

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*Chester, Trans. N. Y. Acad. Sci., XIII, p. 97, 1894.

†Geol. Fören. Förhandl., XII, p. 586.

On the latter basis it agrees in composition with a hydrated manganese phlogopite, having the subjoined admixture of molecules:

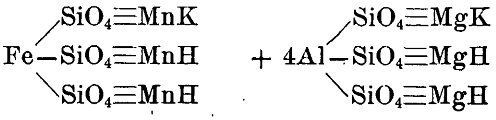
1. $Al(Si_3O_8)_3Mn_3H_3.2aq.$
1. $Al(SiO_4)_3Mn_3H_3.2aq.$
2. $Al(SiO_4)_3Mn_3KH_2.2aq.$
3. $Al(SiO_4)_3Mn_3NaH_2.2aq.$

or, in percentages, as follows:

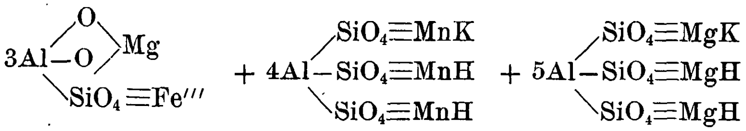
	Found.	Calculated.
SiO_2	39.67	39.99
Al_2O_3	7.95	8.81
Fe_2O_3	.90	
MnO	35.15	36.80
CaO	1.11	
MgO	.20	
PbO	.20	
K_2O	2.70	2.33
Na_2O	2.18	2.29
H_2O	9.79	9.78
	99.85	100.00

Of this water 6.22 per cent is crystalline and 3.56 constitutional.

The associated manganophyll has also phlogopite ratios, but varies so widely in composition as to show that it is, like many other micas, a mixture. Hamberg gives two analyses of this mineral; the first variety, of a reddish-brown color, agrees with



The second variety, which is dark-brown, may be written

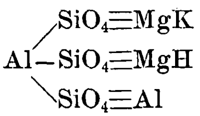


These manganophylls are from Pajsberg, but the manganophyll from Longban, analyzed by Flink, has ratios which indicate the presence of biotitic molecules somewhat similar to those found in alurgite. Manganophyll, however, contains among its constituents a true manganese phlogopite, of which ganophyllite is most probably the hydrate. On this basis both minerals are most easily explained, and all their relations are accounted for.

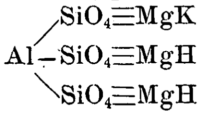
Between the micas and the chlorites the relations are exceedingly close, as regards both composition and physical properties, and from certain points of view the vermiculites are to be regarded as a transitional series connecting the two groups. All the species are highly foliated, all or nearly all are monoclinic, and to each of the definite ferromagnesian micas a chlorite, higher in magnesia and water, seems to correspond. In former publications* I have sought to show that the chlorites may be interpreted as derived from magnesium orthosilicate in the same way that the micas are derived from the normal aluminum salt; but fuller consideration leads me to a more satisfactory generalization, which unites both series under one set of fundamental formulæ.

Returning to the normal micas and ignoring the replacements of magnesium and aluminum by other equivalent bases, we have the following formulæ already developed:

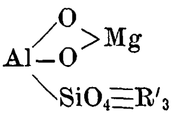
Biotite.



Phlogopite.

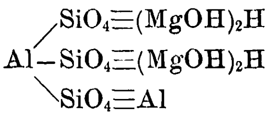


Clintonite.

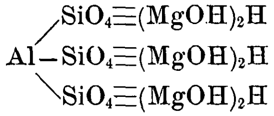


By admixtures of these types all of the ferromagnesian micas are completely explained, and for the orthochlorite series the following parallel expressions are similarly sufficient:

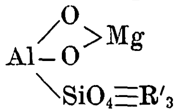
Biotite-chlorite.



Phlogopite-chlorite.



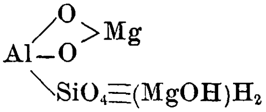
Chloritoid type.



An average pennine consists of the first and second of these types in the ratio 1:1, and an average clinochlore has the same molecules in the ratio 2:1. From these ratios the following composition is deduced:

	Pennine.	Clinochlore.
SiO_2	34.35	34.97
Al_2O_3	14.60	16.51
MgO	38.17	36.27
H_2O	12.88	12.25
	100.00	100.00

In both minerals, as among the corresponding micas, admixtures of molecules of the third type occur, giving a range of variation which is shown in the published analyses. Thus, for leuchtenbergite, we have, with the molecules given above, a large admixture of the compound



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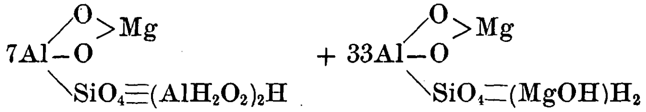
* Bull. U. S. Geol. Survey, No. 78, p. 22; Bull. No. 90, p. 17; Bull. No. 113, pp. 11 and 27.

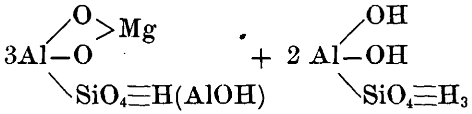
while in prochlorite and corundophilite the latter compound predominates. Prochlorite has the last formula, with trifling admixtures of chloritoid or ottrelite, and corundophilite agrees with the composition



$$7\mathrm{Al}\begin{array}{l}\diagup\mathrm{O}>\mathrm{Mg}\\ -\mathrm{O}\\ \diagdown\mathrm{SiO_4\equiv(AlH_2O_2)_2H}\end{array}+33\mathrm{Al}\begin{array}{l}\diagup\mathrm{O}>\mathrm{Mg}\\ -\mathrm{O}\\ \diagdown\mathrm{SiO_4\equiv(MgOH)H_2}\end{array}$$

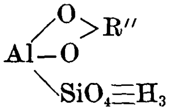
In both prochlorite and corundophilite there are large replacements of magnesium by iron.

To these formulæ some of the rarer or obscurer chlorites offer interesting variations, which, however, are all simple and intelligible. Thus, rumpfite is represented by the formula



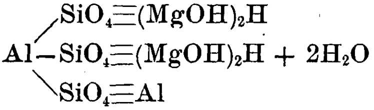
$$3\mathrm{Al}\begin{array}{l}\diagup\mathrm{O}>\mathrm{Mg}\\ -\mathrm{O}\\ \diagdown\mathrm{SiO_4\equiv H(AlOH)}\end{array}+2\,\mathrm{Al}\begin{array}{l}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{SiO_4\equiv H_3}\end{array}$$

the first compound being a magnesian chloritoid, and the second a molecule already indicated in cookeite. The original delessite is very near



$$\mathrm{Al}\begin{array}{l}\diagup\mathrm{O}>\mathrm{R''}\\ -\mathrm{O}\\ \diagdown\mathrm{SiO_4\equiv H_3}\end{array}$$

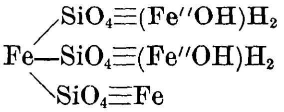
while the Scotch delessites, analyzed by Heddle, agree sharply with the formula



$$\mathrm{Al}\begin{array}{l}\diagup\mathrm{SiO_4\equiv(MgOH)_2H}\\ -\mathrm{SiO_4\equiv(MgOH)_2H}\\ \diagdown\mathrm{SiO_4\equiv Al}\end{array}+2\mathrm{H_2O}$$

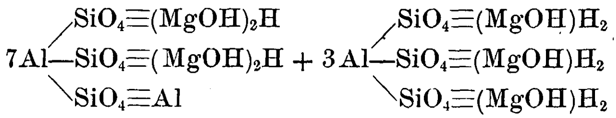
with one-fourth of the Mg replaced by Fe. In the last case the discrimination between hydroxyl and water of crystallization is shown by the analyses, and it is very probable that an analytical revision of the chlorites would bring other instances of the same kind to light.

For melanolite we have very closely the composition



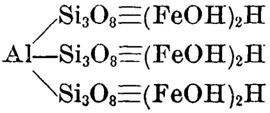
$$\mathrm{Fe}\begin{array}{l}\diagup\mathrm{SiO_4\equiv(Fe''OH)H_2}\\ -\mathrm{SiO_4\equiv(Fe''OH)H_2}\\ \diagdown\mathrm{SiO_4\equiv Fe}\end{array}$$

and for euralite



$$7\mathrm{Al}\begin{array}{l}\diagup\mathrm{SiO_4\equiv(MgOH)_2H}\\ -\mathrm{SiO_4\equiv(MgOH)_2H}\\ \diagdown\mathrm{SiO_4\equiv Al}\end{array}+3\mathrm{Al}\begin{array}{l}\diagup\mathrm{SiO_4\equiv(MgOH)H_2}\\ -\mathrm{SiO_4\equiv(MgOH)H_2}\\ \diagdown\mathrm{SiO_4\equiv(MgOH)H_2}\end{array}$$

Trisilicate molecules, as among the micas, also appear in the chlorite series, and stilpnomelane is a good example of this kind. Its formula is very nearly

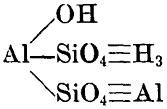


$$\mathrm{Al}\begin{array}{l}\diagup\mathrm{Si_3O_8\equiv(FeOH)_2H}\\ -\mathrm{Si_3O_8\equiv(FeOH)_2H}\\ \diagdown\mathrm{Si_3O_8\equiv(FeOH)_2H}\end{array}$$

with very little SiO_4, and epichlorite is a mixture of this salt with the equivalent $Al(SiO_4)_3(MgOH)_6H_3$, the two compounds being commingled in nearly equal percentages, or about half and half.

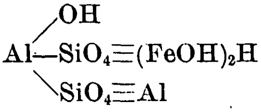
Some of the chlorites, also, are parallel with kaolin and margarite in constitution. Aphrosiderite and strigovite, for example, are well represented, as follows:

Kaolin.



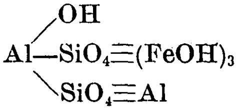
$$\mathrm{Al}\begin{cases}\mathrm{OH}\\ \mathrm{SiO_4\equiv H_3}\\ \mathrm{SiO_4\equiv Al}\end{cases}$$

Strigovite.



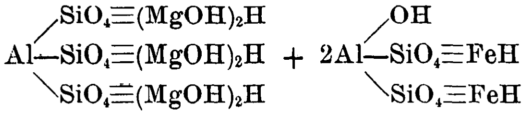
$$\mathrm{Al}\begin{cases}\mathrm{OH}\\ \mathrm{SiO_4\equiv (FeOH)_2H}\\ \mathrm{SiO_4\equiv Al}\end{cases}$$

Aphrosiderite.



$$\mathrm{Al}\begin{cases}\mathrm{OH}\\ \mathrm{SiO_4\equiv (FeOH)_3}\\ \mathrm{SiO_4\equiv Al}\end{cases}$$

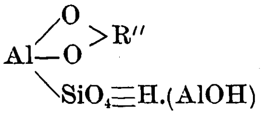
with much ferric iron in strigovite in place of aluminum. In diabantite we find a composition indicative of a mixture between a molecule of this type and one in the normal series. The diabantite from Connecticut, for instance, is very near



$$\mathrm{Al}\begin{cases}\mathrm{SiO_4\equiv (MgOH)_2H}\\ \mathrm{SiO_4\equiv (MgOH)_2H}\\ \mathrm{SiO_4\equiv (MgOH)_2H}\end{cases} + 2\mathrm{Al}\begin{cases}\mathrm{OH}\\ \mathrm{SiO_4\equiv FeH}\\ \mathrm{SiO_4\equiv FeH}\end{cases}$$

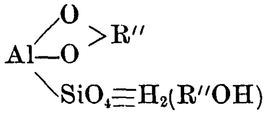
For the minerals daphnite, metachlorite, klementite, chamoisite, thuringite, and cronstedtite, the formulæ are more or less doubtful, for the reason that alternatives are possible. They all, however, reduce to mixtures of the chloritoid or clintonite type, of the forms

A.



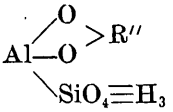
$$\mathrm{Al}\begin{cases}\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\rangle \mathrm{R''}\\ \mathrm{SiO_4\equiv H.(AlOH)}\end{cases}$$

B.



$$\mathrm{Al}\begin{cases}\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\rangle \mathrm{R''}\\ \mathrm{SiO_4\equiv H_2(R''OH)}\end{cases}$$

C.



$$\mathrm{Al}\begin{cases}\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\rangle \mathrm{R''}\\ \mathrm{SiO_4\equiv H_3}\end{cases}$$

Using the letters underneath the formulæ as symbols, the several species become

Chamoisite	B_1C_1, with all $R''=Fe$
Metachlorite	B_3C_1, with all $R''=Fe$
Thuringite	$A_1B_1C_1$, with all $R''=Fe$
Klementite	$A_1B_2C_1$, with R'' mostly Mg
Daphnite	$A_1B_5C_4$, with R'' mostly Fe

In cronstedtite there is a range from $A_1B_1C_1$, as in thuringite, to A_1B_2, and all the aluminum is replaced by ferric iron, while all $R''=Fe$. These expressions give the composition of the several species very closely, and serve to correlate them with delessite, rumpfite, prochlorite. and corundophilite. All of the valid evidence is satisfied, and the micas, clintonites, vermiculites, and chlorites form one systematic group. The facts that garnet and vesuvianite alter into chlorites, and that chloritic pseudomorphs after feldspar are known, serve to still more closely connect the formulæ here adopted with the similar formulæ of the preceding groups of minerals.

When clinochlore or leuchtenbergite is strongly ignited, it yields, like xanthophyllite, a product insoluble in hydrochloric acid, having the composition of spinel. This reaction establishes still more definitely the relationship between the chlorites and the clintonite group, and it is readily intelligible in the light of the structural expressions. The splitting up, under influence of heat, of mixtures containing such groups of atoms as MgOH, AlOH, and AlO_2H_2, ought to generate spinel, and the appearance of a compound of this character is evidence in favor of the formulæ.

VI. THE TOURMALINE GROUP.

Although tourmaline, in its several varieties, is apparently quite complex, the evidence for its interpretation is abundant and ample. Its variations in composition are shown by numerous good analyses, its associations are well known, and its alteration products have been observed in a sufficient number of cases. From the minerals which have been discussed in the preceding chapters, it differs essentially in that it contains boron, and the part played by this element is a new question to be interpreted.

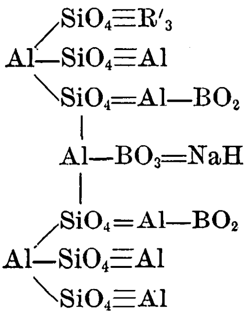
When tourmaline undergoes alteration, the commonest product is a mica, and between the micas and the tourmalines there are very striking analogies. With the lithia micas, lithia tourmalines are generally associated; with muscovite and biotite, iron tourmalines occur, and magnesian tourmalines accompany phlogopite. In each case the composition of the tourmaline seems to bear a relation to that of the associated mica. Furthermore, the varieties of tourmaline shade one into another through an unbroken series of gradations, and this may happen to some extent in one and the same crystal. The genus tourmaline, in short, represents a series of compounds, and these are parallel to the normal mica series. These considerations lead directly to a system of formulæ, which, like those of the micas, are derivable from molecules of the normal aluminum orthosilicate, and which express completely all the known chemical relations of tourmaline.

On studying carefully all the more recent and more trustworthy analyses of tourmaline, a constant ratio appears connecting silicon, boron, and oxygen, which is represented by the figures $Si_6B_3O_{31}$. The variations from constancy are almost all within the limits of accuracy of the analyses, but occasionally a small amount of fluorine is noted, which appears to replace the univalent acid group BO_2. Aluminum, with respect to silicon, varies widely, the ratio ranging from Al_8Si_6 to Al_5Si_6, while the other bases vary reciprocally with aluminum and in the opposite direction. The tourmalines high in aluminum approach, like muscovite, most nearly to the normal ortho-salt; those lowest in aluminum are high in magnesium, like phlogopite; and, like biotite in the mica group, the iron tourmalines lie between these extremes.

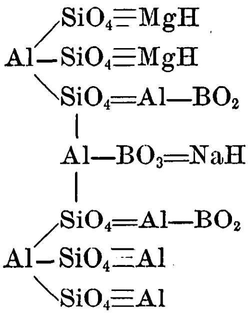
Taking now the smallest amount of aluminum found in the formula of any tourmaline, all varieties of the species may be regarded as containing the nucleus $Al_5(SiO_4)_6(BO_3)(BO_2)_2$, in which 14 units of affinity are still unsatisfied, and among which all of the essential variations in composition take place. The orthoboric group, BO_3, is obviously trivalent, BO_2 being univalent, and the radicle of metaboric acid.

From this nucleus four types of tourmaline are derivable, thus:

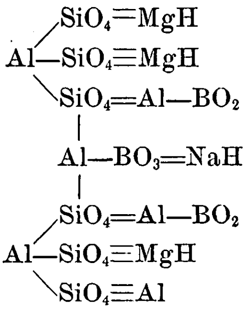
1.



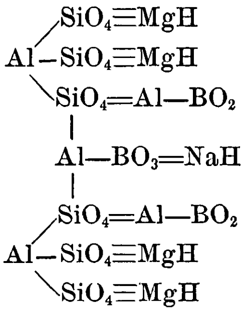
2.



3.



4.



and to all of these, known varieties of the mineral correspond. The only notable variations are due to Cr or Fe replacing Al, Fe or Mn replacing Mg, small quantities of F replacing BO_2, and in No. 4, Ca sometimes replacing NaH. If in No. 1 $R'_3=LiH_2$, and in No. 2 Fe_2 replaces Mg_2, these formulæ give the subjoined percentage compositions:

	1	2
SiO_2	38.05	35.16
B_2O_3	11.10	10.25
Al_2O_3	43.13	34.86
FeO	....	14.06
Na_2O	3.28	3.03
Li_2O	1.58	....
H_2O	2.86	2.64
	100.00	100.00

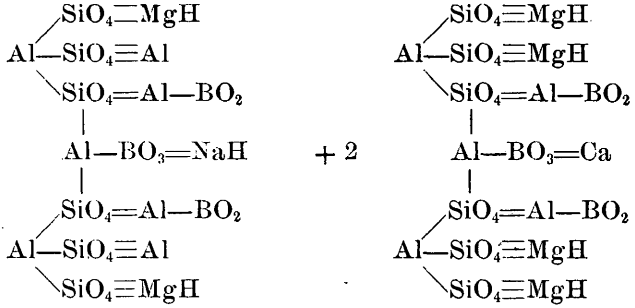
These figures agree well with the best analyses of the lithia tourmalines and the ordinary black tourmalines which are found in the same localities; divergencies being due to trifling admixtures of one with the other, and to the presence of fluorine as previously noted.

Formula No. 3 corresponds to

SiO_2	37.58
B_2O_3	10.96
Al_2O_3	31.94
MgO	12.52
Na_2O	3.24
H_2O	3.76
	100.00

which is very near the composition of the dark-brown tourmalines from Orford, N. H., and Monroe, Conn., except that in them a little Fe replaces Mg, and a little Ca takes the place of NaH.

The brown tourmalines of Hamburg, N. J., and Gouverneur, N. Y., with the white tourmaline from DeKalb, all approximate toward formula No. 4, but with admixtures of No. 3, and with Ca in place of NaH. The mixture



gives the following percentage composition:

SiO_2	37.19
B_2O_3	10.85
Al_2O_3	29.86
MgO	13.77
CaO	3.86
Na_2O	1.06
H_2O	3 41
	100.00

which represents the DeKalb tourmaline fairly well. In the Hamburg mineral there is more of the calcium compound, and in that from Gouverneur rather less. The black tourmaline from Pierrepont gives formula No. 4 very closely, except that about three-tenths of the Mg has been replaced by Fe, and one-half of the NaH by Ca. Calculating for the following mixture of molecules:

$$3Al_5(SiO_4)_6(BO_2)_2BO_3NaFe_4H_5$$
$$2Al_5(SiO_4)_6(BO_2)_2BO_3NaMg_4H_5$$
$$5Al_5(SiO_4)_6(BO_2)_2BO_3CaMg_4H_4$$

we have the following comparison with Riggs's analysis of Pierrepont tourmaline:

	Found.	Calculated.
SiO_2	35.61	35.91
TiO_2	.55	
B_2O_3	10.15	10.48
F	.27	
Al_2O_3	25.29	25.44
Fe_2O_3	.44	
FeO	8.19	8.62
MgO	11.07	11.17
CaO	3.31	2.79
Na_2O	1.51	1.55
K_2O	.20	
H_2O	3.34	4.04
	99.93	100.00

Tourmalines which do not correspond to any one of the four types given agree with mixtures of them, and all of the analyses of this mineral published by Jannasch and Calb or by Riggs can be reduced to suitable formulæ. These formulæ suggest an end product,

$$Al_9(SiO_4)_6(BO_2)_2BO_3NaH$$

which may possibly exist, but is not known. They also indicate the obvious relationship of tourmaline to the micas, and express the ready alterability of the former into the latter. A molecule of tourmaline, with elimination of boric acid and one atom of aluminum, splits into two molecules of the mica type, and the transformation is easily understood. Potash is of course taken up. Certain experiments by Lemberg,* who investigated the action of alkaline solutions upon tourmaline, are in accord with these suppositions.

Although otherwise interpreted by Brögger, the minerals cappelinite, melanocerite, karyocerite, and tritomite seem to be structurally akin to tourmaline. This view of their nature has already been suggested by Wiik,† and it is sustained both by chemical and by morphological considerations. Cappelinite is hexagonal, and the other species, like tourmaline, are rhombohedral. They are silicates of rare earths, which are mostly trivalent, like aluminum; all contain boron, and all but cappelinite contain fluorine also. Furthermore, all four species, considered together, illustrate the reciprocity between boric acid and fluorine, which has been suggested in the discussion of tourmaline.

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* Zeitsch. Deutsch. Geol. Gesell., 1892, p. 239.

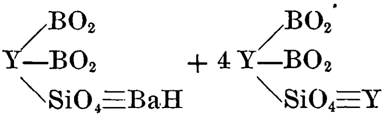
† Zeitsch. Kryst. Min., XXIII, pp. 421, 422, 1894.

Thus, if we compute the atomic ratios from the analyses cited by Brögger,* the following relation appears:

	Si.	B.	F.	B+F.
Cappelinite	236	488	....	488
Melanocerite	218	92	304	396
Karyocerite	216	134	296	430
Tritomite	226	210	226	436

That is, Si:B + F::1:2 nearly, variations being due to the fact that in the first three minerals the boric acid was determined by difference, and also, probably, to the occasional replacement of fluorine by hydroxyl. Another source of variation is found in the presence of tetrad bases, as will be seen later; but for the moment the relation indicated seems to be reasonably clear.

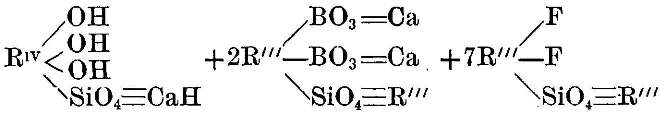
The first member of the group, cappelinite, is a borosilicate of yttrium and barium, and approximates in composition to



$$Y\begin{cases}BO_2\\ BO_2\\ SiO_4\equiv BaH\end{cases} + 4\,Y\begin{cases}BO_2\\ BO_2\\ SiO_4\equiv Y\end{cases}$$

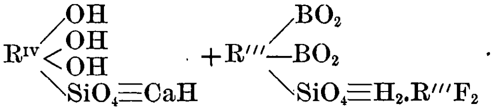
With the earths of uncertain molecular weight designated as "yttria," are a little lanthanum oxide and trifling quantities of ThO_2 and CeO_2, and with the barium are some calcium and alkalies.

The other three members of the group are all more complicated than cappelinite, and vary from it in type by containing tetrad oxides, such as CeO_2, ThO_2, and ZrO_2. In eudialyte and catapleiite we have two rhombohedral silicates of zirconia, which help to explain these compounds. Catapleiite probably has the constitution $(OH)_3Zr.Si_3O_8.R'_3$. If we regard the tetrad bases in the cappelinite group as forming orthosilicates of this same type, the remainder of each mineral may be written as a mixture of molecules like those already designated, but with cerium earths predominating over yttrium, and fluorine replacing some boric radicles. Thus, melanocerite is not far from



$$R^{IV}\begin{cases}OH\\ OH\\ OH\\ SiO_4\equiv CaH\end{cases} + 2R'''\begin{cases}BO_3=Ca\\ BO_3=Ca\\ SiO_4\equiv R'''\end{cases} + 7R'''\begin{cases}F\\ F\\ SiO_4\equiv R'''\end{cases}$$

Karyocerite may be written similarly, and tritomite becomes



$$R^{IV}\begin{cases}OH\\ OH\\ OH\\ SiO_4\equiv CaH\end{cases} + R'''\begin{cases}BO_2\\ BO_2\\ SiO_4\equiv H_2.R'''F_2\end{cases}$$

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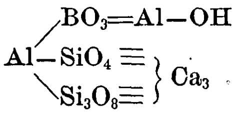
*Zeit. Kryst. Min., XVI, pp. 462–469.

These formulæ are uncertain, and need verification with material from other sources. At present they have only a reasonable probability. The tetrad silicate in them, however, will be seen to be highly probable when we come to the discussion of the other allied compounds in their proper connection later.

There is one other borosilicate containing aluminum, axinite, whose relations are uncertain. Physically it differs widely from tourmaline, being triclinic, but on account of its composition it may fairly be considered here. The analyses of it vary to a considerable extent, partly because of uncertainty in the determinations of water and boron, but also in other respects which indicate a mixture of molecules. Some analyses give orthosilicate ratios, provided that the boron is regarded as basic and equivalent to aluminum, but others show much too little oxygen. Boron, however, is essentially an acid-forming element, and it seems more probable that in axinite it has acid functions. The most typical axinite is that from Bourg d'Oisans, and of this the best analysis is by Jannasch and Locke.* From this the following formula is easily derived:



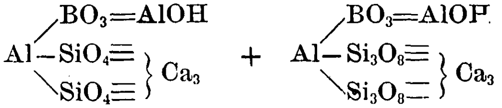
$$\mathrm{Al}\begin{array}{l}\diagup\mathrm{BO_3{=}Al{-}OH}\\ \left.\begin{array}{l}-\mathrm{SiO_4}\equiv\\ \diagdown\mathrm{Si_3O_8}\equiv\end{array}\right\}\mathrm{Ca_3}\end{array}$$

in which the boron is regarded as part of an orthoborate molecule, derived from the acid H_3BO_3.

This may be compared with Jannasch and Locke's analysis directly, and with the latter reduced by recalculating Fe_2O_3 into Al_2O_3, the other bases all into their equivalents in CaO, and then bringing to 100 per cent, thus:

	Found.	Reduced.	Calculated.
SiO_2	42.88	43.13	43.32
B_2O_3	6.02	6.06	6.32
Al_2O_3	18.24	18.73	18.41
Fe_2O_3	.62		
FeO	7.10	29.93	30.33
MnO	1.06		
CaO	19.89		
MgO	2.23		
K_2O	.11		
Na_2O	.36		
H_2O	2.14	2.15	1.62
	100.65	100.00	100.00

The formula may also be written



$$\mathrm{Al}\begin{array}{l}\diagup\mathrm{BO_3{=}AlOH}\\ \left.\begin{array}{l}-\mathrm{SiO_4}\equiv\\ \diagdown\mathrm{SiO_4}\equiv\end{array}\right\}\mathrm{Ca_3}\end{array} + \mathrm{Al}\begin{array}{l}\diagup\mathrm{BO_3{=}AlOH}\\ \left.\begin{array}{l}-\mathrm{Si_3O_8}\equiv\\ \diagdown\mathrm{Si_3O_8}\equiv\end{array}\right\}\mathrm{Ca_3}\end{array}$$

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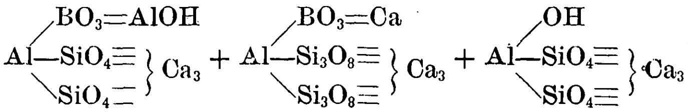
* Zeitsch. Anorgan. Chem., VI, p. 57, 1894.

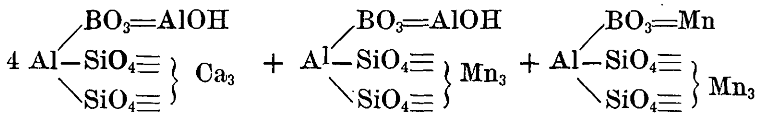
in which form it compares better with other analyses. Thus Baumert's analysis of axinite from the Radauthal* gives



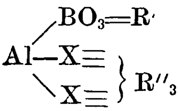
and a comparison as follows:

	Found.	Reduced.	Calculated.
SiO_2	40.76	40.92	41.32
B_2O_3	4.76	4.78	4.82
Al_2O_3	12.47	13.91	14.05
Fe_2O_3	2.17		
FeO	3.60	39.17	38.57
MnO	2.84		
CaO	30.21		
MgO	2.00		
H_2O	1.22	1.22	1.24
	100.03	100.00	100.00

Genth's analyses* of the axinite from Franklin, N. J., give similar ratios, minus the boron-free molecule required in Baumert's case. Approximately they give



with rather less than half the SiO_4 replaced by Si_3O_8. In general, when $X=Si_3O_8+SiO_4$ all axinite except that analyzed by Baumert gives the general formula



in which R″ is partly AlOH, with Ca, Mg, Mn, or Fe. Until further evidence is available this expression may be regarded as valid, but it represents only the composition of the mineral, and no other relations. It is, however, in conformity with the general theory of substitution. Other formulæ, which represent axinite either as metasilicate or as orthodisilicate, are possible, but none of them has any advantage over the one proposed.

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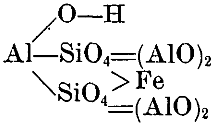
* Dana's System of Min., 6th ed., p. 529.

VII. MISCELLANEOUS SPECIES.

Among the ortho- and trisilicates of aluminum, ferric iron, and other triad elements, there are a considerable number which do not fall conveniently into any of the preceding groups of minerals, or which are doubtful as regards their genetic affinities. Some of them have obvious relationships to other species, and some are quite obscure in character, but all seem to be conformable to the theory of substitution.

First in order of importance is the mineral staurolite, a highly basic silicate, which is evidently akin to andalusite, dumortierite, and sillimanite, and which, like them, is orthorhombic. Like andalusite, furthermore, staurolite alters into muscovite, an entire crystal becoming transformed throughout into an aggregate of mica scales.

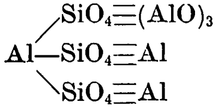
By far the best evidence as to the composition of staurolite is that furnished by the analyses of Penfield and Pratt,[*] who adopt Groth's formula $HAl_5Fe''Si_2O_{13}$. This, structurally, is best written



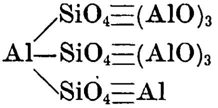
which expresses a partial relation to the micas, andalusite, and so on. The theoretical percentage composition calculated from this formula agrees well with the results of analysis, except that it gives the silica nearly one per cent too low, a discrepancy which Penfield and Pratt attribute to inclusions of silica in the minerals analyzed.

By means of a slightly different formula the relations of staurolite to the other species can be much more clearly shown, but it assumes that the ideal staurolite is not yet known. The expressions proposed are as follows:

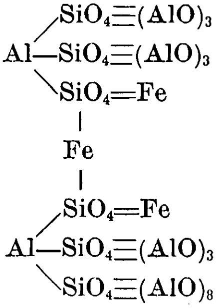
Andalusite.



Dumortierite.



Staurolite.



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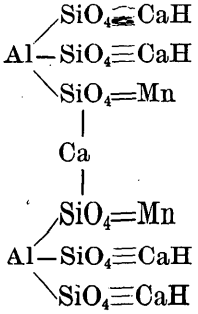
[*] Am. Jour. Sci., (3) XLVII, p. 81, 1894.

This formula, in contrast with that of Penfield and Pratt, and with their reduced analysis of staurolite from Lisbon, N. H., gives the subjoined percentage composition:

	Lisbon.	P. and P.	New formula.
SiO_2	27.44	26.32	27.90
Al_2O_3	55.16	55.92	55.35
FeO	15.72	15.79	16.75
H_2O	1.68	1.97	....
	100.00	100.00	100.00

If, now, we assume that the actual staurolite is slightly altered by hydration, some Fe being replaced by H_2 and by FeOH+H, the discrepancies between formula and analyses are sufficiently accounted for. The new formula is more symmetrical than the old one; it better expresses the alterability of staurolite into muscovite, and it seems to satisfy the evidence with sufficient completeness. When we remember that staurolite is excessively liable to inclusions and alterations, a very sharp agreement between analysis and theory is not to be expected.

Still another orthorhombic species, harstigite, has a formula analogous in some ways to that of staurolite. For harstigite there is but one analysis extant, which gives, nearly

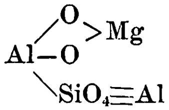


This, in comparison with Flink's analysis, gives

	Found.	Calculated.
SiO_2	38.94	39.13
Al_2O_3	10.61	11.09
MnO	12.81	15.43
MgO	3.27	
CaO	29.23	30.44
K_2O	.35	
Na_2O	.71	
H_2O	3.97	3.91
	99.89	100.00

a result which is fairly satisfactory. More data relative to harstigite are evidently needed.

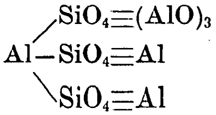
In order to interpret the clintonite micas, the highly basic compound



$$\mathrm{Al}\begin{array}{l}\diagup\!\left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right>\mathrm{Mg}\\ \diagdown\mathrm{SiO_4{\equiv}Al}\end{array}$$

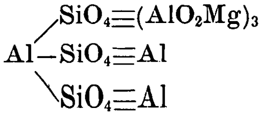
was assumed. This formula also gives, empirically, the percentage composition of the species kornerupine or prismatine, which, unlike the micas, is orthorhombic, and also insoluble in acids. On these grounds it may be compared with andalusite and staurolite; and a clew to its constitution is found in the existence of an alteration product of prismatine, kryptotile, having the composition $\mathrm{HAlSiO_4}$. Tripling the formulæ, we have

Andalusite.



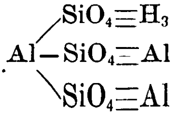
$$\begin{array}{l}\quad\diagup\mathrm{SiO_4{\equiv}(AlO)_3}\\ \mathrm{Al{-}SiO_4{\equiv}Al}\\ \quad\diagdown\mathrm{SiO_4{\equiv}Al}\end{array}$$

Kornerupine.



$$\begin{array}{l}\quad\diagup\mathrm{SiO_4{\equiv}(AlO_2Mg)_3}\\ \mathrm{Al{-}SiO_4{\equiv}Al}\\ \quad\diagdown\mathrm{SiO_4{\equiv}Al}\end{array}$$

Kryptotile.



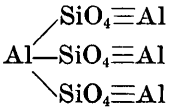
$$\begin{array}{l}\quad\diagup\mathrm{SiO_4{\equiv}H_3}\\ \mathrm{Al{-}SiO_4{\equiv}Al}\\ \quad\diagdown\mathrm{SiO_4{\equiv}Al}\end{array}$$

symbols which express the observed relationship between these and other species. Further than this the formulæ have no real significance, and alternative expressions are considered later in connection with the pyroxenes and amphiboles. Associated with kornerupine the still more basic sapphirine, $\mathrm{Mg_5Al_{12}Si_2O_{27}}$, is found. To the constitution of this species there is no good clew, and any attempt at structural formulation is useless. More than one structural formula is possible for sapphirine, but all are at present meaningless, except in so far as they show that the compound is stoichiometrically conceivable.

A peculiarly difficult group of minerals to interpret constitutionally is the group of clays. One member of this group, kaolin, has already been considered, and this member has the advantage of being crystalline. The other clays are amorphous, and of uncertain origin; they often occur in complicated mixtures, are difficult to identify with certainty, and still more difficult to correlate with other species. They represent undoubtedly the breaking down of crystalline silicates, to which they are related somewhat as kaolin is related to the feldspars; but rarely, if ever, has their actual genesis been observed. Their formulæ, therefore, are merely tentative, and serve only as a first step toward a better study of the several species.

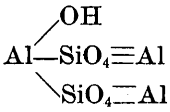
Upon comparing the formula of aluminum orthosilicate with that of kaolin, an indication of serial arrangement becomes evident, which may be written thus:

Normal salt.



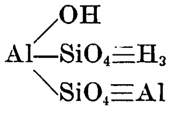
$$\begin{array}{l}\quad\diagup\mathrm{SiO_4{\equiv}Al}\\ \mathrm{Al{-}SiO_4{\equiv}Al}\\ \quad\diagdown\mathrm{SiO_4{\equiv}Al}\end{array}$$

Westanite or woerthite.



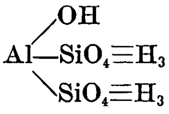
$$\begin{array}{l}\quad\diagup\mathrm{OH}\\ \mathrm{Al{-}SiO_4{\equiv}Al}\\ \quad\diagdown\mathrm{SiO_4{\equiv}Al}\end{array}$$

Kaolin.



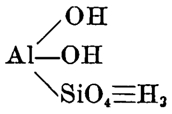
$$\begin{array}{l}\quad\diagup\mathrm{OH}\\ \mathrm{Al{-}SiO_4{\equiv}H_3}\\ \quad\diagdown\mathrm{SiO_4{\equiv}Al}\end{array}$$

Montmorillonite.



$$\begin{array}{l}\quad\diagup\mathrm{OH}\\ \mathrm{Al{-}SiO_4{\equiv}H_3}\\ \quad\diagdown\mathrm{SiO_4{\equiv}H_3}\end{array}$$

Newtonite.



$$\begin{array}{l}\quad\diagup\mathrm{OH}\\ \mathrm{Al{-}OH}\\ \quad\diagdown\mathrm{SiO_4{\equiv}H_3}\end{array}$$

Woerthite is an altered sillimanite, and westanite is perhaps a similar derivative of andalusite. The newtonite compound has already appeared in the mica series among the components of cookeite and rumpfite.

The best that can be said for these formulæ is that they are suggestive. In one respect they are highly questionable, for the reason that the group $—SiO_4{\equiv}H_3$ is indicative of loosely combined water, while in these particular clays the water is quite firmly retained. On this point much fuller information is needed, and future evidence may prove that the serial relation indicated is apparent only.

The composition of rectorite may be $Al_3(SiO_4)_3H_3+2H_2O$, or that of a hydrous kryptotile. Halloysite has the composition of kaolin plus one molecule of water, the latter being removable at or about 100°. Halloysite, however, differs from kaolin in being decomposable by hydrochloric acid, and hence it is unlikely that the two species have similar structure. Allophane is perhaps $(AlO_2H_2)_2H_2SiO_4+3H_2O$, or it may be written analogously to andalusite,

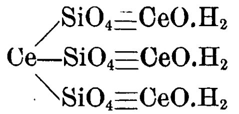
$$Al_3(SiO_4)_3(AlO_2H_2)_3.12H_2O.$$

Neither formula is sustained by any good evidence. Other clays are possibly as follows:

Samoite	$Al_4(SiO_4)_3.10H_2O$
Cimolite	$Al_4(Si_3O_8)_3.6H_2O$
Collyrite	$(AlO)_4SiO_4.6H_2O$
Schrötterite	$(AlO_2H_2)_4SiO_4.6H_2O$

None of these formulæ can be construed as anything more than a temporary suggestion, which may help research. The hydrous ferric silicates are, if anything, less satisfactory than the aluminum salts. Anthosiderite is representable by the formula $Fe_4(Si_3O_8)_3.2H_2O$; and chloropal by the expression $Fe_2(SiO_4)_3H_6$. Hisingerite seems to range from a ferric kaolin to a ferric halloysite, and farther than this it is not worth while to go. The remaining iron clays which have received specific names are altogether doubtful. The chromium clays, wolchonskoite, etc., are also of uncertain character.

To cerite, which is of doubtful composition, the provisional formula



$$\begin{array}{l} \qquad\diagup SiO_4{\equiv}CeO.H_2 \\ Ce—SiO_4{\equiv}CeO.H_2 \\ \qquad\diagdown SiO_4{\equiv}CeO.H_2 \end{array}$$

may be assigned. Other earth metals—lanthanum, the two didymiums, etc.—replace a considerable part of the cerium. With cerium only the formula requires

SiO_2	20.22
Ce_2O_3	73.71
H_2O	6.07
	100.00

Cenosite, $H_4Ca_2Y_2CSi_4O_{17}$, and ardennite, $H_5Mn_4Al_4VSi_4O_{23}$, can each be written structurally in more than one way, with no determining evidence upon which to base a decision. They may be orthosilicates or diorthosilicates; the vanadium in ardennite may be combined as VO_3 or as VO_4, or it may form part of a complex vanadio-silicic acid, and between these alternatives there is no present means of deciding. To carpholite the formula $H_4MnAl_2Si_2O_{10}$ is commonly assigned, but the analyses vary from this composition too widely. Even with this formula carpholite may be either an orthosilicate or a basic metasilicate, and we can only say with regard to this species that further investigation is necessary.

Spodumene, acmite, jadeite, and the corresponding members of the amphibole group will be considered in connection with the metasilicates. It is quite possible that these minerals are really pseudo metasilicates, and that they should properly be discussed now. Their study is deferred on mineralogical grounds solely.

Three other salts of triad bases may be noted here, as having more analogy with the salts of aluminum than with any other silicates. They are pseudobrookite, an orthotitanate of iron, $Fe_4(TiO_4)_3$, and the bismuth silicates, eulytite and agricolite, $Bi_4(SiO_4)_3$. The two last-named species differ in form but are identical in empirical composition. They, therefore, suggest two types of chemical structure among the silicates of trivalent bases.

CHAPTER IV.

THE ORTHOSILICATES OF DYAD BASES.

Although the orthosilicates of the dyad metals are presumably simpler than those of aluminum, the problem of their constitution, studied in the light of mineralogical evidence, is peculiarly difficult. Starting points exist, in the salts of magnesium, iron, manganese, zinc, and glucinum, but the derivatives are fewer than in the case of aluminum, and the evidence upon which to base argument is proportionally limited.

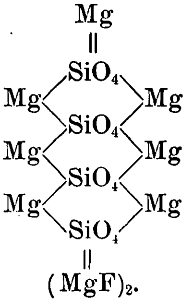
Expressed in the simplest terms, the normal orthosilicates of this group are represented by the general formula R_2SiO_4. To this type the following minerals correspond:

Forsterite	Mg_2SiO_4
Fayalite	Fe_2SiO_4
Tephroite	Mn_2SiO_4
Willemite	Zn_2SiO_4
Phenakite	Gl_2SiO_4
Monticellite	$CaMgSiO_4$
Knebelite	$MnFeSiO_4$

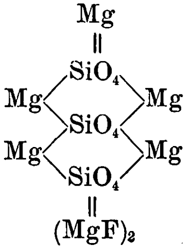
Between these minerals there are many intermediate species or varieties, which may be either isomorphous mixtures or double salts representing polymers of the fundamental type. Thus, chrysolite or olivine may be a mixture of forsterite and fayalite, or, in the case of hyalosiderite, a salt of the formula $Mg_4Fe_2(SiO_4)_3$. So also, allied to knebelite, we have igelströmite, $Fe_4Mn_2(SiO_4)_3$; and in trimerite we find the salt $Gl_3Mn_2Ca(SiO_4)_3$.

Upon studying closely the derivatives of these normal salts, the assumption of polymerization seems to be necessary. If the theory of substitution is valid, then the existence of polymers must be taken for granted; and upon this basis it becomes possible to develop a system of formulæ which satisfies all the conditions imposed by the evidence now at hand. For some of the species already mentioned the degree of polymerization is difficult to determine, and synthetic investigations seem to be needed. In other cases the problem is comparatively simple, and the indications as to the true formulæ are apparently clear. For instance, a good example is furnished by the chondrodite group, for which we have the empirical formulæ established by Penfield and Howe.* Structurally written these become

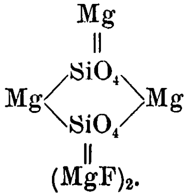
Clinohumite.



Humite.

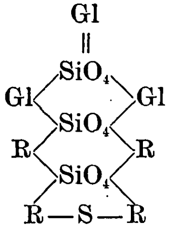


Chondrodite.



or derivatives respectively of the salts $Mg_8(SiO_4)_4$, $Mg_6(SiO_4)_3$, and $Mg_4(SiO_4)_2$, with one atom of magnesium in each case replaced by the two univalent —Mg—F groups. The clinohumite occurs in association with forsterite, and the two species have nearly the same specific gravity. Hence forsterite may be $Mg_8(SiO_4)_4$, and this is the only datum available from which to infer its molecular magnitude. The synthetic transformation of forsterite into clinohumite, if it could be effected, would go far toward settling the question.

In the case of phenakite the triple formula $Gl_6(SiO_4)_3$ is rendered probable by the existence of trimerite, $Gl_3Mn_2Ca(SiO_4)_3$. It is also emphasized by the species helvite and danalite, which contain sulphur, probably combined in the dyad group —R—S—R—. Both of these species, in all of their known occurrences, agree with the general formula



in which R may be either Fe″, Mn, or Zn. The R is variable, but the other constituents are constant. In helvite, Mn and Fe occur, and in danalite zinc appears. In the Colorado danalite Zn predominates largely over Fe, and there is very little Mn. The Rockport danalite has Fe in excess of Zn, and rather more Mn. The Cornish danalite is very low in Zn, and the Fe largely exceeds the Mn. The ratio $Gl:SiO_4::3:3$, however, holds for all.

If phenakite is $Gl_6(SiO_4)_3$, then willemite, which is morphologically similar, is probably $Zn_6(SiO_4)_3$, with zinc partly replaced by manganese in the variety known as troostite.

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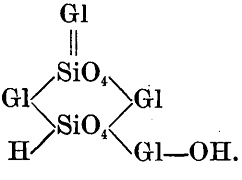
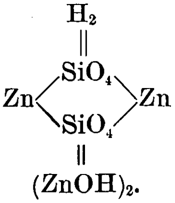
* Am. Jour. Sci. (3), XLVII, p. 188, 1894.

The three orthorhombic species, bertrandite, calamine, and ilvaite, may be most conveniently represented as derivatives of the bipolymer $R_4(SiO_4)_2$, like chondrodite. Crystallographically, ilvaite resembles humite, but bertrandite and calamine are related to each other. The simplest analogous formulæ for the three minerals are as follows:

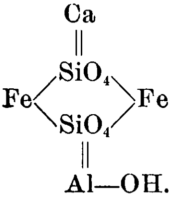
Bertrandite.



Calamine.



Ilvaite.



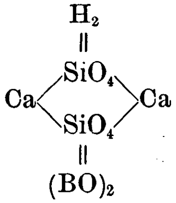
Calamine may also be written as a metasilicate, $(ZnOH)_2SiO_3$, with half of the formula indicated above, but then the analogy with bertrandite disappears. The structure proposed is, therefore, preferable, at least until more evidence has been accumulated.

To the datolite group a similar constitution is ascribable. The species, reduced to their simplest empirical expressions, are these:

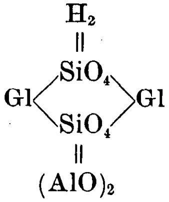
Datolite	$HCaBSiO_5$
Homilite	$Ca_2FeB_2Si_2O_{10}$
Euclase	$HGlAlSiO_5$
Gadolinite	$Gl_2FeY_2Si_2O_{10}$

By doubling the formulæ of datolite and euclase, all four of the minerals become similar in constitution. Hydrogen, here, is evidently basic, and boron must play the same part as aluminum and yttrium. Assuming these elements to be present in the univalent groups BO, AlO, and YO, the subjoined formulæ follow:

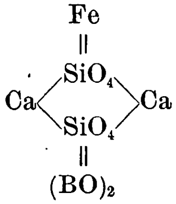
Datolite.



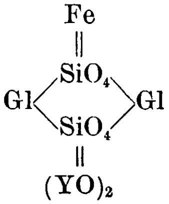
Euclase.



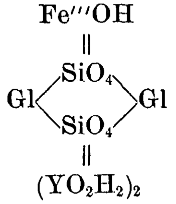
Homilite.



Gadolinite.



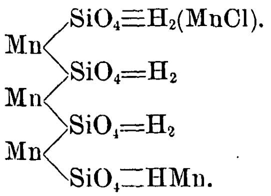
Gadolinite alters with great ease, passing by hydration into a brownish-red earthy substance. The analyses of this substance, which is probably never pure and definite, are not altogether satisfactory; but they indicate in a general way a transformation into the compound



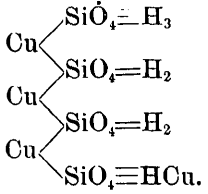
to which the alteration product very roughly approximates.

It will be observed that all of the foregoing structural formulæ in this group of compounds are rings or series of rings. From them, however, chain-like molecules are derivable, and these seem to exist in the cases of friedelite, pyrosmalite, and dioptase. The last-named mineral, simply written, is CuH_2SiO_4; but it is morphologically related to the two other species, which have a much greater complexity of composition. The following expressions derived from the polymer $R_8(SiO_4)_4$ are probably the best to represent existing evidence:

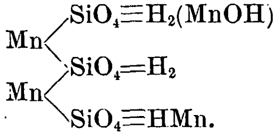
Friedelite.



Dioptase.



Pyrosmalite is like friedelite, but with a large part of the manganese replaced by iron. Possibly karyopilite may be similar, having the formula

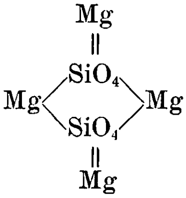


These formulæ are purely tentative and need additional support. By synthetic and genetic investigations they may be supported or overthrown. That they sustain one another, and fit in well with the formulæ of the preceding species, is all that can be said in their favor.

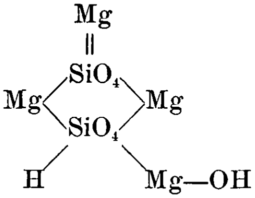
For serpentine, $H_4Mg_3Si_2O_9$, several formulæ are possible, and concerning them there has been much discussion. The species commonly originates in nature from the alteration of olivine on the one hand and from pyroxene or amphibole on the other, and it is therefore conceivable that it may include two or more isomeric compounds. In favor of this supposition there is no direct evidence, but still it should not be left entirely out of account.

By some authorities serpentine is regarded as an orthosilicate, and by others as a salt of the acid $H_6Si_2O_7$. On the latter supposition it becomes $Mg{=}Si_2O_7{\equiv}H_2(MgOH)_2$, which may be derived either from $2\,Mg_2SiO_4$ or $2\,MgSiO_3$, with loss of magnesium in one case and gain in the other. On the orthosilicate basis it is simply derivable from the polymer $Mg_4(SiO_4)_2$, and is related to the intermediate alteration product villarsite, as follows:

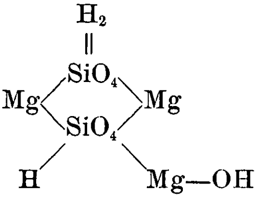
$Mg_4(SiO_4)_2$.



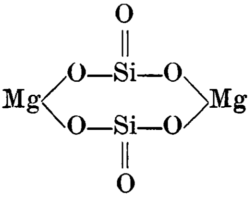
Villarsite.



Serpentine.



On this scheme the formula for serpentine corresponds with that of chondrodite; and the fact that the latter mineral alters readily into serpentine is strong evidence in its favor. If pyroxene is written structurally



the derivation of serpentine from it by action of infiltrating magnesian solutions becomes easy to understand, and the orthosilicate formula for serpentine is rendered still more probable. In short, that formula best indicates the genetic relationships of serpentine, and on these grounds is preferable to the alternative diorthosilicate expression. The latter is not disproved; it is simply rendered less advantageous as regards existing evidence, which is the evidence now to be interpreted.

In some former investigations, carried on jointly with Dr. Schneider,* I sought to obtain experimental data in support of the orthosilicate formula here assigned to serpentine. By acting on serpentine with dry gaseous hydrochloric acid we found that a part of the magnesium could be removed as chloride, while olivine and the magnesian micas were not attacked. At first it seemed probable that the reaction would give a quantitative measure of the magnesium combined as MgOH; but our later experiments and those of Lindner† have shown that the expectation was not well founded. I still believe, however, that the reaction discriminates between those magnesian silicates which contain MgOH and those which contain Mg and H combined otherwise, for only the members which must belong to the first class are acted

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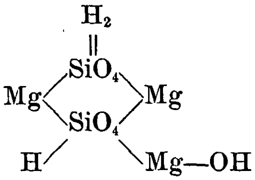
* Bull. U. S. Geol. Survey No. 78, p. 11; Bull. No. 90, p. 11, and Bull. No. 113, pp. 27 and 34.

† A. Lindner, Inaugural Dissertation, Breslau, 1893.

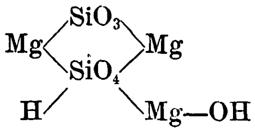
upon by the reagent. Brauns's objections* to this supposition, on the ground that the dry hydrochloric acid becomes moist, are not well taken, for the reaction was always applied at temperatures lower than those at which water is given off. His criticisms may apply to the later stages of the reaction, after it has once fairly begun, but not to its initiation. The magnesian micas which contain several per cent of water are all decomposable by aqueous hydrochloric acid, but are scarcely touched by the dry gas, while on the other hand serpentine and the chlorites are strongly attacked. After the gaseous acid has acted it becomes moist, but very slowly, and most of the moisture is carried past the mineral under investigation before it has had time to produce an appreciable effect. It is possible, however, that a slow stream of the acid may act differently from a rapid current, and that the discordant results of observation may be due to differences of this kind.

When serpentine is ignited, water is expelled, and a residue having the composition $Mg_3Si_2O_7$ is left behind. According to Rammelsberg† the water is given off in two portions—one-half upon weak ignition, the other after heating more strongly. On the orthosilicate theory these stages may be represented thus:

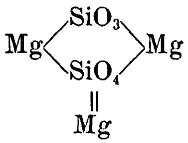
Serpentine.



First stage.

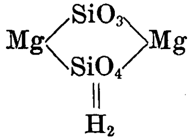


Second stage.



At the end of the second stage, if the ignition has not been too intense, the residue is still decomposable by hydrochloric acid, but by prolonged heating it is broken up quantitatively into soluble olivine and insoluble enstatite.

Allied to serpentine is the somewhat doubtful picrosmine, to which the formula $Mg_2H_2Si_2O_7$ is commonly assigned. Although this expression suggests a diorthosilicate, it may also be written



which represents picrosmine as a dehydrated serpentine altered subsequently by rehydration, with replacement of one magnesium atom by two of hydrogen. This mode of interpretation brings the mineral into line with serpentine, and all the known relations of the species are adequately expressed.

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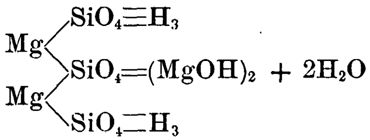
[*] Neues Jahrbuch, 1894. I, p. 205.

[†] Handbuch der Mineralchemie, 2 Aufl., p. 506.

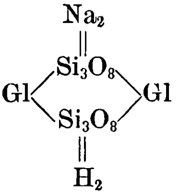
Several other hydrous silicates of magnesium seem to belong in this group, but their nature is altogether doubtful. Thus we have

Aphrodite	$Mg_2H_4(SiO_4)_2$
Kerolite	$Mg(SiO_4)_2H_5(MgOH)$

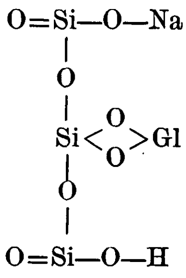
Deweylite is possibly



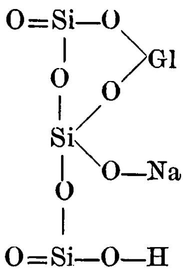
and genthite is similar, with part of the magnesium replaced by nickel. Sepiolite may be a trisilicate, with the formula $H_2{=}Si_3O_8{=}(MgOH)_2$, in which case conarite is the corresponding nickel salt. These symbols are to be regarded as suggestions only. Two other trisilicates—eudidymite and epididymite—should also be noted at this point. The two species have the same empirical formula, $HNaGlSi_3O_8$, which, doubled, becomes



a structure conformable to the type of the orthosilicates already considered. The isomerism between eudidymite and epididymite is explainable by giving one species the constitution just written, while the other, in place of Na_2 and H_2, would have the two groups NaH. It can also be ascribed to a different linking with the oxygen of the acid, and the empirical formula $HNaGlSi_3O_8$ can be put in two forms, thus:



and



a third isomer being also conceivable. The doubled formula, however, brings out analogies with bertrandite and other species and therefore, in default of evidence, is to be preferred.

CHAPTER V.

THE ORTHOSILICATES OF TETRAD BASES.

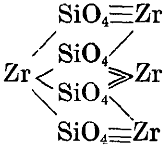
On account of their relatively small number and general scarcity, the silicates of the tetrad metals, titanium, zirconium, and thorium, are difficult to interpret in any satisfactory manner. Evidence exists, however, which seems to show that they are explainable by the same principles which apply to aluminum and the dyads, and that the theory of substitution from normal salts is a good working hypothesis to start from.

One definite normal salt is known in this series, the mineral zircon, $ZrSiO_4$. As with the other inorganic silicates, the true molecular weight of this compound is unknown, and it can be inferred only from a study of its derivatives. If we assume it to be represented by the polymeric expression $Zr_4(SiO_4)_4$, it contains replaceable basic atoms, and a number of other zirconium silicates fall naturally into series derivable from this as the fundamental member. In this connection the mineral auerbachite is peculiarly suggestive, for its composition is best indicated by the formula $Zr_4(Si_3O_8)(SiO_4)_3$; which goes to show an important analogy between this group of silicates and those which have been previously considered. This formula, compared with Hermann's analysis of auerbachite, gives the following results:

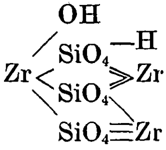
	Hermann.	Calculated.
SiO_2	42.91	42.45
ZrO_2	55.18	57.55
FeO	.93	
H_2O	.95	
	99.97	100.00

Although zircon is a very stable and definite mineral, it alters by hydration into malacone, cyrtolite, and a variety of other indefinite substances which can not as yet be interpreted with any clearness. At the same time other bases, such as lime and the rare earths, are taken up, producing mixtures of great complexity. Malacone is probably the first hydration derivative, and its relations to zircon, regarding the latter as $Zr_4(SiO_4)_4$, may possibly be as follows:

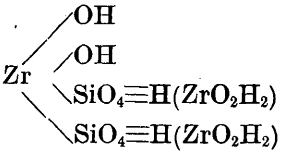
Zircon.



Malacone.



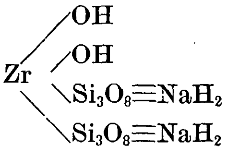
The original cyrtolite from Rockport is near malacone, but the cyrtolite from Colorado, analyzed by Hillebrand, approximates to



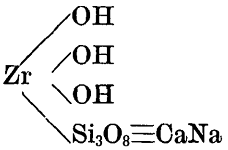
with part of the ZrO_2H_2 replaced by other bases. These formulæ, taken by themselves, are entitled to little consideration; but they become more significant when studied in connection with other compounds later. It will be noticed that one atom of zirconium is represented as linking four groups or radicles together; just as one aluminum atom has a similar triple function in the aluminous orthosilicates. This mode of linkage will be followed throughout this group of compounds.

In eudialyte, elpidite, and catapleiite we have a group of zirconium silicates which form a highly suggestive series. Taking the simpler members first, they may be represented thus:

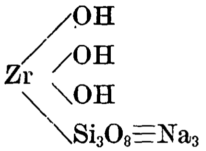
Elpidite.



Lime catapleiite.

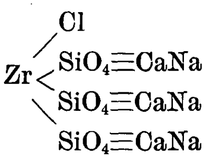


Soda catapleiite.

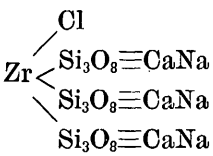


Connecting these formulæ with zircon, we have the facts that Si_3O_8 occurs in auerbachite, and that at Låven, according to Brögger,* zircon is found both intergrown with catapleiite and pseudomorphous after it.

Eudialyte and eucolite are commonly regarded as metasilicates, with the compound $ZrOCl_2$ as an admixture. But the latter is not found in nature by itself, and both minerals, unlike most of the true metasilicates, gelatinize with acids. Furthermore, the analyses of eudialyte and eucolite show a considerable range of variation in the ratio Si : O, although approximating somewhat nearly to the assumed SiO_3. If now we treat eudialyte and eucolite as mixtures of tri- and orthosilicates, like the feldspars, scapolites, and some micas, all difficulties vanish, the chlorine becomes equivalent to hydroxyl, and the minerals fall into line with catapleiite and elpidite as the first members of the series. All varieties of eudialyte and eucolite are then interpretable as mixtures of the two molecules



and



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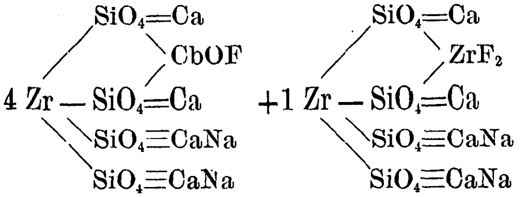
* Zeitsch. Kryst. Min., XVI, p. 105.

commingled in ratios nearly, but not exactly, 1 : 1. Hydroxyl replaces chlorine to some extent, while iron and manganese partly replace calcium; but the ratios shown by the formulæ are constant, and the structural analogies with the allied species are perfectly clear.

The remaining zirconium silicates, wöhlerite, rosenbuschite, låvenite, and hiörtdahlite, are difficult to formulate conclusively. Brögger regards them as meta compounds, and as such they are classed with the pyroxenes; but the ratio Si:O is in each case very nearly 1:4. In wöhlerite, which contains columbium, the latter pentavalent element may be regarded as forming the dyad group $=CbOF$, and as equivalent to the similar group $=ZrF_2$. On this supposition wöhlerite can be written



with small amounts of the groups $R'''F$ replacing ZrF_2. As thus written the calculated composition agrees fairly with Cleve's analysis, thus:

	Cleve.*	Calculated.
SiO_2	30.14	30.27
TiO_2	.42	
ZrO_2	16.12	18.46
Cb_2O_5	12.85	13.52
Fe_2O_3	.48	....
Ce_2O_3	.66	....
FeO	1.26	
MnO	1.00	
MgO	.12	
CaO	26.97	28.26
Na_2O	7.50	7.83
H_2O	.74	....
F	2.98	2.87
	101.24	101.21
Less O	1.24	1.21
	100.00	100.00

* Zeit. Kryst. Min., XVI, p. 347.

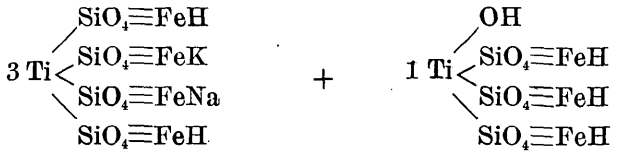
The other "zircon pyroxenes" can be interpreted in a somewhat similar manner, but the results are less satisfactory. The analyses are complicated by the presence of small amounts of titanium, which may be either acid or basic, and more data are needed before formulation can become useful.

The typical silicate of thorium, thorite, or orangite is another unsatisfactory species on account of its wide variations in composition. It is commonly supposed that the mineral, as it exists in nature, has been derived from an original $ThSiO_4$ by hydration; and that that $ThSiO_4$ was isomorphous with zircon. The nearest approach to the type is found in orangite, which may perhaps be regarded as a thorium cyrtolite, or thorium malacone. Yttrialite approximates to the composition

$$Th(Si_3O_8)_4Fe''_2(YO)_8$$

and in steenstrupine a thorium silicate exists which may be $Th(SiO_4)_4Ca_4Na_4$. Further discussion of these minerals at present would be fruitless. The data are wholly inadequate.

To the titanium silicates astrophyllite, johnstrupite, and rinkite similar formulæ to the foregoing are assignable. Indeed, this has already been done for astrophyllite by Brögger, who writes the formula $Ti(SiO_4)_4R''_4R'_4$. This seems to be the dominant molecule in astrophyllite, which, however, varies in composition. To the Colorado mineral we may more precisely give the formula

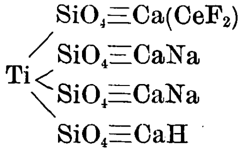


which requires

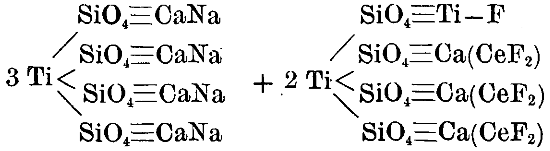
SiO_2	34.30
TiO_2	12.20
FeO	41.16
K_2O	5.36
Na_2O	3.55
H_2O	3.43
	100.00

Some iron is replaced by manganese, and ferric iron, perhaps as $=Fe-OH$, is also present. In the fluoriferous astrophyllites the fluorine should replace hydroxyl.

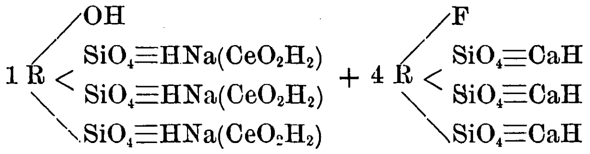
Johnstrupite and rinkite are both fluoriferous, and both contain earths of the cerium groups. In johnstrupite, a little ZrO_2, ThO_2, and CeO_2 replace some TiO_2. For johnstrupite the expression



agrees well with the ratios given by analysis. In rinkite we have, with great probability, the mixture



Even the complex mosandrite reduces to the same general type agreeing very closely with



in which R$=$Ce$^{\text{iv}}$: Zr : Ti :: 1 : 2 : 2. For each of these species the published analyses agree well with the composition calculated from these formulæ.

There is still another group of titaniferous silicates, represented by sphene, keilhauite, and tscheffkinite, which seems to be unconformable with the foregoing scheme of interpretation. Sphene, the typical member of the group, has the empirical formula $CaTiSiO_5$, for which two distinct structures have been proposed. One regards the mineral as the calcium salt of an acid, H_2TiSiO_5, analogous to $H_2Si_2O_5$, while the other treats it as a basic orthosilicate,

$$Ca=SiO_4=TiO.$$

A careful study of the recorded analyses of sphene leads me to prefer the latter expression, for the actual ratios vary in a way which indicates a replacement, sometimes of Ca and sometimes of TiO by other bases. On the meta formula, only the calcium should be replaceable. This variability of ratio is well shown by some of the varieties of sphene, such as grothite, alshedite, and eucolite-titanite, but the data are not absolutely conclusive. If, however, sphene is a basic orthosilicate, it should be placed in the preceding chapter with datolite and the other calcium salts. On the other hand, the acid character of the titanium is suggested by the remarkable hydration derivative of sphene, xanthitane, of which the composition is approximately represented by the formula $Al\equiv Ti_2O_7\equiv H_3$.

For tscheffkinite, as shown by Eakins' analyses, the composition is approximately $(FeCa)_3Ce_6Ti_4Si_6O_{32}$, but the constitution of the mineral is very doubtful. Keilhauite appears to be like sphene, with Ca or TiO replaced by $R'''OH$ or $R'''O_2H_2$, but the analyses are widely discordant. The orthorhombic guarinite is generally assumed to be isomeric with sphene, although there is but one incomplete analysis from which to calculate.

Some light may possibly be shed upon the sphene groups of mineral by a study of the columbo-titanates æschynite and polymignite. The composition of æschynite is very well represented by a mixture of molecules

$$\begin{array}{l} 2\ O=Ti=TiO_4=Ca \\ 2\ (CbO_3)_2=Ti=TiO_4=Fe \\ 3\ (CbO_3)_2=Th=TiO_4=(CeO)_2 \end{array}$$

which compares with Rammelsberg's analysis as follows:

	Found.	Calculated.
TiO_2	21.20	20.70
ThO_2	17.55	18.63
Cb_2O_5	32.51	31.52
$(Ce, La, Di)_2O_3$	19.41	23.14
$(Y, Er)_2O_3$	3.10	
FeO	3.34	3.38
Ca	2.50	2.63
	99.61	100.00

For polymignite a similar expression gives equally good results. It is

$$
\begin{aligned}
&5\ (CbO_3)_2{=}Zr{=}TiO_4{=}(Fe'''O)_2\\
&4\ O{=}Zr{=}TiO_4{=}(CeO)_2\\
&15\ O{=}Zr{=}TiO_4{=}Ca\\
&1\ O{=}Th{=}TiO_4{=}Na_2
\end{aligned}
$$

The similarity in type of these expressions to the orthosilicate formula for sphene is obvious. It is also obvious that the entire group is greatly in need of further study.

CHAPTER VI.

THE DIORTHOSILICATES.

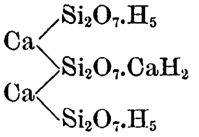
Although the existence of the sexbasic acid $H_6Si_2O_7$ has been well established by the preparation of its ethers, its metallic salts are little known and uncertain. I have already shown, in the case of serpentine, that a mineral may be apparently a diorthosilicate, and yet equally well explainable otherwise; and what is true in that instance may be true in others. For the following species the diorthosilicate formulæ seem to be the best and simplest, even though they are not wholly free from objection. They fit existing evidence, but are not absolutely conclusive.

The typical member of this group of minerals is the hexagonal lead silicate, barysilite, $Pb_3Si_2O_7$. The artificial compound from the slags of Bonneterre, Mo., described by Dana and Penfield, is near this, and may have the composition $Pb_2CaSi_2O_7$. The tetragonal ganomalite is another similar compound, approximating to $3Pb_3Si_2O_7+2Ca_3Si_2O_7$, although the latest analysis agrees rather better with $Pb_3Si_2O_7+Ca_2SiO_4$. Two other orthorhombic species, kentrolite and melanotekite, may be regarded as basic salts derived from barysilite, thus:

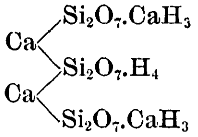
Barysilite	$Pb_2Si_2O_7Pb$
Melanotekite	$Pb_2Si_2O_7(Fe'''O)_2$
Kentrolite	$Pb_2Si_2O_7(Mn'''O)_2$

The group of zeolitic calcium silicates, okenite, gyrolite, and apophyllite, are unquestionably related to one another, and are best represented as salts of $H_6Si_2O_7$. In nature, gyrolite may be derived from apophyllite, and apophyllite also from gyrolite, while Doelter has generated apophyllite from okenite by artificial means.* First, by heating okenite with potassium silicate and water to 200°, crystals of apophyllite were obtained. Secondly, by heating okenite with aluminum chloride, sodium carbonate, and carbonated water together at 220°, apophyllite, analcite, and chabazite were produced. The most satisfactory general formulæ for the three species are these:

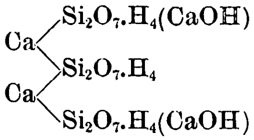
Okenite.



Gyrolite.



Apophyllite.



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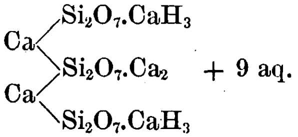
* Neues Jahrb., 1890, I, p. 118.

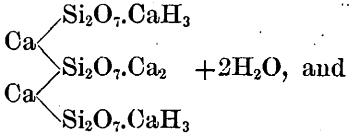
In apophyllite fluorine may partly replace hydroxyl, and K may replace the univalent CaOH. With K : CaOH : : 1 : 1 the composition of apophyllite becomes

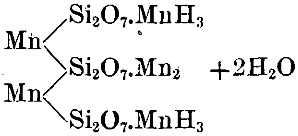
SiO_2	52.03
CaO	24.27
K_2O	6.79
H_2O	16.91
	100.00

The uncertain mineral plombierite may be a fourth member of this group, with the formula



To the calcium-manganese silicate, inesite, various formulæ are assignable. By Flink it is regarded as $2(CaMn)SiO_3.\ H_2O$. But part of the water is stable at temperatures above 300°; and this fact is expressed by Schneider's formula $(CaMn)Si_3O_8(MnOH)_2.\ H_2O$. Both formulæ agree with the analyses approximately, but the latest analysis, that of Lundell,* is better represented by the following mixture:

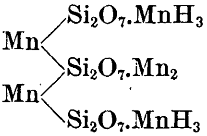




which requires:

	Found, Lundell.	Calculated.
SiO_2	42.92	42.18
PbO	.73	
MnO	36.31	37.44
MgO	.37	
CaO	8.68	9.84
H_2O	10.48	10.54
	99.49	100.00

With inesite another manganese silicate, bementite, is perhaps related, having the formula



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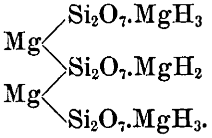
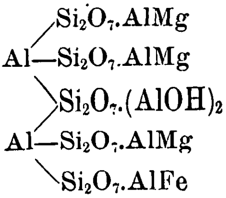
* See Hamberg, Geol. Fören. Förhandl., XVI, p. 325.

and the magnesian spadaite may be similar, with the composition



Another magnesian silicate, saponite, is perhaps normally $H_4(MgOH)_2Si_2O_7$, although the analyses all show admixtures of some aluminous compound.

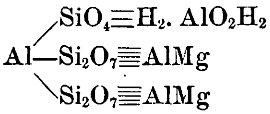
Among the silicates of aluminum, salts of diorthosilicic acid are very rare. The only one which seems to be at all well defined is iolite, which agrees best with the formula



which requires

SiO_2	49.26
Al_2O_3	33.50
MgO	9.85
FeO	5.91
H_2O	1.48
	100.00

in close concordance with the best recorded analyses. By alteration, iolite passes into mica, going through an intermediate stage, however, known as chlorophyllite. This substance may be regarded as formed by hydration, in which the linking group of Si_2O_7 in iolite is split into two orthosilicic radicles, yielding two molecules of the type

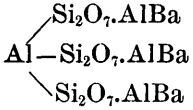


from which the final transition into a mica is easy. If we take Rammelsberg's analysis of chlorophyllite, recalculate the ferric oxide into alumina and lime into magnesia, reducing afterwards to 100 per cent, we get the following comparison between observed fact and the composition of chlorophyllite computed from the foregoing formula:

	Found.	Reduced.	Calculated.
SiO_2	46.31	47.99	48.39
Al_2O_3	25.17	33.34	32.90
Fe_2O_3	10.99		
MgO	10.91	11.74	12.90
CaO	.58		
H_2O	6.70	6.93	5.81
	100.66	100.00	100.00

The agreement is as close as could be reasonably expected. The replacement of a little magnesia by a little water in the original alteration product accounts for the discrepancies.

Two other aluminous silicates possibly belong in this group. One, barylite, is near

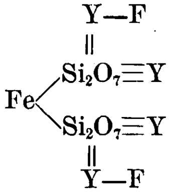


which requires

SiO_2	35.19
Al_2O_3	19.94
BaO	44.87
	100.00

The other silicate, sphenoclase, is approximately $Al_2(Si_2O_7)_3Ca_6$; which may be analogous to barylite in structure, or written as a calcium salt similar in type to okenite. Both barylite and sphenoclase, however, are uncertain, and their relations are not definitely known. The species glauconite, pholidolite, and celadonite, all of doubtful composition, seem also to have diorthosilicate ratios.

To the rare mineral rowlandite, in accordance with Hillebrand's analysis,[*] a diorthosilicate formula belongs, viz:



which expresses the composition of the species very closely.

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[*] Bull. U. S. Geol. Survey No. 113, p. 45.

CHAPTER VII.

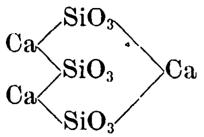
THE META- AND DIMETASILICATES.

Although the metasilicates appear at first sight to be extremely simple, they are actually quite difficult to interpret. It is easy enough to deduce their empirical formulæ, and to write them afterwards in structural terms; but this is not sufficient. The structural formulæ must express all known relations in the case of each species, and in attempting to satisfy the established conditions the difficulties begin to appear. In the first place, metasilicic acid itself is defectively known, and no ether of the form R_2SiO_3 has yet been certainly obtained. Troost and Hautfeuille's ether $(C_2H_5)_8Si_4O_{12}$ suggests the possibility that metasilicic acid, like metaphosphoric acid, may polymerize, but an attempt to draw general conclusions on so important a supposition from one datum only would be most unwise. The possibility of polymeric acids, however, must be recognized.

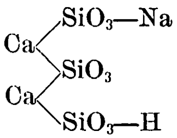
Again, as we have repeatedly seen, a mineral may be apparently a metasilicate and yet really a mixture of ortho- and trisilicates. Even a basic trisilicate can have seemingly metasilicate ratios. All of these considerations complicate the identification and study of the true metasilicates to such an extent that only provisional conclusions can be drawn from the data now on hand.

A crystallized silicate of sodium, $Na_2SiO_3.8H_2O$, is well known. A solution of this salt added to a solution of calcium chloride precipitates a compound which, dried over sulphuric acid, has, according to my own observations, the composition $Ca_2Si_2O_6.5H_2O$. This, minus the water, is analogous to the mineral wollastonite, from which another mineral, pectolite, is derived. If wollastonite, instead of the formula $Ca_2Si_2O_6$, be given the formula $Ca_3Si_3O_9$, it may be compared structurally with pectolite, as follows:

Wollastonite.



Pectolite.



It must be remembered that the molecular weights of the inorganic silicates are not known, but only assumed; and the problem suggested by the foregoing expressions is to find a set of structural formulæ which shall represent all of the available evidence. Now, wollastonite is commonly classed with the pyroxenes, on crystallographic grounds; and so too is pectolite. But both species are very easily decomposed by even dilute and weak acids, while the normal pyroxenes are quite refractory; and furthermore, wollastonite has a lower density than any pyroxene which approaches it in composition. Chemically, then, these species are dissimilar, and it is very doubtful whether they can properly be grouped together.

Empirically, however, the nonaluminous pyroxenes resemble wollastonite in their ratios. Thus we have, according to the commonly accepted formulæ developed by Tschermak, Doelter, and others:

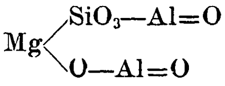
Enstatite, orthorhombic	$Mg_2Si_2O_6$
Diopside, monoclinic	$CaMgSi_2O_6$
Hedenbergite, monoclinic	$CaFeSi_2O_6$
Rhodonite, triclinic	$Mn_2Si_2O_6$

There is also a great variety of other intermediate species or isomorphous mixtures in the pyroxene series, such as bronzite, hypersthene, schefferite, sahlite, jeffersonite, and fowlerite, in which we find, variously replacing one another, salts of magnesium, calcium, iron, manganese, and zinc. All of these minerals, however, conform to the general formula $RSiO_3$, or $R_2Si_2O_6$, which adequately expresses their constitution so far as they alone are concerned. This, structurally, can be written

$$R\left\langle\begin{matrix}SiO_3\\SiO_3\end{matrix}\right\rangle R$$

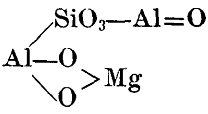
which would be satisfactory if the pyroxene series ended here and if the amphiboles were unknown.

Going a step farther we find in augite a pyroxene containing aluminum, and having an oxygen ratio greater than $Si:O_3$. In place of aluminum, ferric iron also occurs, and alkalies are sometimes present. Leaving these variations out of account, for consideration later, we have in augite, as interpreted by Tschermak, together with the normal compound $R_2Si_2O_6$, the basic salt $RAlAlSiO_6$; which, as shown by Groth, is empirically analogous to kornerupine. It is also similar in composition to the silicate which is characteristic of the clintonite micas; but the two are probably not identical. A metasilicate isomer of the clintonite molecule might be written either as



$$Mg\left\langle\begin{matrix}SiO_3-Al=O\\O-Al=O\end{matrix}\right.$$

or as



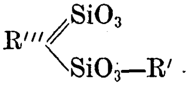
$$Al\left\{\begin{matrix}SiO_3-Al=O\\ \left.\begin{matrix}-O\\O\end{matrix}\right\rangle Mg\end{matrix}\right.$$

having in the first form some resemblance in structure to the metasilicate formula for the nonaluminous pyroxenes. The compound, however, unless represented by kornerupine, is not known by itself, but is assumed as existent in mixtures; its reality, therefore, is still questionable. Its simplest representation would be as a basic orthosilicate, $Mg(SiO_4)(AlO)_2$, and it will be seen later that a polymer of this form is far more satisfactory than any metasilicate expression.

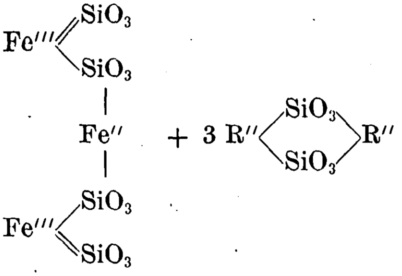
Still another series of silicates containing triad bases and also alkalies are classed with the pyroxenes, as follows:

Spodumene	$AlLiSi_2O_6$
Jadeite	$AlNaSi_2O_6$
Acmite	$Fe'''NaSi_2O_6$

and their empirical formulæ are fairly satisfactory. Structurally, these expressions become, as metasilicates,



and babingtonite, which contains no alkalies, is similar, thus:

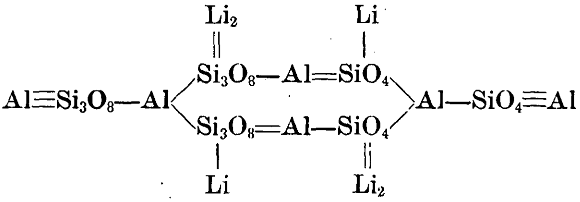


R'' being = Ca, Fe'', and Mn. The ferric molecule is evidently equivalent to two acmite molecules, with Na_2 replaced by a linking atom of iron.

So far, except partially in the comparison between wollastonite and pectolite, the formulæ cited for the pyroxenes express composition and composition only. But spodumene, as shown by the elaborate research of Brush and Dana, splits upon alteration into a mixture of eucryptite, an orthosalt, and albite, a trisilicate. This observation suggests two alternatives: either that spodumene is derived from a polymetasilicic acid, or else that it is a pseudometasilicate, a mixed ortho- and tri-salt, like some of the species which have already been explained. An analogy with leucite, for example, will at once be inferred, and that species, empirically, is strikingly like spodumene, thus:

Leucite	$AlKSi_2O_6$
Spodumene	$AlNaSi_2O_6$

Like spodumene, leucite alters into a feldspar and a member of the nepheline group; but it differs from spodumene in form and in density. The specific gravity of the isometric leucite is 2.5, that of the monoclinic spodumene is nearly 3.2, and hence we may reasonably infer that the latter species has the larger and more condensed molecule. In order to explain the relations of leucite, its empirical formula was quadrupled, and in that way a relation with the garnet group was brought out. For spodumene, regarding it also as a mixed silicate, a sixfold multiplication of its formula indicates its greater density, and its splitting up into eucryptite and albite, with partial replacement of lithium by sodium, is representable as follows:

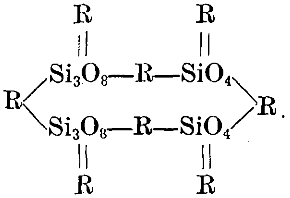


From this grouping of atoms the transition into $Al_3(Si_3O_8)_3Na_3 + Al_3(SiO_4)_3Li_3$ is hardly more than a simple case of cleavage, and the relations between the three species are intelligibly expressed. Acmite, which yields pseudomorphs of analcite, and jadeite also, probably follow the same rule, the formula of one being typical of the others. The ferric molecule in babingtonite should be still another instance of the same kind, with Fe''_3 in place of Li_6, and Fe''' instead of Al.

If the formula just developed for spodumene should be sustained, it would seem necessary to adjust the other pyroxenes with it. In the case of Tschermak's aluminous constituent of augite this adjustment is easily made by taking the formula Al_2MgSiO_6 six times, as in the case of spodumene. The parallelism between the two species is then representable as follows:

Spodumene	$Al_6(Si_3O_8)_3(SiO_4)_3Li_6$
Al. augite	$Al_6(SiO_4)_3(SiO_4)_3(AlO_2Mg)_6$

the univalent AlO_2Mg having been recognized among the micas. This formula serves to explain the well-known alterability of augite into epidote and into mica, and so far at least is useful. I do not, however, feel inclined to put very much stress upon it, for as yet it is only an expression of analogy, which may or may not prove to be valid. It would seem to require the recognition of all the pyroxenes as pseudometasilicates, in which case the normal series, containing only dyad bases, would become

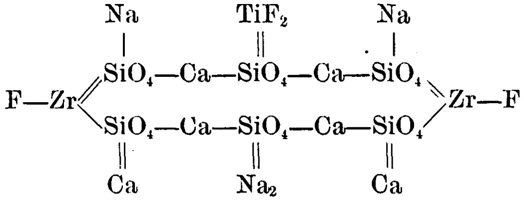


with four atoms of R given linking functions, while the other four are, so to speak, replaceably combined. On this basis we should write

Diopside	$Mg_4Ca_4(Si_3O_8)_2(SiO_4)_2$
Hedenbergite	$Fe_4Ca_4(Si_3O_8)_2(SiO_4)_2$

The formula $R''_4(AlO)_8(SiO_4)_2(SiO_4)_2$ would be exactly parallel with these, and affords another expression for Tschermak's compound Al_2RSiO^6. On the ground of simplicity this is preferable to the more complex expression based on the formula of spodumene.

The so-called "zircon pyroxenes," rosenbuschite, wöhlerite, låvenite, and hiörtdahlite, I have already mentioned among the orthosilicates of zirconium. They can be given metasilicate ratios, following Brögger, by regarding the zirconium as present in the form of a metazirconate. If this explanation is correct, we should expect to find zirconates in nature, free from admixtures; but no such minerals are yet known. Artificial zirconates have, indeed, been prepared; but zirconium is more markedly basic than acid in its functions, and the analogy furnished by the orthosilicate, zircon, has been my guide in the interpretation of these species. Rosenbuschite, however, can be represented as a definite compound having structural analogies with the pyroxenes, as here formulated, with the composition



$$\begin{array}{ccccccc}
 & Na & & TiF_2 & & Na & \\
 & | & & \| & & | & \\
 & SiO_4- & Ca- & SiO_4- & Ca- & SiO_4 & \\
F-Zr\langle & & & & & & \rangle Zr-F \\
 & SiO_4- & Ca- & SiO_4- & Ca- & SiO_4 & \\
 & \| & & \| & & \| & \\
 & Ca & & Na_2 & & Ca &
\end{array}$$

which compares well with Cleve's analysis,* thus:

	Found.	Calculated.
SiO_2	31.36	30.30
ZrO_2	20.10	20.54
TiO_2	6.85	6.73
Fe_2O_3	1.00	
La_2O_3	.33	
MnO	1.39	
CaO	24.87	28.29
Na_2O	9.93	10.44
F	5.83	6.40
	101.66	102.70
Less O	2.47	2.70
	99.19	100.00

This mode of interpreting the pyroxenes is so remote from our usual conceptions that I bring it forward with great diffidence. It unifies the group, however, it expresses the observed alterations of the several species, and despite its complexity it will be found to be sustained and strengthened by evidence brought out in the study of the amphiboles.

This last-named group of highly important minerals resembles the pyroxenes in composition, and is explained by Tschermak in essentially the same way. Their molecular weights, however, are taken as double

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*Zeit. Kryst. Min., XVI, p. 383.

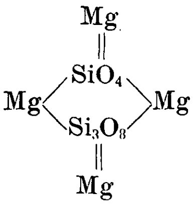
those of the pyroxenes, for the reason that the atomic replacements seem to occur by fourths rather than by halves. This point is exemplified by a comparison between diopside and tremolite; which, reduced to their simplest empirical formulæ, become

Diopside	$CaMgSi_2O_6$
Tremolite	$CaMg_3Si_4O_{12}$

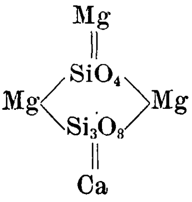
The pyroxenes, however, are somewhat heavier than the amphiboles, and from their greater density we may suppose them to have the larger molecules. Hence the formula of diopside should be a multiple of that just cited, and presumably greater than $Ca_2Mg_2Si_4O_{12}$. Upon this point the phenomenon of uralitization has definite bearing. In this process pyroxene is converted into amphibole, with increase of volume and little or no change of composition. In other words, a complex molecule has been dissociated into simpler molecules—a phenomenon the direct opposite of polymerization. In the face of this evidence it is difficult to see how the current views as to the relative molecular magnitudes of pyroxene and amphibole can be maintained. The pyroxenes must form the more complex group, and the amphiboles the simpler.

In the amphibole group the orthorhombic anthophyllite is the equivalent or isomer of enstatite and hypersthene. Then follows a monoclinic series, containing tremolite, actinolite, cummingtonite, dannemorite, etc., all being represented by the general empirical formula $RSiO_3$, with calcium, magnesium, iron, or manganese as the bivalent metal. In grünerite the salt $FeSiO_3$ exists by itself, and in richterite and astochite alkaline silicates appear. If we regard the minerals as pseudometasilicates, having molecular weights lower than the pyroxenes, and, with the bases replaceable by fourths, the typical amphiboles are most simply represented by formulæ like the following:

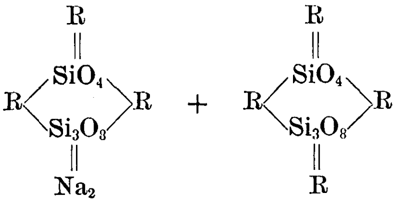
Anthophyllite.



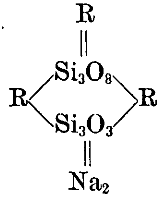
Tremolite.



Richterite becomes a mixture of salts,

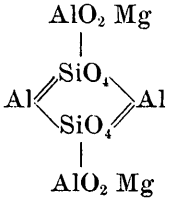


commingled in ratios near 1:1, and astochite is similar, but with NaH in place of Na_2. Potassium may also partly replace sodium. Another alkaline amphibole of doubtful character, waldheimite, approximates to

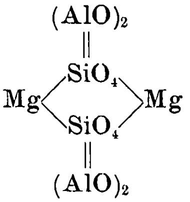


which is the formula of a trisilicate pure and simple, with R=Ca, Fe, Mg. The existence of this compound is strong evidence in favor of the pseudometasilicate theory; and, as will be seen later, it does not stand alone. The formulæ as written suggest a close analogy between the pyroxene-amphibole minerals and the olivine group, which may have some future significance.

Among the amphiboles, as among the pyroxenes, aluminous and ferric compounds are common, and with these the minerals approach to orthosilicate ratios. Tschermak's interpretation of these ratios is practically the same as in the pyroxene series, namely, by the assumption of molecules of the form Al_2RSiO_6 or $Al_4R_2Si_2O_{12}$. An alternative to this view is offered by Scharizer,* who shows that the hornblendes can be explained as mixtures of actinolite, $R_4Si_4O_{12}$, with an orthosilicate called syntagmatite $(R'_2R'')_3Al_2(SiO_4)_3$, whose ratios are similar to those of garnet. An amphibole from Jan Mayen's Island approaches very nearly to syntagmatite in composition. If a compound of this type is present in the amphiboles it would explain at once their alterability into epidote, micas, and chlorites; but so far as the composition of the group is concerned neither Tschermak's view nor Scharizer's is absolutely necessary. The Tschermakian molecule, however, can be written either as



or as



the latter form resembling that of tremolite, and also connecting the group still more closely with the olivines. It is also parallel to the last formula suggested for the corresponding pyroxene compound, being one-half of the latter and identical with it in type.

No amphibole is yet known which, by itself, corresponds precisely in its constitution to acmite and spodumene. In glaucophane we find a species, which, as a metasilicate, may be written $AlNaSi_2O_6+(MgFe)SiO_3$; and in crocidolite another similar salt, $Fe'''NaSi_2O_6+FeSiO_3$. Crocidolite alters easily; and one of the products of alteration, which

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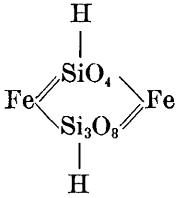
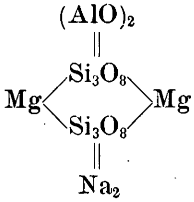
*Neues Jahrbuch, 1884, (2), p. 143.

has been named griqualandite, is very near $Fe'''HSi_2O_6$, the equivalent of acmite in general type. This last compound can be written

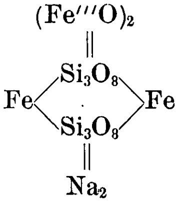


and so adjusted as an amphibole-hydrogen-acmite to the remainder of the group; but glaucophane and crocidolite are best formulated as follows:

Glaucophane.

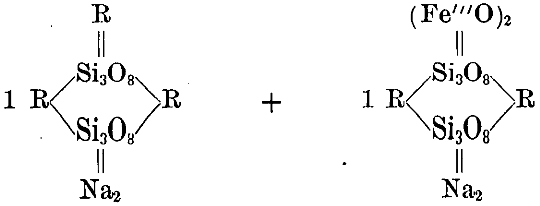


Crocidolite.



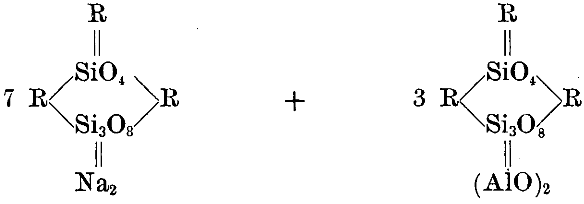
which makes them, as trisilicates, precisely equivalent in structure to the normal amphiboles. These compounds, and their corresponding orthosilicates, commingled with salts like tremolite or actinolite, give mixtures which conform in composition to the aluminous hornblendes.

Closely allied to crocidolite and glaucophane is the recently described amphibole crossite;* in which the ratio of Si:O is distinctly less than 1:3. This species may be written as a mixture of the two molecules



with some Al in place of Fe''', and R being=Fe, Mg, Ca. Gastaldite and riebeckite are similar species, but the analyses are not perfectly conclusive. It is, perhaps, necessary with these minerals to assume the presence of acmite-like molecules, riebeckite being empirically near $2Fe'''NaSi_2O_6+FeSiO_3$.

Arfvedsonite, in which R'' is mainly Fe, may be represented quite closely as a mixture of this order:



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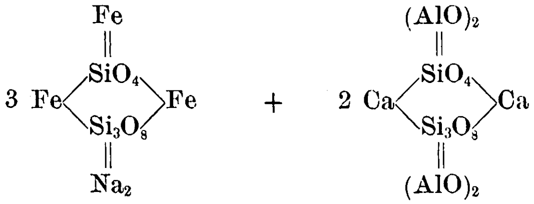
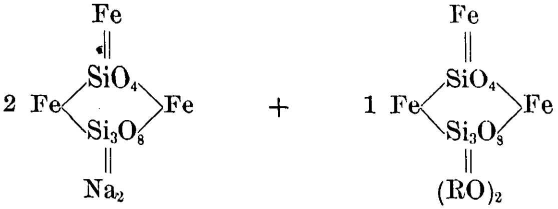
* Palache, Geol. Bulletin, Univ. of California, I, p. 181. 1894.

a little aluminum being replaced by iron. Barkevikite, a more basic species still, has its composition well indicated by the following expression, with some Fe replacing Al as in arfvedsonite:



Finally, in the triclinic aenigmatite, if we assume that the titanium (7.57 per cent TiO_2) is equivalent to silica, we find the mixture



with $RO = AlO : FeO :: 1 : 1$ almost exactly, and $Si : Ti :: 7 : 1$. Calculating with these ratios, ænigmatite has the following composition in comparison with Forsberg's analysis:*

	Found.	Calculated.
SiO_2	37.92	38.11
TiO_2	7.57	7.26
Fe_2O_3	5.81	4.85
Al_2O_3	3.23	3.08
FeO	35.88	39.20
MnO	1.00	
CaO	1.36	
MgO	.33	
Na_2O	6.58	7.50
K_2O	.51	
	100.19	100.00

The variations here are plainly due to the replacements of Fe by Mn, Ca, and Mg, and of Na by K.

A careful study of the best analyses in the pyroxene and amphibole groups will strengthen very materially the view here developed that the species are not true metasilicates. Although in most cases the approximation to metasilicate ratios is very close, there are distinct variations toward orthosilicates on one side and toward trisilicates on the other, and it is only by assuming that we have mixed silicates to deal with that all the anomalies can be made to disappear. On this

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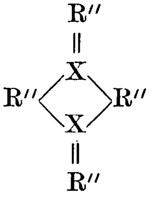
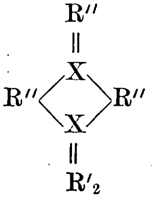
*Zeit. Kryst. Min., XVI, p. 428.

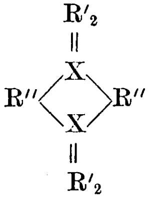
theory, if we represent Si_3O_8 and SiO_4 groups indiscriminately by the general symbol X, all of the amphiboles are covered by the following typical symbols, in which R″ stands for any dyad metal, and R′ for K, Na, H, AlO, or Fe‴O:

$$R''_4X_2$$
$$R''_3X_2R'_2$$
$$R''_2X_2R'_4$$

or, structurally,





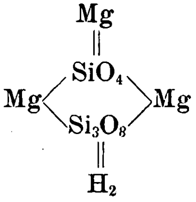


In a similar way, all the pyroxenes, except the acmite-spodumene group, which has the special formula discussed previously, may be represented as formed by mixtures of

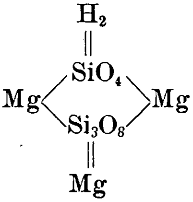
$$R''_4X_4R''_4$$
$$R''_4X_4(R'''O)_8$$

which is in accordance with the theory developed by Tschermak except as to the molecular magnitude of the compounds—that is, the pyroxenes are essentially bipolymers of the amphiboles, and the character of the structure is the same for both groups. The olivine minerals are represented by similar orthosilicate formulæ, $R_4(SiO_4)_2$ being the constitutional equivalent of $R_4(SiO_4)(Si_3O_8)$. Pseudomorphs of pyroxene (fassaite) after monticellite, have been found at Monzoni, and are well known. Furthermore, Becke* has described pseudomorphs of anthophyllite and actinolite after olivine, so that a connection between the two groups is clearly indicated. The tracing of this connection in a more general way would seem to offer a profitable field for investigation.

By the hydration of pyroxene or amphibole either serpentine or talc may be generated. The latter species has the composition $H_2Mg_3Si_4O_{12}$, and may be written structurally like amphibole either



or



Both expressions are in accord with the fact recorded by Schneider and myself,† that upon the ignition of talc one-fourth of the silica is

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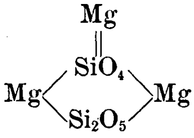
* Min. Pet. Mitth. (N. F.), 4, pp. 355 and 450.

† Bull. U. S. Geol. Survey No. 78, p. 13.

set free quantitatively. This would give the ignited residue the composition shown by the subjoined alternative formulæ:



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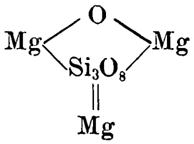
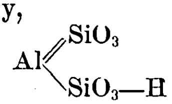


and of these the first would seem to accord the better with the remarkable stability and insolubility of the material. A metasilicate formula, $H_2Mg_3(SiO_3)_4$, is also admissible, and accords equally well with the evidence concerning talc. The pseudometasilicate expression, however, seems to be preferable in view of what is known as to the genesis of the species.

Pyrophyllite and kyanite are two aluminous metasilicates which seem to be related; at all events the former is not infrequently the gangue or matrix of the latter. Empirically they are

Pyrophyllite	$AlHSi_2O_6$
Kyanite	Al_2SiO_5

or, structurally,



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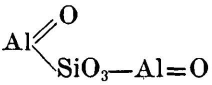
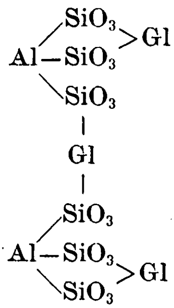


To these formulæ I attach very little significance, except in so far as they represent a single observed relation. Probably the true formulæ should be multiples of these; for kyanite is much denser than its isomer, andalusite, $Al_3(SiO_4)_3(AlO)_3$. Both kyanite and andalusite, at very high temperatures, are transformed, with disengagement of heat, into a third isomer, sillimanite,* a phenomenon which indicates dissociation. Sillimanite doubtless has the smallest molecule of the three species, and may be $Al\equiv SiO_4—AlO$, but even this is so purely hypothetical that it would be useless at present to discuss the species farther.

With beryl, $Gl_3Al_2Si_6O_{18}$, the evidence in favor of a metasilicate structure is fairly good, although the composition can also be expressed as that of a basic trisilicate. There are thus two alternatives,



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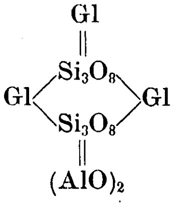

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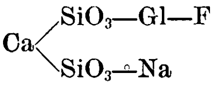
* Vernadsky, Bull. Soc. Min., XII, p. 447, and XIII, p. 256.

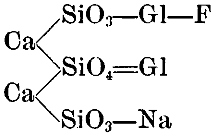
But beryl alters into mica, a fact which is favorable to the first of these formulæ, and all of its commoner alterations seem to take place by replacement of glucinum. In the trisilicate formula the alumina should be equally replaceable, and so far the evidence is adverse to it. Furthermore, Traube* has effected the synthesis of beryl by precipitating a mixture of glucinum and aluminum sulphates with a solution of sodium metasilicate, and then crystallizing by fusion of the precipitate with boron trioxide. Since the starting point was a metasilicate, there is a fair presumption that the product was a metasilicate also. Beryl can be written as a pseudometasilicate, but there are no data to justify doing so.

Two other minerals containing glucinum, leucophanite, and meliphanite, appear to be essentially metasilicates with the subjoined formulæ:

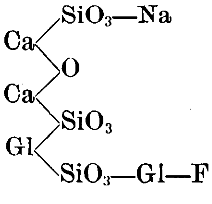
Leucophanite	$NaCaGlFSi_2O_6$
Meliphanite	$NaCa_2Gl_2FSi_3O_{10}$

These are capable of several interpretations. The simplest regards meliphanite as a mixed meta- and orthosilicate, when both species can be written





or else with the glucinum as the linking element, and with the calcium united to fluorine. This involves no change of type, but only an exchange of position between Ca and Gl. Brögger,† to whom the empirical formulæ are due, also represents meliphanite as a basic metasilicate



which is also justifiable. Between the several alternatives there is no ground for deciding. The stability of meliphanite toward ordinary acids would seem to favor the formula first given, for a basic calcium salt would probably be more easily decomposable.

Danburite, $CaB_2Si_2O_8$, is sometimes regarded as the equivalent of barsowite, $CaAl_2Si_2O_8$, a doubtful isomer of anorthite. But barsowite

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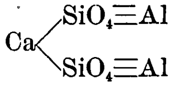
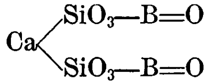
* Neues Jahrbuch., 1894, I, p. 275.

† Zeit. Kryst. Min., XVI, pp. 289-291.

gelatinizes with hydrochloric acid, while danburite is attacked by the reagent only after ignition. Possibly the difference may be as follows:



$$Ca\left\langle\begin{matrix}SiO_4\equiv Al\\ SiO_4\equiv Al\end{matrix}\right.$$

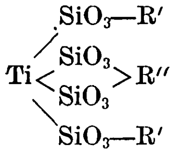


$$Ca\left\langle\begin{matrix}SiO_3-B=O\\ SiO_3-B=O\end{matrix}\right.$$

danburite being a metasilicate. Other formulæ are also possible, and more data are needed before any conclusion can be reached. The associations of danburite with feldspars, mica, pyroxene, etc., suggest that it may be a pseudometasilicate, allied in structure to the aluminous constituent of augite.

Chrysocolla is probably a metasilicate, and perhaps, empirically, $CuSiO_3.2H_2O$. It can not be well regarded as impure dioptase, for the latter gelatinizes with hydrochloric acid, while chrysocolla does not. The species, which may be a mixture of compounds, needs careful investigation.

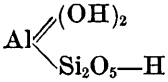
Among the titanosilicates, the recently described neptunite* appears to be a meta compound,



$$Ti\left\langle\begin{matrix}SiO_3-R'\\ \left.\begin{matrix}SiO_3\\ SiO_3\end{matrix}\right\rangle R''\\ SiO_3-R'\end{matrix}\right.$$

with $R'=Na, K$, and $R''=Fe, Mn$. The analogy between this formula and the formulæ of the titanium orthosilicates is its sole justification. The ratios given by analysis, however, are sharply in accord with the proposed expression.

The salts which are fairly ascribable to dimetasilicic acid, $H_2Si_2O_5$, are few in number and comparatively rare. Among them, petalite, $AlLi(Si_2O_5)_2$, is the best known and most characteristic. Its formula, as here written, is closely similar to the metasilicate formula for spodumene, and the two species are commonly associated. Petalite, however, has far the lower density of the two, and is therefore presumably composed of smaller molecules. An alteration product of petalite, hydrocastorite, approximates roughly to



$$Al\left\langle\begin{matrix}(OH)_2\\ Si_2O_5-H\end{matrix}\right.$$

which requires

SiO_2	60.60
Al_2O_3	25.75
H_2O	13.65
	100.00

The actual hydrocastorite contains about 4.3 per cent of lime, and is doubtless impure. By Doelter† petalite is interpreted somewhat

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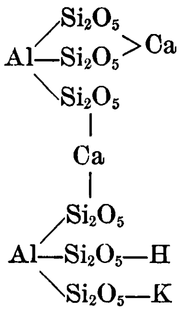
[*] Flink. Geol. Fören. Förhandl., XV, p. 196.

[†] Min. Pet. Mitth., 1878, I, p. 529.

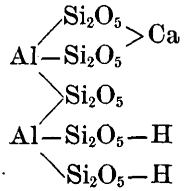
differently, being given the empirical formula $Al_2Li_2Si_{10}O_{24}$; but the formula here adopted is the one most generally received.

Milarite, $HKCa_2Al_2(Si_2O_5)_6$, is, like beryl, hexagonal; and its formula is analogously to be written

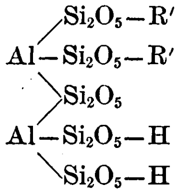


For this species the only evidence is that of its composition. Its genesis and its possible alterations are unknown.

The two closely allied zeolitic minerals, mordenite and ptilolite, are also to be classed as dimetasilicates. Their constitution, which I have fully discussed elsewhere,* is easily expressed by regarding both minerals as mixtures of the two molecules



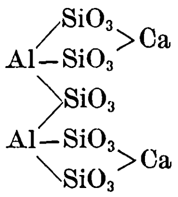
$+6H_2O$ and



$+6H_2O$

in which $R' = Na$ or K. In one occurrence of ptilolite the water is lower than is required by these formulæ, and it seems probable that a trihydrate may exist.

The metasilicate zeolite, laubanite, is the precise equivalent of ptilolite and mordenite, and is easily interpreted thus:



$+6H_2O$

Pilinite, a similar mineral, seems to be $Al_2(SiO_3)_5Ca_2.H_2O$, a monohydrate corresponding to the hexhydrated laubanite. Unlike laubanite, pilinite is undecomposed by hydrochloric acid; but physically all four of the species here grouped together resemble one another very closely.

The rare mineral hyalotekite, which contains boron, agrees very closely with the empirical formula $R''_4BFSi_6O_{17}$, if we regard the water

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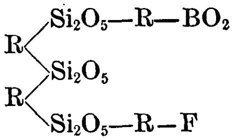
* Am. Jour. Sci., August, 1892.

in it as hydroxyl replacing fluorine. This can be interpreted either as a dimetasilicate or as a trisilicate, with the following alternative formulæ:



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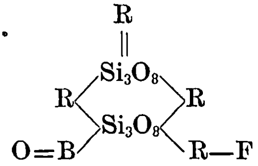


Its association with feldspar and schefferite rather favors the trisilicate formula, but the two are empirically identical. If we reduce Lindström's analysis to 100 per cent, after calculating the water (ignition) into its equivalent of fluorine, rejecting as impurities the traces of Al_2O_3 and Fe_2O_3, and consolidating like bases, we get the following comparison with theory:

	Found.	Reduced.	Calculated.
SiO_2	39.47	38.60	38.10
B_2O_3	3.73	3.63	3.71
PbO	25.11	25.71	26.22
CuO	.09		
MnO	.29		
GlO	.75		
Na_2O	.17		
CaO	7.82	9.43	9.22
BaO	20.08	21.32	21.59
MgO	.09		
K_2O	.89		
Al_2O_3	.18	....	....
Fe_2O_3	.06	....	....
F	.99		
Cl	.06	2.26	2.01
Ign	.59		
	100.37	100.95	100.85
Less O	....	.95	.85
		100.00	100.00

In computing, R'' has been regarded as Ca:Ba:Pb::7:6:5—that is, hyalotekite is a mixture of isomorphous calcium, barium, and lead salts in the indicated ratio. The agreement between analysis and theory is as close as could be reasonably expected.

There still remain a few natural silicates which are definitely recognized as species, but which do not fall distinctly into any one of the chapters of this work. Their constitution is obscure, and I shall not attempt to discuss them. Still, they may properly be recorded at this point for the sake of completeness.

Cuspidine.—A fluosilicate of calcium, supposed to be orthosilicate in structure. It may be allied to chondrodite, but it has not yet been completely analyzed.

Långbanite.—A silicate of manganese and iron containing antimony. Allied on crystallographic grounds to the oxides hematite and ilmenite.

Uranophane.—Composition represented by the empirical formula $CaU_2Si_2O_{11}.6H_2O$.

Thaumasite.—$CaSiO_3,CaSO_4,CaCO_3,15H_2O$. To the molecular constitution of this extraordinary substance there is as yet no tangible clew. A structural formula can be assigned to it, but would be meaningless.

Neotocite.—Hydrous silicates of manganese and iron, of variable composition. Several distinct compounds are probably covered by this name.

A multitude of other silicates have been described as species, but without, as yet, securing full recognition. Some of these are doubtless mixtures, or impure varieties of well known minerals; while others may be ultimately established as good and definite compounds. A discussion of the records, without experimental investigation of the various minerals, would have very uncertain value. I therefore omit these doubtful species from consideration.

CHAPTER VIII.

SUMMARY.

The formulæ developed in the body of this memoir are so varied and so interlinked, one with another, that a summary of them in concise form seems to be desirable. I accordingly append such a summary, with occasional notes intended to make the subject, if possible, more clear.

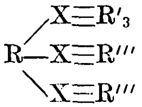
1. *Ortho- and trisilicates of triad bases.*

A. Normal salts.

Xenolite	$Al_4(SiO_4)_3$(?)
Samoite	$Al_4(SiO_4)_3.10H_2O$(?)
Cimolite	$Al_4(Si_3O_8)_3.6H_2O$(?)
Anthosiderite	$Fe_4(Si_3O_8)_3.2H_2O$(?)
Pseudobrookite	$Fe_4(TiO_4)_3$
Eulytite	$Bi_4(SiO_4)_3$
Agricolite	

Of these species the last three are definitely established, but the others are more or less uncertain.

B. First substitution series.

Type

$$R\begin{cases} X\equiv R'_3 \\ X\equiv R''' \\ X\equiv R''' \end{cases}$$

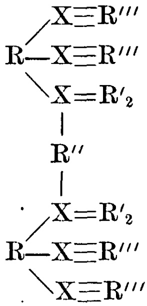
Eucryptite	$Al_3(SiO_4)_3Li_3$
Nephelite	$Al_3(SiO_4)_3Na_3$
Kaliophilite	$Al_3(SiO_4)_3K_3$
Kryptotile	$Al_3(SiO_4)_3H_3$(?)
Albite	$Al_3(Si_3O_8)_3Na_3$
Orthoclase	$Al_3(Si_3O_8)_3K_3$
Paragonite	$Al_3(SiO_4)_3NaH_2$
Muscovite	$Al_3(SiO_4)_3KH_2$
Andalusite	$Al_3(SiO_4)_3(AlO)_3$
Sillimanite	
Topaz	$Al_3(SiO_4)_3(AlF_2)_3$
Kornerupine*	$Al_3(SiO_4)_3(AlO_2Mg)_3$
Rectorite	$Al_3(SiO_4)_3H_3.2H_2O$(?)
Hydronephelite	$Al_3(SiO_4)_3Na_2H.3H_2O$

---

*Doubtful. Compare with formulæ given for pyroxenes and amphiboles.

Offretite	$\left[\begin{array}{l} 2Al_3(Si_3O_8)_3K_2H.8H_2O \\ 1Al_3(SiO_4)_3CaH.8H_2O \end{array}\right]$
Gmelinite Soda chabazite	$Al_3(SiO_4)(Si_3O_8)_2Na_3.9H_2O$

Double type

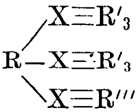


Anorthite	$Al_6(SiO_4)_6Ca_3$
Meionite	$Al_6(SiO_4)_6Ca_2.(CaOCa)$
Thomsonite	$Al_6(SiO_4)_6Ca_3.7H_2O$
Gismondite	$Al_6(SiO_4)_6Ca_3.12H_2O$
Phillipsite	$Al_6(SiO_4)_3(Si_3O_8)_3Ca_2K_2.14H_2O$
Levynite	$Al_6X_6Ca_3.15H_2O$
Heulandite Epistilbite	$Al_6(Si_3O_8)_6Ca_3.16H_2O$
Stilbite	$Al_6(Si_3O_8)_6Ca_3.18H_2O$
Chabazite	$Al_6(SiO_4)_3(Si_3O_8)_3Ca_3.18H_2O$

Also the barium feldspars, and the barium-strontium zeolites harmotome and brewsterite. X represents the tetrad groups SiO_4 and Si_3O_8 indiscriminately.

C. Second substitution series.

Type



Natrolite	$Al_2(SiO_4)_3Na_2H_4$
Dumortierite	$Al_2(SiO_4)_3(AlO)_6$
Zunyite	$Al_2(SiO_4)_3R'_6$
Chloropal	$Fe_2(SiO_4)_3H_6$
Cancrinite	$Al_2(SiO_4)_3Na_4H(AlCO_3)$
Microsommite	$Al_2(SiO_4)_3CaR'_4$
Prehnite	$Al_2(SiO_4)_3Ca_2H_2$
Arctolite	$Al_2(SiO_4)_3CaMgH_2$
Biotite	$Al_2(SiO_4)_3Mg_2KH$
Siderophyllite	$Al_2(SiO_4)_3Fe_2KH$
Biotite-vermiculite	$Al_2(SiO_4)_3Mg_2H_2.3H_2O$
Biotite-chlorite	$Al_2(SiO_4)_3(MgOH)_4H_2$
Scolecite	$Al_2(SiO_4)_3CaH_4.H_2O$
Sodalite	$Al_2(SiO_4)_3Na_4(AlCl)$

Haüynite	$Al_2(SiO_4)_3Na_2Ca(AlSO_4Na)$
Nosite	$Al_2(SiO_4)_3Na_4(AlSO_4Na)$
Lazurite	$Al_2(SiO_4)_3Na_4(AlS_3Na)$
Garnet group	$R'''_2(SiO_4)_3R''_3$
Epidote group	$R'''_2(SiO_4)_3R''_2(R'''OH)$
Leucite	$Al_2(SiO_4)(Si_3O_8)_2K_4(AlSiO_4Al)$
Analcite	Similar to leucite.
Pollucite	Similar to leucite.
Marialite	$Al_2(Si_3O_8)_3Na_4(AlCl)$

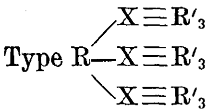
Double type, $R'''_4X_6R''_6$.

Mesolite	$Al_4(SiO_4)_6CaNa_2H_8.H_2O$
Foresite	$Al_4(SiO_4)_6CaH_{10}.H_2O$

Conjugate type, $R'''_2X_5R''_7$.

Vesuvianite	$Al_2(SiO_4)_5R''_6(AlOH)$
Gehlenite	$Al_2(SiO_4)_5R''_6(AlO_2Mg)_2$
Melilite	$Al_2(SiO_4)_4(SiO_3)R''$

D. Third substitution series.



$$\text{Type } R\begin{cases} X\equiv R'_3 \\ X\equiv R'_3 \\ X\equiv R'_3 \end{cases}$$

Phlogopite	$Al(SiO_4)_3Mg_3KH_2$
Phlogopite-vermiculite	$Al(SiO_4)_3Mg_3H_3.3H_2O$
Phlogopite-chlorite	$Al(SiO_4)_3(MgOH)_6H_3$
Manganophyll	$(AlFe)(SiO_4)_3(MnMg)_3KH_2$
Ganophyllite	$AlX_3Mn_3R'_3.2H_2O$
Stilpnomelane	$Al(Si_3O_8)_3(FeOH)_6H_3$
Faujasite	$Al(Si_3O_8)_3R'_5R''_2.15H_2O$
Cerite	$Ce(SiO_4)_3(CeO)_3H_6$

Double type, $R'''_2X_6R'_{18}$.

Staurolite	$Al_2(SiO_4)_6Fe''_3(AlO)_{12}$
Harstigite	$Al_2(SiO_4)_6Ca_5Mn_2H_4$

E. Basic salts.

Westanite	$AlOH(SiO_4)_2Al_2$
Kaolin	$AlOH(SiO_4)_2AlH_3$
Montmorillonite	$AlOH(SiO_4)_2H_6$
Newtonite	$Al(OH)_2(SiO_4)H_3$
Margarite	$AlOH(SiO_4)_2CaH(AlO)_3$
Strigovite	$AlOH(SiO_4)_2AlH(FeOH)_2$
Aphrosiderite	$AlOH(SiO_4)_2Al(FeOH)_3$
Lepidolite type	$AlF_2(Si_3O_8)R'_3$
Cookeite type	$Al(OH)_2(SiO_4)R'_3$
Clintonite type	$AlO_2Mg(SiO_4)R'_3$
Clintonite-vermiculite	$AlO_2Mg(SiO_4)R'_3.3H_2O$
Chloritoid	$AlO_2Fe(SiO_4)H(AlOH)$
Ottrelite	$AlO_2Fe(Si_3O_8)H(AlOH)$

With many members of the chlorite group, such as prochlorite, leuchtenbergite, etc.

F. Borosilicates, etc.

Tourmaline, A	$Al_8(SiO_4)_6(BO_3)(BO_2)_2R'_5$
Tourmaline, B	$Al_7(SiO_4)_6(BO_3)(BO_2)_2Mg_2R'_4$
Tourmaline, C	$Al_6(SiO_4)_6(BO_3)(BO_2)_2Mg_3R'_5$
Tourmaline, D	$Al_5(SiO_4)_6(BO_3)(BO_2)_2Mg_4R'_6$
Axinite	$Al(SiO_4)(Si_3O_8)(BO_3)Ca_3(AlOH)$

And the species cappelinite, karyocerite, melanocerite, and tritomite.

G. Complex silicates.

Spodumene	$Al_6(Si_3O_8)_3(SiO_4)_3Li_6$
Jadeite	$Al_6(Si_3O_8)_3(SiO_4)_3Na_6$
Acmite	$Fe_6(Si_3O_8)_3(SiO_4)_3Na_6$
And in babingtonite the molecule	$Fe'''_6(Si_3O_8)_3(SiO_4)_3Fe''_3$

To this group of triad silicates, the largest and most important group of all, other species belong which I have not clearly interpreted. Such species are halloysite, allophane, collyrite, schrötterite, sapphirin, ardennite, carpholite, cenosite, sarcolite, etc. The formulæ of the tabulated species must all be construed in a general way—that is, with common replacements of aluminum by ferric iron, magnesium by ferrous iron, and so on. In every case details are suppressed, and these are to be found in the text. The same rule applies to the species in the groups which follow:

2. *Ortho- and trisilicates of dyad bases.*

Forsterite	$n.Mg_2SiO_4$
Fayalite	$n.Fe_2SiO_4$
Tephroite	$n.Mn_2SiO_4$
Willemite	$n.Zn_2SiO_4$
Phenakite	$n.Gl_2SiO_4$
Monticellite	$CaMgSiO_4$
Knebelite	$MnFeSiO_4$
Hyalosiderite	$Mg_4Fe_2(SiO_4)_3$
Igelströmite	$Fe_4Mn_2(SiO_4)_3$
Trimerite	$Gl_3Mn_2Ca(SiO_4)_3$
Chondrodite	$Mg_3(SiO_4)_2(MgF)_2$
Humite	$Mg_5(SiO_4)_3(MgF)_2$
Clinohumite	$Mg_7(SiO_4)_4(MgF)_2$
Helvite Danalite	$Gl_3R''_2(SiO_4)_3(R—S—R)$
Bertrandite	$Gl_3(SiO_4)_2H(GlOH)$
Calamine	$Zn_2(SiO_4)_2H_2(ZnOH)_2$
Lievrite	$Fe_2Ca(SiO_4)_2(AlOH)$
Datolite	$Ca_2(SiO_4)_2H_2(BO)_2$
Homilite	$Ca_2Fe(SiO_4)_2(BO)_2$

Euclase	$Gl_2(SiO_4)_2H_2(AlO)_2$
Gadolinite	$Gl_2Fe(SiO_4)_2(YO)_2$
Friedelite	$R''_4(SiO_4)_4H_7(R''Cl)$
Pyrosmalite	
Dioptase	$n.CuH_2SiO_4$
Karyopilite	$Mn_3(SiO_4)_3H_5(MnOH)$
Villarsite	$Mg_3(SiO_4)_2H(MgOH)$
Serpentine	$Mg_2(SiO_4)_2H_3(MgOH)$
Picrosmine	$Mg_2(SiO_3)(SiO_4)H_2$
Aphrodite	$Mg_2(SiO_4)_2H_4$
Kerolite	$Mg(SiO_4)_2H_5(MgOH)$
Deweylite	$Mg_2(SiO_4)_3H_6(MgOH)_2.2H_2O$
Eudidymite	$HNaGlSi_3O_8$
Epididymite	

3. *Ortho- and trisilicates of tetrad bases.*

Zircon	$n.ZrSiO_4$
Thorite	$n.ThSiO_4(?)$
Auerbachite	$Zr_4(SiO_4)_3(Si_3O_8)$
Malacone	$Zr_3(SiO_4)_3(OH)H$
Eudialyte	$ZrX_3Cl.Ca_3Na_3$
Elpidite	$Zr(Si_3O_8)_2(OH)_2Na_2H_4$
Catapleiite	$Zr(Si_3O_8)(OH)_3Na_3$
Wöhlerite	$Zr(SiO_4)_4R''_5Na_2$
Yttrialite	$Th(Si_3O_8)_4Fe''_2(YO)_8$
Astrophyllite	$Ti(SiO_4)_4Fe''_4R'_4$
Johnstrupite	$Ti(SiO_4)_4Ca_4(CeF_2)Na_2H$
Sphene	$Ca(SiO_4)(TiO)$

With rosenbuschite, låvenite, and hiörtdahlite, allied to wöhlerite; rinkite and mosandrite, allied to johnstrupite; and keilhauite and tscheffkinite, allied to sphene.

4. *The diorthosilicates.*

Barysilite	$Pb_3(Si_2O_7)$
Melanotekite	$Pb_2(Si_2O_7)(Fe'''O)_2$
Kentrolite	$Pb_2(Si_2O_7)(Mn'''O)_2$
Ganomalite	$(PbCa)_3(Si_2O_7)$
Okenite	$Ca_3(Si_2O_7)_3H_{12}$
Gyrolite	$Ca_4(Si_2O_7)_3H_{10}$
Apophyllite	$Ca_2(Si_2O_7)_3H_{12}(CaOH)_2$
Plombierite	$Ca_6(Si_2O_7)_3H_6.\ 9H_2O$
Inesite	$R_6(Si_2O_7)_3H_6.\ 2H_2O$
Bementite	$Mn_6(Si_2O_7)_3H_6$
Spadaite	$Mg_5(Si_2O_7)_3H_8$
Saponite	$(MgOH)_2H_4(Si_2O_7).(?)$
Iolite	$Al_6(Si_2O_7)_5Mg_4(AlOH)_2$

Barylite	$Al_4(Si_2O_7)_3Ba_3$
Sphenoclase	$Al_2(Si_2O_7)_3Ca_6$
Rowlandite	$Fe''(Si_2O_7)_2Y_2(YF)_2$

5. *The metasilicates.*

Laubanite	$Al_2(SiO_3)_5Ca_2.6H_2O$
Talc*	$Mg_3(SiO_3)_4H_2(?)$
Pyrophyllite	$Al(SiO_3)_2H$
Kyanite	$AlO(SiO_3)(AlO)$
Beryl	$Al_2Gl_3(SiO_3)_6$
Leucophanite	$Ca(SiO_3)_2Na(GlF)$
Meliphanite	$Ca_2(SiO_3)_2(SiO_4)GlNa(GlF)$
Wollastonite	$Ca_3(SiO_3)_3$
Pectolite	$Ca_2(SiO_3)_3NaH$
Danburite	$Ca(SiO_3)_2(BO)_2$
Chrysocolla	$CuSiO_3.2H_2O(?)$
Neptunite	$Ti(SiO_3)_4R''R'_2$

Leucite, pollucite, analcite, eudialyte, etc., have been treated as pseudometasilicates. To these species must be added the pyroxenes and the amphiboles, with the following general formulæ:

Pyroxene	$R''_8(SiO_4)_2(Si_3O_8)_2$
Amphibole	$R''_4(SiO_4)(Si_3O_8)$

Glaucophane and crocidolite may be written

$$R''_2(Si_3O_8)_2(R'''O)_2Na_2$$

or all trisilicate, and crossite, waldheimite, etc., seem to be similar. The evidence for these expressions appears in the text.

6. *The dimetasilicates.*

Petalite	$Al(Si_2O_5)_2Li$
Milarite	$Al_2(Si_2O_5)_6HKCa_2$
Mordenite	$Al_2(Si_2O_5)_5CaH_2.6H_2O$
Ptilolite	$Al_2(Si_2O_5)_5R'_2H_2.6H_2O$
Hyalotekite	$R''_2(SiO_5)_3(RF)(RBO_2)$

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* Possibly a pseudometasilicate.

INDEX TO SPECIES.