Isle Royale. Prehnite has been reported from several places along the north shore of Lake Superior in Minnesota, and Grout[8] has given an analysis of the mineral from Pine County.

The writer is indebted to the Minnesota School of Mines Experiment Station for analyses, and to Dr. F. F. Grout for much assistance.

[8] Grout, F. F., Contributions to the petrography of the Keweenawan: *Jour. Geol.*, **18**, 654 (1910).

A NEW THEORY OF THE COMPOSITION OF THE ZEOLITES*

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INTRODUCTION

The great similarities in composition between the zeolites and the feldspars have been pointed out many times, but in a summary of previous studies Dana[1] expressed correctly the conclusion reached by all investigators of the subject, as follows: "Unlike the feldspars (in zeolites) . . . calcium and sodium seem to replace one another and an increase in alkali does not go with an increase in silica." The formulas given by Dana and all other authorities known to the writer show that in zeolites alkalies are supposed to replace lime under the control of valence, that is, two atoms of Na or of K are supposed to take the place of one atom of Ca.

It may be worth while to be more specific in regard to the present situation as to the composition of the zeolites. Dana gives the following formulas as representing the composition of the zeolites named:

Thomsonite	$(Na_2, Ca) Al_2Si_2O_8.2.5 H_2O$
Chabazite	$(Ca, Na_2) Al_2Si_4O_{12}.6 H_2O$
Gmelinite	$(Na_2, Ca) Al_2Si_4O_{12}.6 H_2O$
Wellsite	$(Ba, Ca, K_2) Al_2Si_3O_{10} .3 H_2O$
Phillipsite	$(K_2, Ca) Al_2Si_4O_{12}.4.5 H_2O$
Harmotome	$(K_2, Ba) Al_2Si_5O_{14}.5 H_2O$
Stilbite	$(Na_2, Ca) Al_2Si_6O_{16}.6 H_2O$
Mordenite	$3(Ca, Na_2, K_2) Al_2Si_{10}O_{24}.20 H_2O$
Ptilolite	$(Ca, K_2, Na_2) Al_2Si_{10}O_{24}.5 H_2O$

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* Presented at the annual meeting of The Mineralogical Society of America, Ithaca, New York, December 31, 1924.

[1] System of Mineralogy, 6th Ed., p. 570, (**1892**).

According to Dana the other common zeolites have invariant composition. The same or very similar formulas are given by Groth, and all other authorities, so far as known to the writer. That is, according to standard authorities, any zeolite which is not invariant is supposed to show a variation in the Ca : Na (or K) ratio, and no other corresponding variation.[2] Furthermore, in this variation two atoms of Na or K are supposed to replace one atom of Ca.

Zeolites are commonly regarded as more or less exactly hydrous equivalents of feldspars. In plagioclase and other feldspars it is well known that one atom of Ca is replaced, not by two atoms of Na (or K), but by one atom of alkali with a simultaneous replacement of one atom of Al by one atom of Si. Therefore it may be worth while to study the best analyses of the various zeolites to learn whether they resemble the feldspars in this respect, rather than showing variations in composition as represented by the formulas universally used for them. Such a study is a long and difficult matter except by means of graphs. By plotting the best analyses of each kind of zeolite on a square[3] so arranged that the horizontal coordinate expresses variation in the Ca : Na ratio and the vertical coordinate expresses variation in the Al : Si ratio, the distribution of the points, each of which represents an analysis, shows at a glance whether the composition varies as in the feldspars, or as in the formulas now accepted. It is evident that the points representing the variations in composition in one kind of zeolite must lie along a horizontal line in such a diagram if the usual formulas are correct. Also, if the variation in the Ca : Na ratio is accompanied by a simultaneous variation in the Al : Si ratio the points representing the variations in composition in one kind of zeolite must lie along a line taking a diagonal course on the square.

Such diagrams are not difficult to prepare nor entirely novel, but, since they do not seem to be familiar to mineralogists, it seems necessary to explain the method of preparation.

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[2] Groth (Mineral. Tabellen, **1921**) and Tschermak (*Sitz. Akad. Wiss. Wien*, **CXXVI** (1917), p. 541 and **CXXVII**, (1918), p. 177) recognize variations in the Al:Si ratio in some zeolites, but fail to show any relation between such variations and those in the Ca:Na ratio. Gordon (*Proc. Phila. Acad. Sci.*, **LXXVI**, (1924), p. 103) has found the approximate relationship in these ratios in thomsonite, but did not discover the atom-for-atom type of replacement, recognizing instead a replacement of Ca by 2Na, and of 2Si by 3Si

[3] Full details regarding the preparation of the graphs are given later.

Starting with any molecule, for example $Ca_3Al_6Si_{10}O_{32}$.Aq. at one corner of a square, as at A in the figure, let us assume that this molecule may change gradually to the corresponding sodium salt, $Na_6Al_6Si_{10}O_{32}$.Aq. and let us represent this entire change by a horizontal line as AB. By dividing this line into ten equal parts, each division point represents these two molecules mixed in simple decimal ratios.

Starting again with the molecule $Ca_3Al_6Si_{10}O_{32}$.Aq. at A let us assume another kind of variation, in this case variation in the Al : Si ratio. In the first molecule assumed this ratio is 6 : 10. Let us assume in a second molecule that it changes to 10:6. If there were no other change this would lead to the molecule $Ca_3Al_{10}Si_6O_{30}$.Aq. However, all authorities are agreed that in zeolites the $Ca+Na_2:Al_2$ ratio is always 1:1. Therefore the molecule should be written: $Ca_5Al_{10}Si_6O_{32}$.Aq. This molecule may be placed at C, and the line AC made equal to AB, and divided in the same way, so that the divisions represent simple decimal mixtures of the two molecules A and C.

Now the molecule $Ca_5Al_{10}Si_6O_{32}$.Aq. at C may obviously be assumed to vary to a corresponding sodium molecule just as was assumed for the molecule at A. This variation is properly represented along the line CD, which is divided in ten parts like the other lines. Also, the molecule $Na_6Al_6Si_{10}O_{32}$.Aq. may be assumed to vary in its Al:Si ratio without variation in its Na:Al ratio, just as the molecule at A was assumed to do, and this variation may be represented along the line BD.

Since the zeolites do not form a single isomorphous system like the feldspars, but include several disconnected series, it is necessary to discuss them separately; for convenience they will be treated in the following order:

1. The composition of thomsonite.
2. The composition of natrolite, mesolite, scolecite, gismondite and laumontite.
3. The composition of chabazite and related zeolites.
4. The composition of phillipsite and related zeolites.
5. The composition of heulandite and related zeolites.
6. Comparative study and summary.

1. The Composition of Thomsonite

The theory that variation in composition of crystals is accomplished by change of one atom for another of similar size has been very useful in attacking the difficult problems involved in reaching a rational explanation of the constitution of the pyroxene, amphibole, mica and other important groups of silicate minerals.

The zeolites form a complex group of hydrous aluminum silicates which are truly extraordinary in many ways. For example, the water in them is unlike the water in most other minerals since it can be expelled without destroying (or materially changing) the crystal which contained it; the water goes off through a considerable temperature range rather than at any fixed temperature; any other fluid will enter the crystal in large amounts in the absence of water, but does not remain if water becomes available to the crystal. Furthermore, in many zeolites, a base, such as sodium, can be artificially replaced by another base, such as potassium or calcium.

Since the zeolites are so exceptional, it is quite possible that a theory which applies to other silicates will not apply to them. For example, the theory of similar-sized atom-for-atom control of isomorphous systems may not hold in the zeolite group. In fact, many analyses made by Lemberg,[4] Thugutt,[5] Gans,[6] Zoch[7] and others indicate that in the artificial exchange of bases in zeolites valence controls the process, so that, for example, Ca is replaced, not by Na, but by 2Na. It remains to be determined whether a similar valence-control exists in the natural formation of zeolite crystals.

Wherry[8] has recently discussed the composition of thomsonite with special reference to this problem, and reached the conclusion that "thomsonite" is not one mineral, but two, each a double salt of fixed formula. That is, according to Wherry, thomsonite does not illustrate the usual condition of isomorphous relationships shown in so many silicates, but should be assigned to one or the other of two definite formulas. This attitude reminds the writer of the attempt of Fouqué to refer the plagioclase feldspars to a few definite formulas rather than to a continuous isomorphous series. The view of Wherry is all the more remarkable since he himself states[9] that "the lime varies inversely as the soda" in

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[4] *Zeit. Dtsch. Geol. Gesell.*, **XXVII,** (1887) p. 973; **XXXIX,** (1888) p. 561; **XL,** (1888) p. 651.

[5] *N. Jahrb. Min. B. B.*, **IX,** (1894) p. 555.

[6] *Jahrb. preuss. geol. Landesan.*, **XXVII**, (1906) p. 63.

[7] *Chemie der Erde*, **I,** (1915) p. 219.

[8] *Am. Mineral.*, **8,** (1923) p. 121.

[9] *Loc. cit.*, p. 122, footnote.

thomsonite and his diagram shows clearly a continuous gradation from one of his types to the other.

Still more recently Gordon[10] has discussed the composition of thomsonite and reached the conclusion that there is a continuous variation in composition from $CaO.Al_2O_3.2SiO_2.3H_2O$ to mix crystals containing up to 40 percent of $Na_2O.Al_2O_3.3SiO_2.H_2O$. Gordon argues that Wherry must be wrong in adopting the notion of fixed composition since Lemberg has shown that the composition of thomsonite can be changed artificially. The writer would call attention to the fact that Lemberg's analyses show that Ca is replaced by 2Na without a simultaneous increase in SiO_2, and therefore the artificial change is not a confirmation of Gordon's theory.

The evidence presented by Gordon seems very convincing, but the writer is unwilling to accept it as conclusive because it involves the necessity of believing that in the crystal space-lattice which may be assumed to be built first of $CaO.Al_2O_3.2SiO_2.3H_2O$, half the Ca atoms may be replaced by twice as many Na atoms and simultaneously half the Si atoms may be replaced by other Si atoms 50 percent more in number, that is, Ca may be replaced by 2Na and simultaneously 2Si may be replaced by 3Si. In anhydrous silicates no isomorphous series of such a kind is known to the writer. Therefore it seems desirable to study the problem further.

Doelter[11] has listed 67 analyses of thomsonite, but some of these are clearly inaccurate, and a few are averages or duplicates. It is obviously of great importance to use only the very best analyses made on carefully selected material as a basis for comparative studies aimed at the determination of the constituent molecules. Therefore only the modern analyses, made since 1880, will be used. Next, analyses of later date which are clearly abnormal or inaccurate or on impure material must be excluded, as illustrated by some which include more than trifling amounts of CO_2, or MgO, or Fe_2O_3, or have unsatisfactory totals. After these omissions, the list of preferred analyses includes the following: Doelter's Nos. 6, 9, 11, 18, 22, 23, 27, 28, 36-44, 48, 50-54, 56, 57, 61, 66, 67.

Furthermore, the following analyses belong in the same group:

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[10] *Proc. Phila. Acad. Sci.*, **LXXVI,** (1924) p. 103.

[11] Hdb. Mineral Chem. **II,** 3, (1921) p. 16.

68. Thomsonite, Quirang, Scotland, F. Heddle: *Mineral. Mag.*, **V,** (1882) p. 119.

69. Thomsonite, Borschom, Transcaucasia. K. D. Glinka: *Tr. Soc. Nat. St. Petersburg*, **XXIV,** (1906) p. 1; *Zeit. Kryst.*, **XLVI,** (1909) p. 287.

70. Thomsonite, Amethyst Cove, Nova Scotia. T. L. Walker. *U. Toronto Studies, Geol. Ser.* **14,** (1922) p. 72.

71. Thomsonite, Port George, Nova Scotia. T. L. Walker. *loc. cit.*

72. Thomsonite, Franklin, N. J. S. G. Gordon: *Proc. Acad. Nat. Sci. Phila.*, **LXXV,** (1923) p. 273, and *Am. Mineral.*, **8,** (1923) p. 125.

73. "Harringtonite," Antrim, Ireland. A. and R. Brauns: *Cent. Min.*, **(1924)** p. 545. Analysis I.

74. "Harringtonite," Antrim, Ireland, A. and R. Brauns: *Cent., Min.*, **(1924)** p. 545. Analysis II.

In thomsonite, as in other zeolites, the molecular ratio of Al_2O_3 to $CaO+Na_2O$ is very nearly unity in most cases; the largest variations from this ratio in the preceding list of analyses are found in the analyses of Chauvenet (No. 41-ratio = .91), Heddle (68-.91), Todd (70-.93), Heddle (11-.94), Chauvenet (42-.94), Todd (71-.94), Manasse (22-1.06), Heddle (57-1.07), Görgey (43-1.10), Manasse (23-1.12), Luedecke (6-1.14), Prior (54-1.15) Lacroix (48-1.16), and Whitfield (72-1.16). If some variation in this ratio actually exists the writer has found no explanation for it; the evidence at present is not conclusive, but it seems reasonable to assume that the ratio is constant and unity. Since this assumption underlies all the subsequent discussion it may be worth while to add that all writers on the subject of the constitution of the zeolites make this assumption, so far as known to the writer.

Contrary to the view of Wherry, the writer finds that the analyses show a considerable range in the Al_2O_3:SiO_2 ratio, as well as in the Na_2O:CaO ratio. The former varies from about 1:2 to about 1:2.5, and the latter varies from about 1:2 to about 1:4 (Whitfield's ratio is 1:5).

If sodium be omitted for the moment the constant unit Al_2O_3: $CaO+Na_2O$ ratio and the first of the Al_2O_3:SiO_2 ratios give the formula $CaAl_2Si_2O_8$; if lime be omitted, this becomes $Na_2Al_2Si_2O_8$. A careful study of the best analyses of thomsonite shows that alumina decreases as silica increases. Therefore it is reasonable to test the idea that in this zeolite, as in plagioclase, one atom of aluminum may take the place of one atom of silicon, or *vice versa*. In order to do so it is desirable to use molecules both more siliceous and less siliceous than the standard thomsonite formula already derived. To avoid too great differences the series may be written thus:

	Lime	Soda
More siliceous	$Ca_3Al_6Si_{10}O_{32}.Aq.$	$Na_6Al_6Si_{10}O_{32}.Aq.$
Standard	$Ca_4Al_8Si_8O_{32}.Aq.$	$Na_8Al_8Si_8O_{32}.Aq.$
Less siliceous	$Ca_5Al_{10}Si_6O_{32}.Aq.$	$Na_{10}Al_{10}Si_6O_{32}.Aq.$

By taking these more siliceous and less siliceous lime and soda molecules as the corners of a square, as in Fig. 1, various points in the square represent varying proportions of the four molecules which may be read directly from the diagram. For example, analysis 66 contains 26% of soda molecules (B and D) and 74% of lime molecules (A and C); it also contains 57% of the more siliceous molecules (A and B) and 43% of the less siliceous molecules (C and D); therefore it contains 74% of 57 % or 42% of $Ca_3Al_6Si_{10}O_{32}$, 26% of 57% or 15% of $Na_6Al_6Si_{10}O_{32}$, 74% of 43% or 32% of $Ca_5Al_{10}Si_6O_{32}$, and 26% of 43% or 11% of $Na_{10}Al_{10}Si_6O_{32}$. It is evident that various points in the square represent varying ratios so far as $Al_2O_3:SiO_2$ and $CaO:Na_2O$ are concerned, but a constant unit ratio between Al_2O_3 and $CaO+Na_2O$.

In order to calculate from a chemical analysis the molecular percentage of the molecules of the square which are represented by the analysis (that is in order to find the point which represents the analysis on the square) it is, of course, necessary, first, to obtain the relative number of oxide molecules by dividing each weight percentage of the analysis by the molecular weight of the given oxide.[12] It is then possible to obtain the percentage of soda molecules by dividing the Na_2O (including K_2O) by the sum of CaO (including MgO, etc.) and Na_2O molecules. Finally, to obtain the percentage of the more siliceous molecules, let

$x = Al_2O_3$ molecules in the less siliceous molecules
$y = Al_2O_3$ molecules in the more siliceous molecules.
then $x+y =$ total number of Al_2O_3 molecules in the analysis, and
$6/5x + 10/3y =$ total number of SiO_2 molecules in the analysis.

After solving for x and y, it may be noted that there are $y/3$ of the more siliceous molecules (since each contains $3Al_2O_3$) and $x/5$ of the less siliceous molecules; therefore $y/3 \div y/3 + x/5 =$ percentage of more siliceous molecules.

Since the diagram is based on the assumption that the $Al_2O_3:CaO+Na_2O$ ratio is unity, it is desirable to use, first, only those

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[12] To reduce the labor involved the writer uses the molecular weight only to the nearest whole number; it is customary to multiply by 1000 to eliminate decimals.

analyses which do not depart appreciably[13] from this condition. In this way the numbered points on Fig. 1 are found, the numbers corresponding with the list already given. Analyses which do not give a unit ratio for Al_2O_3:CaO+Na_2O cannot be calculated into the molecules of Fig. 1, without leaving discrepancies, whose magnitude varies with the departure from unit ratio. If these discrepancies are equally divided between Al_2O_3 and CaO+Na_2O points can be found; if the discrepancies are attributed wholly to Al_2O_3 other points can be found; if they are attributed wholly to CaO+Na_2O still other points can be found. A line connecting the second and third of these points for a given analysis is bisected by the first point named and represents all possible assumptions regarding elimination of the condition that the Al_2O_3:CaO+Na_2O

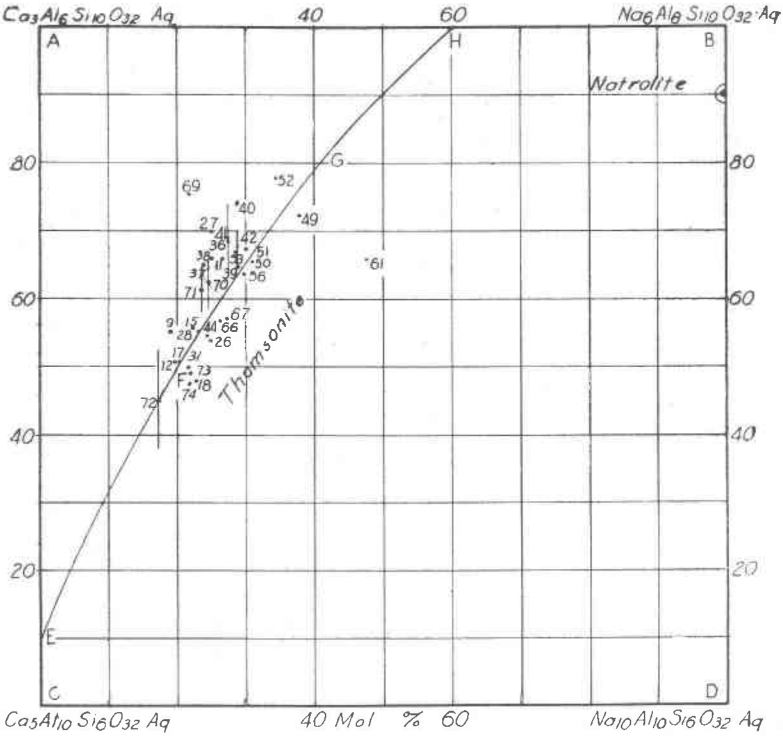

Fig. 1. The composition of thomsonite. Each dot represents an analysis.

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[13] Any small discrepancy is divided equally between Al_2O_3 and CaO+Na_2O in the actual computations.

ratio is not unity. Such lines are vertical in Fig. 1 since the $CaO:Na_2O$ ratio is not affected by the various methods of eliminating the discrepancy.

By plotting all the "superior" analyses as points and some[14] of the other modern analyses as lines; as just described, the range of variations in composition can be seen very readily, as shown in Fig. 1. The diagram shows, not two species, but a continuous series between limits which are not clearly defined. Only two analyses (61 and 69) depart rather widely from the main series. It is reasonable to disregard these as due to impurities or inaccuracies (61 is rather old and 69 was made on massive rather than crystal material) and conclude that thomsonite varies in composition essentially as expressed by a line running about NE and SW in Fig. 1, such as EFGH (the reason for the curvature of this line will be given later).

The complete formula for the point F may be written $Na_4Ca_8Al_{20}Si_{20}O_{80}$ and the complete formula for the point H is, $Na_9Ca_3Al_{15}Si_{25}O_{80}$. These formulas are very complex, but the first one is (four times) the formula deduced by Wherry for one of his types. However, the striking and most important feature about them is that they contain exactly the same number of atoms, and the replacements are just the same as in plagioclase. In fact the series can be considered to parallel part of the plagioclase series, differing only in the fact that there are in thomsonite (about) 12 (Ca+Na) atoms for each 80 oxygen atoms, while in plagioclase there are only 10 (Ca+Na) atoms for each 80 oxygen atoms.

In Fig. 1 the four components of the system do not have the same (Ca+Na):O ratio, although this ratio is the same for the points F and G. Therefore a straight line from F to H would not express simple mixtures of F and H (which have the same ratio). Such mixtures are expressed by the curved line EFGH whose position can be found by plotting a few points along its course. It is evident that the points which represent the analyses all fall near this curve. It seems clear that the isomorphous series in thomsonite may be considered to be one in which Ca is replaced not by 2Na, nor 2Si by 3Si nor by 6Si, as has been suggested,[15]

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[14] It seems quite unnecessary to calculate all of these; enough of these and of good older analyses have been calculated to make sure that they would not alter the conclusions reached.

[15] S. G. Gordon: *Proc. Phila. Acad. Sci.*, **LXXVI,** (1924) p. 103, and C. F. Rammelsberg: Min. Chem. Erg. Heft **II,** (1895) p. 389.

but that, as in plagioclase, Ca is replaced by Na with a simultaneous replacement of Al by Si.

Therefore, in thomsonite as in the anhydrous silicates, a natural isomorphous series is formed not between molecules which are unlike in number and size of atoms, but between molecules having exactly the same number of atoms of nearly the same sizes; the replacement is not 2Na for Ca and 3Si for 2Si, but, Na for Ca and Si for Al.

Accordingly, accepting the conclusions of Gordon regarding the water in thomsonite (with which this article does not deal) the mineral is an isomorphous series from about the point F whose composition is $Na_4Ca_8Al_{20}Si_{20}O_{80}.25H_2O$ nearly to the point G whose composition is $Na_7Ca_5Al_{17}Si_{23}O_{80}.20H_2O$.

(To be continued)

FOSHAGITE, A NEW SILICATE FROM CRESTMORE, CALIFORNIA[1]

ARTHUR S. EAKLE, *University of California*

The Riverside Portland Cement Company which quarried the crystalline limestone at Crestmore, has transferred most of its operations to a hill, lying further west, of white crystalline limestone containing few associated minerals, and the original quarries have been practically deserted. The old Commercial quarry on Sky Blue Hill where the wilkeite and other minerals described by the writer[2] were found has been cleaned up and is not now of special interest. Some later quarrying has been done on the north side of the hill at what is locally known as the Wet Weather quarry, and there was a large accumulation of boulders at the base of this quarry last May, when visited by the writer. Brown and yellow vesuvianite and light blue calcite, principally, formed the boulders, but other minerals occur in the vesuvianite masses which make a visit to the deposit of great interest to the mineralogist. The solutions connected with the intrusive pegmatitic and monzonitic dikes in the limestone mass were magmatic siliceous waters which were in all probability responsible for the conversion of the

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[1] Presented at the annual meeting of The Mineralogical Society of America, Ithaca, New York, December 31, 1924.

[2] Minerals associated with the crystalline limestone at Crestmore, Riverside County, California. Arthur S. Eakle. *Bull. Dept. Geol. Univ. Calif.*, **10**, 327-360 (1917).