the chemical and optical properties of members of this mineral series.

A NEW THEORY OF THE COMPOSITION OF THE ZEOLITES. PART III

(Continued from page 117)

A. N. WINCHELL, *University of Wisconsin*

3. THE COMPOSITION OF CHABAZITE AND RELATED ZEOLITES

The composition of chabazite is usually given as (Ca,Na_2) $Al_2Si_4O_{12}.6H_2O$, which means that two atoms of sodium may replace one atom of calcium in the crystal space lattice. Since such a change, although apparently possible in artificial alterations of zeolites, and especially of the artificial zeolite known as permutite, is contrary to the condition in all anhydrous silicates, it seems worth while to test the matter somewhat carefully, particularly since it has been found that a different explanation can be applied to thomsonite.[1]

After a careful study of all available analyses, including the ninety-nine listed by Doelter[2] and a few others,[3] it seemed necessary to reduce the number in order to concentrate attention on the best or "superior" analyses. In chabazite and in many other zeolites the ratio of Al_2O_3 to $CaO+Na_2O$ is more constant than any other ratio which can be derived from the analyses, and varies very little from 1:1. By rejecting all the old analyses, and all those not made on selected crystal material and also five analyses in which this ratio was not satisfactory, the thirteen "best" analyses were selected.

The results of plotting these analyses on a square, on which the variables are the Al_2O_3-SiO_2 ratio and the CaO-Na_2O ratio, as described in the discussion of natrolite, are shown in Fig. 3. The distribution of these points seems to the writer to indicate the existence of an isomorphous series along the line ABC which is curved through those points which represent mix-crystals having the same number of $Ca+Na$ atoms, and of $Al+Si$ atoms for a

[1] A. N. Winchell: *Am. Min.*, **X**, (1925).

[2] Hdb. Mineralchemie, **II**, 3, 1921, pp. 73-128.

[3] G. T. Prior: *Mineral. Mag.*, **XVII**, 1916, p. 274; and G. Stoklossa: *N. Jahrb. Min.*, *Beil. Bd.* **XLII**, 1919, p. 39.

constant number of O atoms.   The line represents a series from
$Ca_7Al_{14}Si_{26}O_{80}$ at A to $Na_4Ca_3Al_{10}Si_{30}O_{80}$ at C.
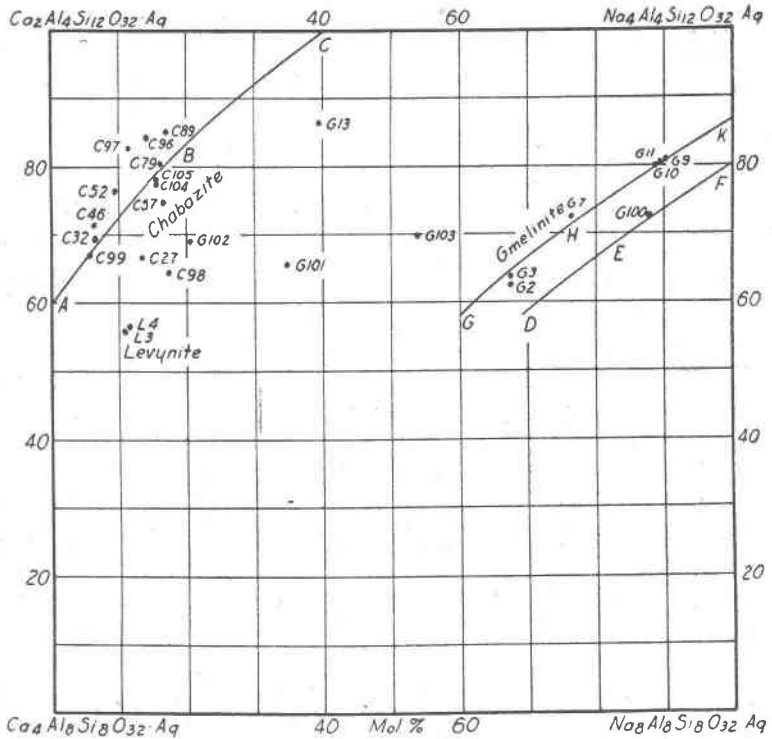

FIG. 3.   The Composition of Chabazite and Related Zeolites

Smith, Ashcroft and Prior[4] have recently argued that gmelinite
is merely a soda-rich chabazite in spite of the difference in cleavage
and in crystal habit.   Therefore the composition of gmelinite
should be compared with that of chabazite.   Unfortunately there
are very few modern analyses of gmelinite; in order to obtain
enough analyses to show the range in composition it is necessary to
use some of the older ones, of course selecting the best of these.
In this way eleven analyses were selected which are plotted on Fig.
3. The correct interpretation of the meaning of the distribution of
these points is not obvious, but the writer believes gmelinité is

4 *Mineral. Mag.*, **XVI**, 1916, p. 274.

essentially a series varying in composition along the line DEF,[5] which is curved through those points which represent mix-crystals having the same number of $Na + Ca$ atoms, and of $Al + Si$ atoms, for a constant number of O atoms. The line represents a series from $Na_4Ca_2Al_7Si_{13}O_{40}$ at D to $Na_6Al_6Si_{14}O_{40}$ at F. If this view is correct there is a distinct chemical difference between chabazite and gmelinite, since the former contains 7 $Ca + Na$ atoms for each 80 atoms of oxygen while the latter contains 12 $Ca + Na$ atoms for the same number of oxygen atoms.

There are some analyses which are intermediate between these two conditions; these are responsible for the ordinary view that there is a gradation from chabazite to gmelinite. Such intermediate types are abnormal, as shown by their relative scarcity, and the writer believes that they have nothing to do with a correct interpretation of the normal types. It is possible that they are incorrect on account of faulty execution or methods of analysis, or on account of impurities in the material analyzed. However, some of the intermediate points (for example 101 and 102) represent modern analyses made on carefully selected material. For these a different explanation is needed.

It is well known[6] that zeolites can be changed in composition artificially in such a way that a Ca-zeolite can be changed into a Na-zeolite. Such an exchange of bases in zeolites is the foundation of the modern method of water-softening. The exchange of bases is controlled by valence so that, for example, two atoms of sodium enter the zeolite in place of one atom of calcium which goes into the salt solution. At first thought this fact seems to demonstrate that in zeolites isomorphous systems are controlled by valence alone. However, principles which apply to the exchange of bases in crystals already formed do not necessarily apply to the formation of new crystals, that is, the writer believes that in the formation of isomorphous zeolite crystals as in the formation of all other isomorphous crystals *one* atom takes the place in the crystal space lattice of *one* other atom regardless of their respective valences.[7]

The zeolites are exceptional and remarkable because in crystals already formed (perhaps on account of inertia) bases can be ex-

[5] Or, perhaps along a line parallel to DEF and a short distance to the left of it, such as GHK.

[6] I. Zoch: Chemie der Erde, I, **1915.**

[7] Of course all valences in each end-member molecule must be satisfied.

changed with those in a solution surrounding the crystal under the control of valence, so that two monovalent atoms take the place of one divalent atom, or *vice versa*. This process is fully demonstrated and in current use artificially; there is no reason to doubt its occurrence in nature, though the necessary conditions seem to be uncommon in nature. It is to this process that the writer would appeal to explain the occurrence of crystals of chabazite abnormally rich in soda,[8] and also the occurrence of gmelinite crystals abnormally rich in lime.

In general, exchange of bases in zeolites is facilitated by the presence of much water;[9] that is, those zeolites containing much water exchange their bases more freely than those with less water. Chabazite contains the maximum water content known in zeolites (except for the rare faujasite) followed by minerals of the phillipsite group, gismondite, heulandite, laubanite, mordenite, epistilbite, scolecite, thomsonite, etc.

This theory regarding the constitution of chabazite and gmelinite can be tested at any place where complete information is available regarding the nature of the solutions in which crystals have been immersed.

Levynite is commonly referred to the chabazite group and it is true that a resemblance in axial ratios can be shown. However, the crystal habit is distinctly different and the inferior cleavage of levynite does not correspond with the distinct cleavage of chabazite. The mineral is so rare that the only good analyses are the two made by Hillebrand of crystals from Table Mt., Colo. These are shown in Fig. 3 at L3 and L4. The position of these points shows that levynite is not the same as chabazite nor intermediate between chabazite and gmelinite. It is an entirely distinct and independent species. Crystallographic similarities between it and chabazite do not exist because the two belong to a chemically isomorphous series, but in spite of chemical differences. Chabazite has a ratio of 7 Ca+Na atoms to 80 oxygen atoms while levynite has 8 Ca+Na atoms to the same number of oxygen atoms. The composition of levynite can be expressed quite accurately as $NaAlSi_4O_{10}.5H_2O+4CaAl_2Si_3O_{10}.5H_2O$ or $NaCa_4Al_9Si_{16}O_{50}.25H_2O$; no data are available to show whether it is a double salt of this

---

[8] Point 98 is a chabazite abnormally rich in K_2O rather than Na_2O.

[9] I. Zoch; Chemie der Erde, I, 1915.

composition or merely a member of an isomorphous series between the limits suggested. Its scarcity perhaps makes the former view the more probable.

4. THE COMPOSITION OF PHILLIPSITE AND RELATED ZEOLITES.

Phillipsite is a zeolite which varies in composition very considerably. The formula is commonly written (Ca, K_2) $Al_2Si_4O_{12}.4.5H_2O$. Without discussing in detail other formulas which have been proposed, it is sufficient to say that, so far as known to the writer, they all involve the theory that Ca and K_2 are equivalent. Since such a condition is contrary to that found in the anhydrous silicates it may be worth while to test the commonly accepted view by the new method recently described.[10]

After a study of all the forty-three analyses listed by Doelter[11] the most accurate were carefully selected by eliminating (1) those made before 1900, and (2) those in which the ratio of Al_2O_3 to CaO+alkalies does not approximate very nearly to 1:1. The twelve analyses thus selected are shown on Fig. 4, which is a diagram entirely similar in construction to that described in the discussion of natrolite. With the exception of two analyses (18 and 19) these indicate clearly that phillipsite is an isomorphous series probably along the line ABC which is curved through those points which represent mix-crystals having the same number of $Ca+K$ atoms, and of $Al+Si$ atoms for a constant number of O atoms. The line represents a series from $K_4Ca_7Al_{18}Si_{22}O_{80}$ at A to $K_{11}Al_{11}Si_{29}O_{80}$ at C. Therefore, in phillipsite, as in thomsonite, chabazite and gmelinite, the isomorphous relationships are between molecules of the same number of atoms of each group, $(Ca+Na)$, $(Al+Si)$, and O.

The analyses of Zambonini[12] are of special importance because they include the least siliceous as well as the most siliceous types as yet fully known. They are also of importance in showing very clearly that the tenor of water decreases markedly in phillipsite with increase in tenor of silica. The decrease is not easily explained, and, in fact, is not recognized in the ordinary view first proposed

[10] A. N. Winchell. The Composition of Thomsonite, *Am. Min.*, **10**, 90, (1925)·

[11] Hdb. Mineralchemie, **II**, 3, 1921, pp. 138-150.

[12] F. Zambonini: *Bull. Soc. Fr. Min.*, **XXV**, 1902, p. 360; and Mineral. Vesuv., **1910**, p. 294.

by Fresenius[13] and adopted by Dana,[14] Groth[15] and others, that phillipsite is an isomorphous series from $R''_2Al_4Si_4O_{16}.6H_2O$ to $R''Al_2Si_6O_{16}.6H_2O$, since the change of two atoms of Si for two of Al makes no important change in volume. The new theory furnishes an excellent reason for the decrease since it recognizes that the more siliceous types contain a corresponding increase of K in
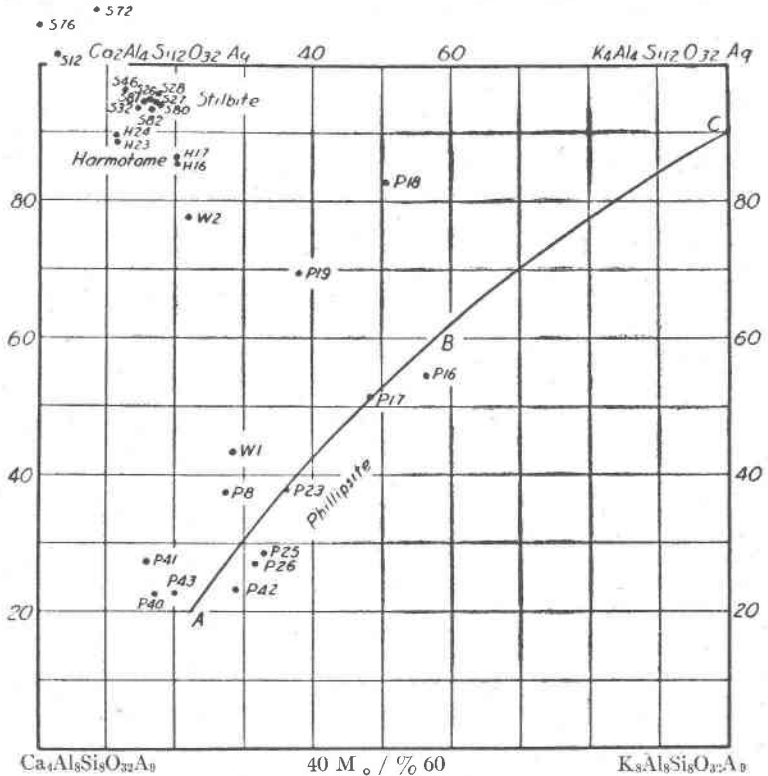

FIG. 4. The Composition of Phillipsite and Related Zeolites

place of Ca. The volume of a K atom is nearly twice as great as the volume of a Ca atom; therefore the increase of K atoms leaves decidedly less space to be occupied by water. Including the water, the composition of known phillipsite can be expressed as a series from $K_4Ca_7Al_{18}Si_{22}O_{80}.40\pm H_2O$ to $K_6Ca_5Al_{16}Si_{24}O_{80}.30\pm H_2O$.

[13] *Zeit. Kryst.*, **III**, 1880, p. 67.
[14] Syst. Mineral., **1892**, p. 579.
[15] Mineral. Tabel., **1921**, p. 124.

The two analyses which do not lie along this line may owe their peculiar character to faulty execution or methods of analysis or to impurities in the material used for analysis.   However, one of them (19) is a very recent analysis of carefully selected material made under Tschermak's supervision and published by him; it seems more likely that the abnormal character of both is, therefore, due to change in composition by partial exchange of bases (Ca for K_2) as more fully explained in the discussion of chabalite.

Stilbite, harmotome and wellsite are crystallographically related to phillipsite.

Some of the best analyses of stilbite are plotted on the figure;[16] they show that the mineral varies very little in composition; it is near $CaAl_2Si_6O_{16}$, but nearly always contains a small and nearly constant amount of soda; the precise formula is not readily determined from data at present available, but is nearly Na_3Ca_9 $Al_{21}Si_{59}O_{160}.60H_2O$. The fact that stilbite contains sodium rather than potassium shows that it is not an end-member of the phillipsite series, as has been suggested.

Harmotome analyses are not numerous; two pairs of "duplicates" are shown on the figure: they are not sufficient to show the variations in composition, but suggest a formula of the type of that of stilbite, perhaps $KBa_5Al_{11}Si_{29}O_{80}.25H_2O$.

There are only two analyses of wellsite on record; the first one —made on material from the original locality in North Carolina by Pratt and Foote[17]—seems to be phillipsite with part of its calcium replaced by barium and strontium (which are considered equal to calcium in computing the position of the point (W_1) in the figure.) The other analysis (W_2) by Fersman[18] of a sample from Russia is apparently a lime-rich harmotome rather than wellsite. Wellsite like the potash-rich phillipsites contains relatively little water, since the barium atom like the potassium atom is much larger than the calcium atom.

Incidentally, it may be remarked that the new orientation for phillipsite, stilbite and harmotome recently proposed by Tscher-

[16] Stilbite contains Na rather than K, so that in reading its composition from the diagram the right hand corners must be assumed to be sodium instead of potassium molecules.

[17] *Am. Jour. Sci.*, III, 1897, p. 443.

[18] *Trav. Mus. Géol. Acad. Sci. St. Petersbourg*, **III**, 1909, p. 129; *Zeit. Kryst.*, **LI**, 1915, p. 291.

mak[19] seems to the writer to be a decided improvement. It is as follows:

Dana		Tschermak
001	=	100
010	=	010
100	=	$10\bar{1}$
$\bar{1}01$	=	001
011	=	120
110	=	$12\bar{1}$

With this new orientation the phillipsite group, like all the other fibrous zeolites and many other fibrous minerals, is elongated in the vertical direction instead of parallel to *a*. Furthermore, the experiments of Rinne[20] on stilbite show that when it becomes orthorhombic at about 250°C. the axes Y and Z coincide with Dana's axes *b* and *a*, but X is normal to 001 and not parallel with *c*. With Tschermak's orientation the orthorhombic substance has $X = a$, $Y = b$, $Z = c$.

(To be continued)

A FULGURITE FROM SOUTH AMBOY, NEW JERSEY[1]

W. M. Myers[2] and Albert B. Peck[3]

Fulgurites, the glassy irregular tubes produced by the fusion of sand or silicous soil, which has been struck by lightning, have attracted attention from very early times. Their rare occurrence, unusual appearance and association with localities where lightning has been observed have lead to many strange conjectures concerning them. Before the true nature of lightning had been established by Franklin, there was even some popular belief that they were the actual "thunder bolts" which descended from the sky.

The infrequency with which fulgurites are encountered together with the difficulty of extracting them from the surrounding soil and the fact that their true identity often is not recognized has

---

[19] *N. Jahrb. Min.*, 1897, **I,** p. 41.

[20] *Sitz. Akad. Wiss. Wien,* **CXXVI,** 1917, p. 541 and **CXXVII,** 1918, p. 177.