Only a small quantity of foreign material need be adsorbed to control the crystallization. Analyses of various epidotes show a varying amount of impurities. The greater portion of this foreign material was occluded during the process of crystallization and was not added by the process of adsorption.

The elongation of epidote crystals along the b axis is believed to be satisfactorily explained as a result of the reaction of introduced material with rock material amenable to such reactivity. During the process of crystallization, due to adsorption of foreign material, the growth of the crystals along the b axis is retarded to a greater extent than along the c axis.

Lindgren's[6] contention, that replacement is essentially a process of adsorption and super-saturation, receives, then, additional support from the foregoing observations, with regards to the importance of adsorption.

[6] Mineral Deposits, p. 26, New York, 1919.

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

(Continued from page 152)

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5. THE COMPOSITION OF HEULANDITE AND RELATED ZEOLITES

Doelter[1] has collected 47 analyses of heulandite and three more have been published since the date of his compilation. However, many of these are too old to be of high quality, and some were made on impure material. In heulandite, as in other zeolites, the ratio between Al_2O_3 and $\ddot{R}O + \dot{R}_2O$ is very nearly constant and very nearly unity. Excluding therefore a few analyses because this ratio is unsatisfactory, the "superior" analyses of heulandite are the following:

Doelter's Nos. 11, 19, 23, 25, 37, 38, 40, 41, and 47.
A. L. Parsons:[2] Heulandite from Digby Cut, Nova Scotia.
K. H. Scheumann:[3] Heulandite from Berufiord, Iceland.

[1] Hdb. Mineralchemie, **II**, 3, (1921), p. 171.
[2] *U. Toronto Studies, Geol. Ser.*, **14**, (1922), p. 52.
[3] *Ber. Sachs. Akad. Wiss.*, Leipzig, **LXXIII**, (1921), p. 1; *Zeit. Kryst.*, **LVII**, (1923), p. 657.

In spite of the fact that the differences in composition are not very great it may be useful to study these analyses by the method recently described.[4] However, in this case the corners of the square must be more highly siliceous than in the case of thomsonite, or even natrolite, since the points for heulandite cannot be plotted on the square as used for those minerals. As a matter of convenience the following molecules are chosen as the corners of the square:

	Lime	Soda
More siliceous	$CaAl_2Si_{14}O_{32}.Aq.$	$Na_2Al_2Si_{14}O_{32}.Aq.$
Less siliceous	$Ca_3Al_6Si_{10}O_{32}.Aq.$	$Na_6Al_6Si_{10}O_{32}.Aq.$

It is evident that the ratio between Al_2O_3 and $CaO+Na_2O$ is unity at all points on the square, and it is easy to see that the horizontal axis expresses the $CaO:Na_2O$ relation while the vertical axis expresses the $Al_2O_3:SiO_2$ relation. It will be readily understood that CaO and Na_2O in the figure stand for $CaO+MgO+SrO+BaO$ and Na_2O+K_2O, respectively. It is easily seen that the lower half of this square is the same as the upper half of the square used for natrolite.

The results of calculating the "superior" analyses into these molecules and plotting them on the square are shown in Fig. 5, on which are also shown points representing similarly selected analyses of epistilbite, mordenite and brewsterite, which are isomorphous with heulandite. The variations in composition in heulandite are not sufficiently great to put the proper interpretation beyond question, but they are as favorable to the theory that the composition of heulandite varies like that of feldspars as they are to any other theory, that is, the points should lie along a curve if the composition varies as in the feldspars, while, if it varies, as is commonly supposed in all zeolites, so that Na₂ takes the place of Ca the points should lie along a horizontal line. The writer has already pointed out that such a variation in composition as would be expressed in the diagram by a horizontal line can be produced in zeolites (already crystallized) by artificial means, and it seems probable that some variations of this kind may occur in nature *after formation* of the zeolite crystals.

It is not clear precisely what ratio of Ca+Na atoms to oxygen atoms is found in heulandite, but the writer would suggest that the mineral may be represented approximately as isomorphous mix-

[4] A. N. Winchell: The Composition of Thomsonite, *Am. Min.*, **X**, (1925), p. 90.

tures in variable proportions of the molecules: $NaCa_5Al_{11}Si_{29}O_{80}$. $25H_2O$ and $Na_2Ca_4Al_{10}Si_{30}O_{80}.25H_2O$.

In these formulas the writer is merely expressing the ordinary view regarding the water. Neither the amount nor the condition of the water is considered in this discussion, except that it is
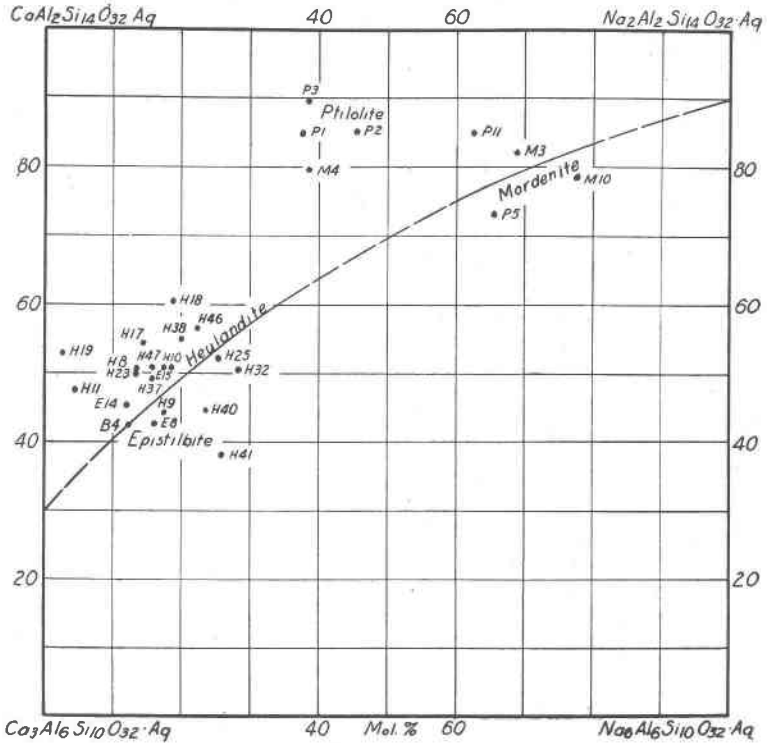

Figure 5
The Composition of Heulandite and Related Zeolites

assumed that the water takes no part in the main formula. This assumption is in harmony with the fact that the water can be driven out without destroying the zeolite crystal.

Tschermak[5] has recently made it clear that mordenite and epistilbite (as well as brewsterite) belong to the heulandite group by adopting a new orientation for epistilbite, so that the ratios become:

Mordenite　　$a:b:c = 0.401 : 1 : 0.428$　　$\beta = 88°31'$
Heulandite　　$a:b:c = 0.404 : 1 : 0.429$　　$\beta = 88°34'$

[5] *Sitz. Akad. Wiss. Wien*, **CXXVI**, (1917), p. 601.

Epistilbite	$a:b:c=0.419 : 1 : 0.432$	$\beta=89°20'$
Brewsterite	$a:b:c=0.405 : 1 : 0.420$	$\beta=86°20'$

Mordenite is so rare that only three satisfactory analyses have been found. These are shown on the figure (M10 the analysis by E. W. Todd published by T. L. Walker: *Toronto U. Studies, Geol. Ser.,* 14, (1922), p. 59; the others are Doelter's Nos.). Except for analysis M4, mordenite belongs to the same series as heulandite, and is nearly free from lime, the formula being roughly $Na_4Ca_2Al_8Si_{32}O_{80}.25H_2O$.

Epistilbite is chemically nearly the same as one end member of the heulandite series: no modern analyses are available, but two, carefully selected from the old analyses, are shown on Fig. 5. Therefore the composition of epistilbite may be indicated as $NaCa_5Al_{11}Si_{29}O_{80}.25H_2O$.

Brewsterite is rare and only one superior analysis is on record. So far as shown by the diagram it is practically the same as epistilbite, but it is characterized by the presence of much strontium and some barium.

So far as the optic properties of the epistilbite-heulandite-mordenite series are concerned, the mean index of refraction and the birefringence seem to decrease regularly with increase of soda and silica, but the sign and optic orientation do not seem to be those that should belong to such a series. However, when it is remembered that small temperature changes produce marked changes in these properties, as shown by Rinne for stilbite[6] and heulandite,[7] and that heulandite and epistilbite both become orthorhombic with similar optic orientations at moderate temperatures, the theory that they belong to a single isomorphous series does not seem unreasonable.

It may be noted that, if brewsterite is isomorphous with heulandite and epistilbite, as seems clearly to be the case from the chemical and crystallographic data, the index of refraction in the literature for the former[8] ($n=1.45$) must be incorrect since its composition as compared with that of the latter would require a higher index than possessed by heulandite and epistilbite (namely 1.50 and 1.51). It may be suggested that the index of brewsterite should be 1.55, the 1.45 being perhaps a typographical error.

[6] *N. Jahrb. Min.*, (1897), I, p. 41.

[7] *Sitz. preus. Akad. Wiss. Berlin,* **XLVI**, (1890), p. 1183.

[8] Minéraux des Roches, **1888**, p. 301.

Ptilolite is chemically closely related to mordenite, but Böggild[9] has shown that it is normally orthorhombic. The analysis (P11 in Fig. 5) by Prof. Kossmat recently published by Tschermak[10] suggests that the mineral has the composition $Na_3Ca_2Al_7Si_{33}O_{80}$. $25H_2O$, differing from mordenite in having $5(Na+Ca)$ atoms, instead of 6, for 80 atoms of oxygen. However, Lindström's analysis (P5 in Fig. 5) of ptilolite from Teigarhorn, Iceland,[11] has the same ratio as found in mordenite; it may be significant that Böggild found the mineral in this occurrence to differ optically from all others, being apparently monoclinic like mordenite. There are three other good analyses of ptilolite, two by Eakins[12] (P1 and P2 in Fig. 5) and one by Colomba[13] (P3 in Fig. 5). This is the first instance discovered among the zeolites in which the data indicate a series by substitution of two atoms of Na for one of Ca. The analyses are not numerous and the condition is perhaps due to change in composition after formation of the crystals, as previously suggested.

6. Comparative Study and Summary

A summary of the composition of the zeolites as determined in this study may be arranged as follows:

Thomsonite	$Na_4Ca_8Al_{20}Si_{20}O_{80}.25H_2O$ to $Na_7Ca_5Al_{17}Si_{23}O_{80}.20H_2O$.
Gmelinite	$Na_4Ca_2Al_7Si_{13}O_{40}.20H_2O$ to $Na_6Al_6Si_{14}O_{40}.20H_2O$
Levynite	$Na_4Ca_4Al_8Si_{16}O_{50}.25H_2O$
Chabazite	$Ca_7Al_{14}Si_{26}O_{80}.40H_2O$ to $(Na, K)_4Ca_3Al_{10}Si_{30}O_{80}.40H_2O$
Phillipsite	$K_4Ca_7Al_{18}Si_{22}O_{80}.40H_2O$ to $K_6Ca_5Al_{16}Si_{24}O_{80}.30H_2O$
Stilbite	$Na_3Ca_9Al_{21}Si_{59}O_{160}.60H_2O$
Harmotome	$KBa_5Al_{11}Si_{29}O_{80}.25H_2O$
Natrolite	$Na_2Al_2Si_3O_{10}.2H_2O$
Mesolite	$Na_2Ca_2Al_6Si_9O_{30}.8H_2O$
Scolecite	$CaAl_2Si_3O_{10}.3H_2O$
Edingtonite	$BaAl_2Si_3O_{10}.3H_2O$
Gismondite	$KCa_{10}Al_{21}Si_{19}O_{80}.40H_2O$ to $K_4Ca_7Al_{18}Si_{22}O_{80}.36H_2O$
Laumontite	$Ca_7Al_{14}Si_{26}O_{80}.25H_2O$ to $Na_2Ca_5Al_{12}Si_{28}O_{80}.25H_2O$
Heulandite	$NaCa_5Al_{11}Si_{29}O_{80}.25H_2O$ to $Na_2Ca_4Al_{10}Si_{30}O_{80}.25H_2O$
Mordenite	$Na_4Ca_2Al_8Si_{32}O_{80}.25H_2O$?
Epistilbite	$NaCa_5Al_{11}Si_{29}O_{80}.25H_2O$
Brewsterite	$Na(Sr,Ba,Ca)_5Al_{11}Si_{29}O_{80}.25H_2O$
Ptilolite	$Na_3Ca_2Al_7Si_{33}O_{80}.25H_2O$?

[9] *Kgl. Danske Vid. Selsk. Math. fys. Meddel.*, **IV,** 8, (1922).

[10] *Sitz. Akad. Wiss. Wien*, **CXXVI,** (1917), p. 547.

[11] *Geol. För. Förh. Stockholm*, **XX,** (1907), p. 106.

[12] *Am. J. Sci.*, **XXXII,** (1886), p. 117, and **XLIV,** (1898), p. 96.

[13] *Zeit. Kryst.*, **XL,** (1904), p. 100.

The most striking feature of these formulas is their remarkable complexity. It is possible that in some cases more accurate information will permit some simplifications, but, in general, this will probably not be considerable, and it must be concluded that the zeolites are remarkable in one other respect, besides those mentioned at the beginning of this discussion, namely, in the extraordinary complexity of their formulas.
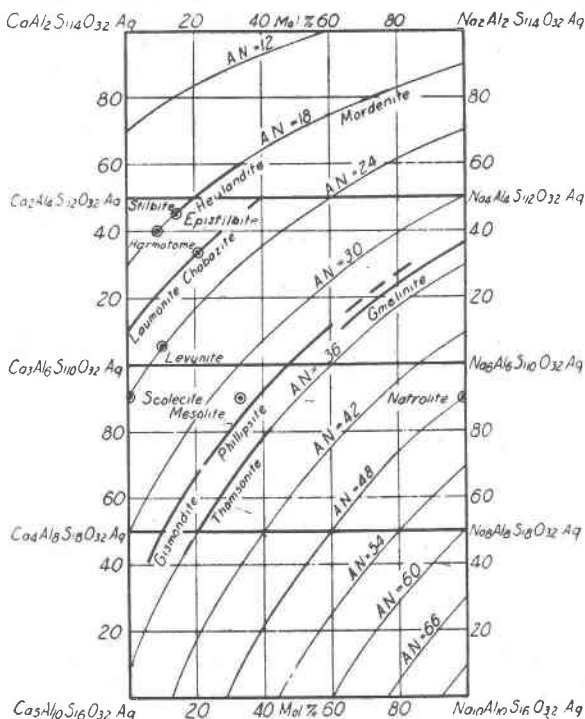
Figure 6
Summarized Composition of the Zeolites
AN (alkali number) = number of $(Ca+Na)$ atoms to 240 oxygen atoms.

However, the preceding discussion shows that the zeolites are like the feldspars in their composition in certain important respects: namely,

1. The Al_2O_3:$CaO+Na_2O$ ratio is always unity in the whole zeolite group.

2. The $Al+Si$:O ratio is always 1:2 in the whole group.

3. In any given strictly isomorphous part of the zeolite group the $Ca+Na$:O ratio is constant.

4. The composition of all the zeolites can be expressed very simply in a suitable graph, in which the composition of certain zeolites is shown by points, while that of others varies along simple lines, as shown in Fig. 6.

If the number of $(Ca+Na)$ atoms in each portion of the zeolite space lattice containing 240 oxygen atoms be called the alkali number then it appears from the preceding study that the following tabulation is possible:

Name	Alkali number
Ptilolite	15?
Mordenite	18
Heulandite	18
Epistilbite	18
Brewsterite	18
Stilbite	18
Harmotome	18 or 21?
Laumontite	21
Chabazite	21
Levynite	24
Scolecite	24
Edingtonite	24
Feldspar	30
Mesolite	32
Gismondite	33
Phillipsite	33
Gmelinite	34 or 36?
Thomsonite	36
Natrolite	48

This suggests a new study of the crystallographic relationships of the zeolites, but the subject will not be pursued farther here.

The writer believes that the preceding study of the zeolites has shown that:

1. Thomsonite is certainly an isomorphous series of the feldspar type.

2. Natrolite, mesolite and scolecite are three independent zeolites of fixed composition, which are not isomorphous in the sense of forming intermediate mix-crystals. They have similar crystal forms, but unlike space lattices, as shown both by their inability to form mutual crystal solutions and by their differences of symmetry.

3. Laumontite is probably a short isomorphous series of the feldspar type; it is chemically related to chabazite, but contains less water.

4. Gismondite is probably a short isomorphous series of the feldspar type; it is chemically closely related to phillipsite.

5. Chabazite probably forms a short isomorphous series of the feldspar type; it is chemically related to laumontite but contains more water.

6. Gmelinite probably forms an isomorphous series of the feldspar type; the variation of some crystals toward the composition of chabazite is believed to be due to change in composition after formation of the crystals just as "permutite" and many natural zeolites are known to change composition in various solutions under valence-control.

7. Levynite is unlike chabazite in composition and may be of fixed formula.

8. Phillipsite is an isomorphous series of the feldspar type, though variations in composition under valence-control, believed to be secondary, as in the case of gmelinite, are also known. Phillipsite is chemically closely related to gismondite.

9. With three exceptions, perhaps misnamed, stilbite is an independent zeolite of fixed composition; it is related to epistilbite and heulandite in composition.

10. Harmotome is perhaps of fixed composition; it is related to stilbite, but is rich in barium.

11. Heulandite varies in composition rather lawlessly, but may be referred reasonably to an isomorphous series (with mordenite) of the feldspar type.

12. Epistilbite belongs at one end of the heulandite series.

13. Brewsterite is like epistilbite in composition except that strontium and barium replace much of the calcium of the latter.

14. Disregarding one analysis, as perhaps due to secondary changes under valence-control, mordenite belongs, with heulandite, to a discontinuous (?) isomorphous series of the feldspar type.

15. Ptilolite seems to form an isomorphous series in which 2Na takes the place of Ca, or *vice versa*, but analyses are few and the variations may be due to changes after formation of the crystals, such as can be produced artificially in several zeolites.

16. The general conclusion which seems justified may be stated as follows:

With a few exceptions which can reasonably be explained as due to secondary changes after formation of the crystals, the zeolites show no evidence of isomorphous replacement under valence-control (so that 2Na replaces Ca, or *vice versa*), but, con-

trary to the theories of all authorities, they are either of fixed composition, like natrolite and mesolite, or they vary in composition exactly as the feldspars do; that is, variation occurs by replacement of Ca by Na (or K) with simultaneous replacement of Al by Si.   The isomorphous molecules are composed of the same number of atoms, and these are divisible into three groups of atoms, the smallest oxygen atoms, the intermediate Al and Si atoms, and the largest Ca and Na atoms; in all zeolite molecules the oxygen atoms are just twice as numerous as the $(Al+Si)$ atoms, while the number of $Ca+Na$ atoms is constant in each part of the zeolite group whose molecules are capable of forming mix-crystals, but differs widely in different parts of the whole group.

The zeolites differ from the feldspars (1) in forming many isomorphous systems rather than one such system, (2) in apparently showing a limited range of formation of mix-crystals rather than an unlimited range, and (3) in consisting of very complicated molecules instead of very simple ones.

17. This theory of the isomorphous relationships of the zeolites can be tested by comparative studies of the composition of zeolites under varying conditions of composition of the solutions surrounding them. If the theory is correct, it can be used to learn something about the nature of solutions in given regions.

It seems very strange to the writer that Tschermak, the able exponent of isomorphous systems in silicates and the scientist who established the correct explanation of the composition of the feldspars, was unable even after years of elaborate studies and calculations[14] to discover that a similar explanation should be applied to the zeolites, and recently presented instead a theory which is so complicated that it seems destined to fall of its own weight.[15]

[14] See his elaborate discussion of the zeolites: *Sitz. Akad. Wiss. Wien*, **CXXVI,** (1917), pp. 541-606 and **CXXVII,** (1918), pp. 177-289.

[15] While this is the view of E. T. Wherry (*Am. Min.*, **VIII,** 1923, p. 122) and the writer, it should in fairness be added that Tschermak's theory is discussed favorably by Doelter (Hdb. Mineralch. **II,** 2, 1917 and **II,** 3, 1921) and by Niggli (*Zeit. Kryst.*, **LVII,** 1923, p. 647).   It is not accepted nor mentioned by Groth (Mineral. Tabellen, **1921,** p. 120).