FURTHER STUDIES OF THE ZEOLITES

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Twelve years ago the writer proposed a new theory of the composition of the zeolites[1] according to which those zeolites which are not essentially fixed in composition show variations in their alkali or alkaline earth metal, not under the control of valence, but in the same way as in the feldspars. It was recognized at that time that variations in composition under valence control are found in nature, and can be produced artificially, but it was suggested that such variations are secondary in origin, even when found in nature. Although this theory was unlike any previous conception of the composition of the zeolites and even directly contrary to most of them, it has not been seriously challenged[2] since that time, and seems to be winning gradual acceptance by those who are making careful studies of the hydrous equivalents of the feldspars.

In the original study of the zeolites the relation between variations in the Na:Ca ratio and the Si:Al ratio was studied by means of square diagrams essentially based on these two ratios. At the same time the diagrams were intended to be devised in such a way that any single point on one of them would represent a complete analysis in terms of the four molecules at the corners of the square. In this respect the diagrams were not accurate, since the center point should represent equal parts[3] of the two molecules at the ends of each diagonal, but cannot do so since these sums are not equal to each other.

During the last decade many new analyses of zeolites have been published. Accordingly it is now possible, not only to correct the diagrams previously published, but also to prepare diagrams based on much new information, some of which is doubtless more accurate than previously available. This article describes an attempt to accomplish these ends.

Considering the square formerly used for the study of thomsonite, the molecules concerned were

$$Ca_3Al_6Si_{10}O_{32}\cdot Aq \qquad Na_6Al_6Si_{10}O_{32}\cdot Aq$$
$$Ca_5Al_{10}Si_6O_{32}\cdot Aq \qquad Na_{10}Al_{10}Si_6O_{32}\cdot Aq.$$

In order to change these so that they will satisfy the condition already explained those in the first line must be taken five times and those in the second line three times. Then the Ca molecules will have the same

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[1] *Am. Mineral.*, vol. **10**, pp. 88, 112, 145 and 166, 1925.

[2] E. T. Wherry (*Am. Mineral.*, vol. **10**, p. 342, 1925) took exception to the theory as applied to thomsonite; he asked for optical evidence (of an isomorphous series), which the writer supplied. (*Am. Mineral.*, vol. **11**, p. 82, 1926.)

[3] Dr. N. L. Bowen kindly called the writer's attention to this method of testing a square diagram. See also *Am. Mineral.*, vol. **20**, p. 773, 1935.

number of Ca atoms and of Al atoms; they will differ only in Si atoms and O atoms. The same is true of the Na molecules. This shows that the Al:Si ratio must be changed by increasing the Si atoms without changing the Al atoms. Accordingly, if we begin with $CaAl_2Si_2O_8$ and $Na_2Al_2Si_2O_8$ which are the molecules containing the minimum tenor of silica in zeolites, an increasing tenor of silica must be represented by $CaAl_2Si_3O_{10}$, $CaAl_2Si_4O_{12}$, etc. In order to show a considerable difference it may be desirable to use $CaAl_2Si_6O_{16}$ and $Na_2Al_2Si_6O_{16}$ as the other corner molecules of the square, as shown in Fig. 1. On this square the lines connecting points having equal numbers of (Ca+Na) atoms for a given number of oxygen atoms are straight. They are not parallel, but are diagonal in their general direction. The numbers on them in the figure express the number of (Ca+Na) atoms for 80 oxygen atoms. The composition of many zeolites

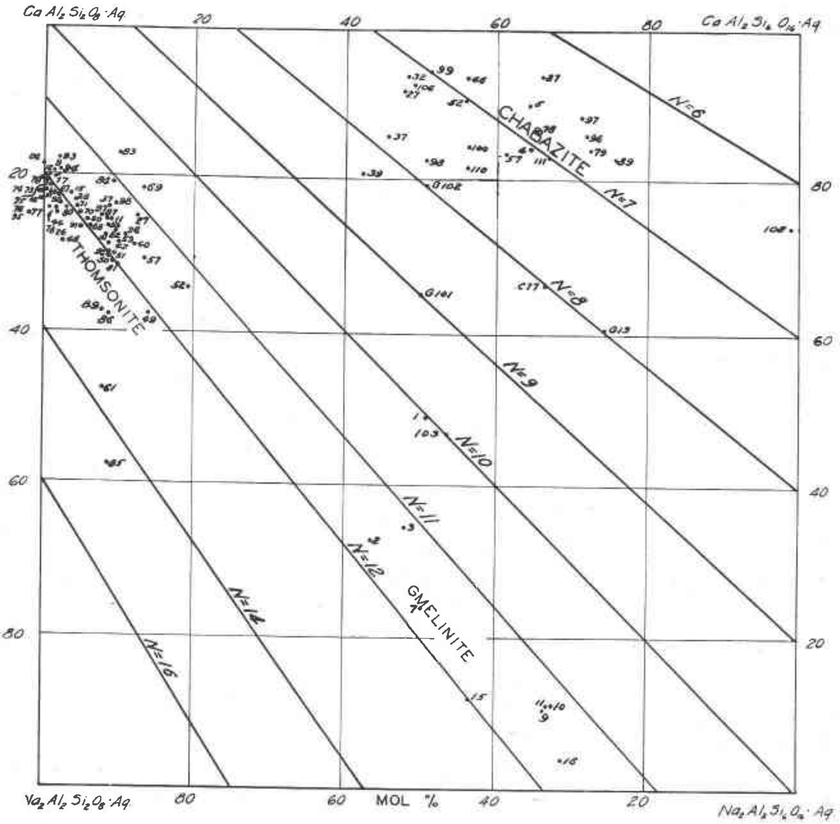

FIG. 1. Variations in composition in thomsonite, chabazite, and gmelinite.

can be shown on this square, but stilbite and heulandite may contain more SiO_2, and mordenite and ptilolite contain much more silica. To show these zeolites it is necessary to use a square which may be shown adjoining the first one; it has $CaAl_2Si_{10}O_{24} \cdot Aq$ and $Na_2Al_2Si_{10}O_{24} \cdot Aq$ as the silica-rich molecules. A few samples of ptilolite are even more siliceous than can be expressed inside this square.

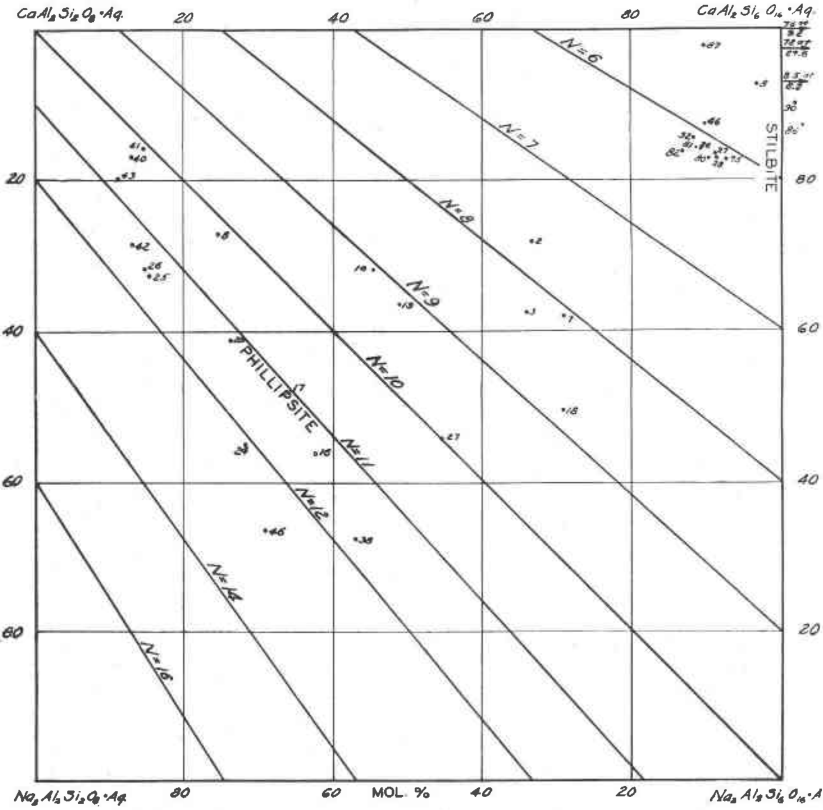

FIG. 2. Variations in composition in phillipsite and stilbite.

The distribution of points[4] expressing the best analyses of thomsonite

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[4] To find the position of the point representing any analysis it is only necessary to find: (a) the per cent. of Na_2O molecules in the total Na_2O+CaO molecules, and (b) the per cent. of silica-rich molecules in the total of silicate molecules; this may be accomplished from the silica and alumina molecules by means of the relation:

$$\% \text{ silica-rich molecules } (Si_6) = \frac{1/4(SiO_2-2Al_2O_3)100}{Al_2O_3} \text{ for Figs. 1 and 2.}$$

$$\% \ Si_{10} \text{ molecules} = \frac{1/4(SiO_2-6Al_2O_3)100}{Al_2O_3} \text{ in right hand square of Fig. 3.}$$

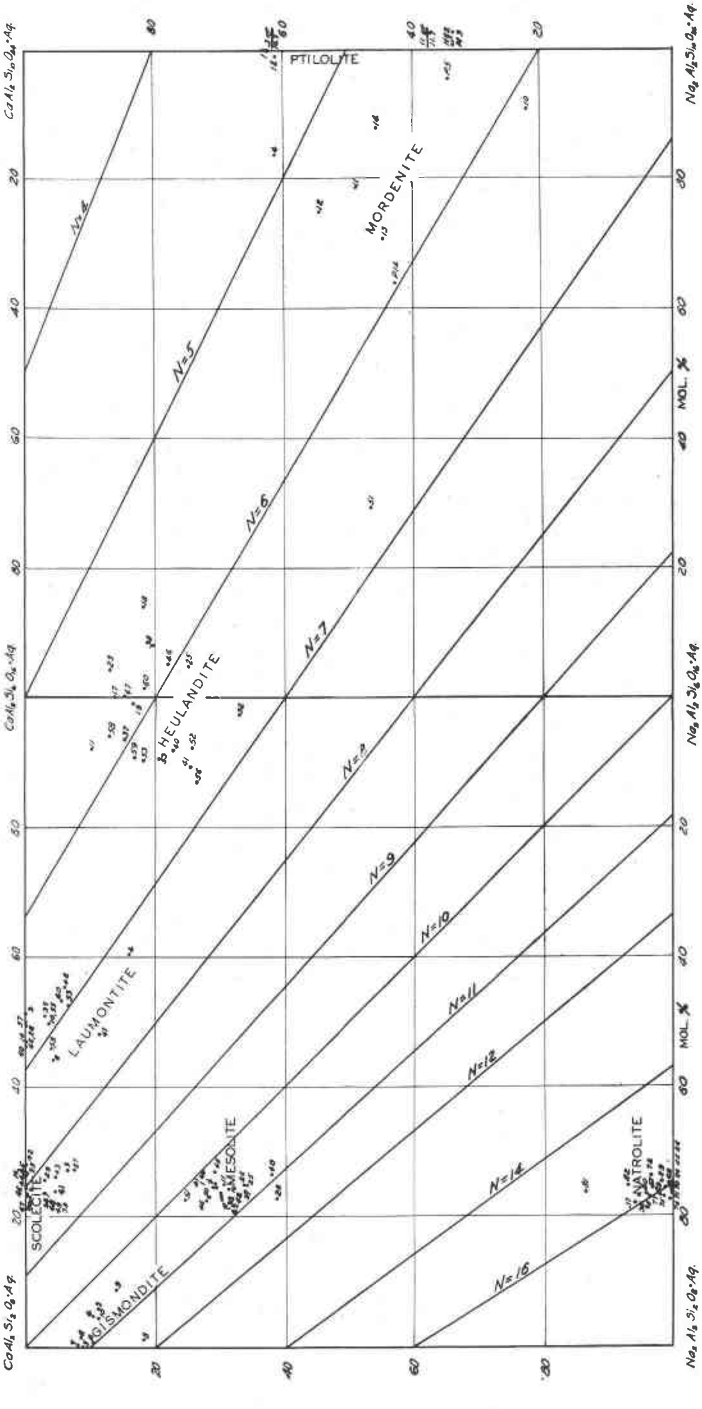

FIG. 3. The composition of gismondite, scolecite, mesolite, natrolite, laumontite, heulandite, mordenite, and ptilolite.

shown on Fig. 1 indicates some variation of composition under valence control (secondary?), as well as distinct and more common variation as in feldspars. On the same figure the composition of chabazite is seen to vary chiefly as in the feldspars, but that of gmelinite varies chiefly under valence control; the writer has suggested that this is due to secondary changes.

The remarkably random distribution of points expressing the best analyses of phillipsite is shown in Fig. 2, as well as the more compact grouping of good analyses of stilbite.

Two squares are shown side by side in Fig. 3 so as to give the complete picture of the distribution of points representing heulandite and their relation to mordenite and ptilolite. On the same diagram are shown the variations of composition of laumontite and of gismondite, as well as the approximately constant composition of scolecite, mesolite, and natrolite. It is possible to find variation of composition under the control of valence in nearly all zeolites, but in many cases this is subordinate to variation of the feldspar type, and it is perhaps always secondary.

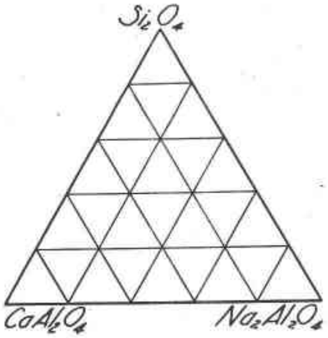

FIG. 4. Theoretical components (not end-members) of zeolites.

These squares express variations of composition in terms of addition of equal parts of silica to an original molecule and, therefore, equal distances on them do not express equal changes of composition. This may be more readily understood by noting the fact that it would be necessary to add an *infinite* amount of a molecule, B, to the original molecule, A, in order to complete the change from A to B, which is half accomplished when one molecule of B is added to one of A, and only changed from 90 per cent. to 90.9 per cent. when one molecule of B is added to a mixture of A+9B. Therefore it is highly desirable to devise a different diagram.

As already explained, one extreme of the change in composition of zeolites is pure silica; it follows that another extreme must be a molecule with no silica. Disregarding soda it is easy to see that this must contain

CaO and Al_2O_3 in equal parts. Therefore the molecule is $CaAl_2O_4$; and a silica molecule of equal oxygen content must be Si_2O_4. The soda molecule corresponding to $CaAl_2O_4$ is clearly $Na_2Al_2O_4$. These may be arranged on a triangle as shown in Fig. 4.

What part of this triangle represents the composition of zeolites? The minimum tenor of SiO_2 in zeolites is found in some samples of thomsonite, the composition of which (omitting Na_2O and H_2O) may be written: $CaAl_2Si_2O_8$. This is the composition expressed by a point midway between $CaAl_2O_4$ and Si_2O_4. The corresponding sodium molecule is $Na_2Al_2Si_2O_8$ and pure silica with the same oxygen content must be written Si_4O_8. Thus we obtain the molecules of Fig. 5, which corresponds with the upper half of Fig. 4. The same molecules are used in Figs. 6–8. In these triangular diagrams there is no distortion, and equal distances represent equal changes of composition. Horizontal lines express variation of composition under valence control (Ca for 2 Na), and diagonal lines express variations of composition of the feldspar type (CaAl for NaSi); the numbers on these diagonal lines give the number of (Ca+Na) atoms for 80 oxygen atoms. It is impracticable to number the points representing analyses since they are too close together.

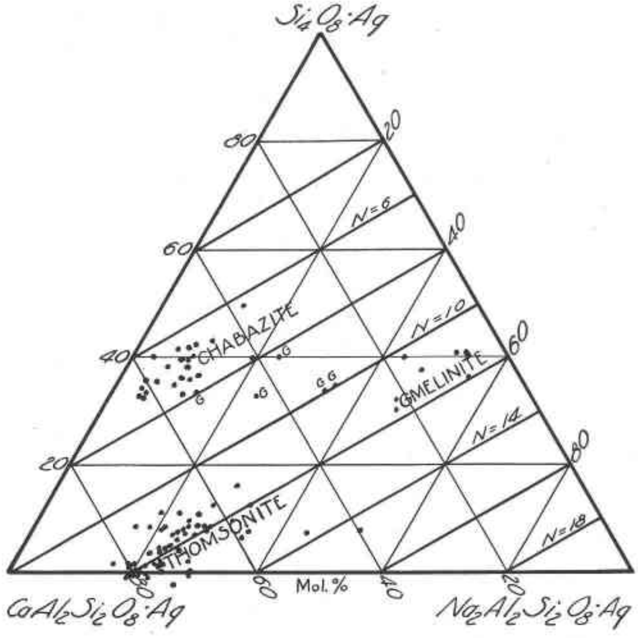

FIG. 5. Variations in composition of thomsonite, chabazite, and gmelinite.

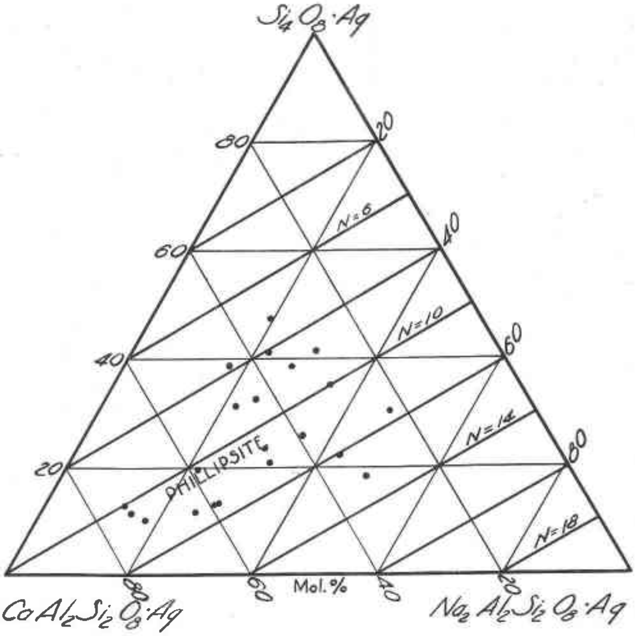

FIG. 6. Variations of composition in phillipsite.

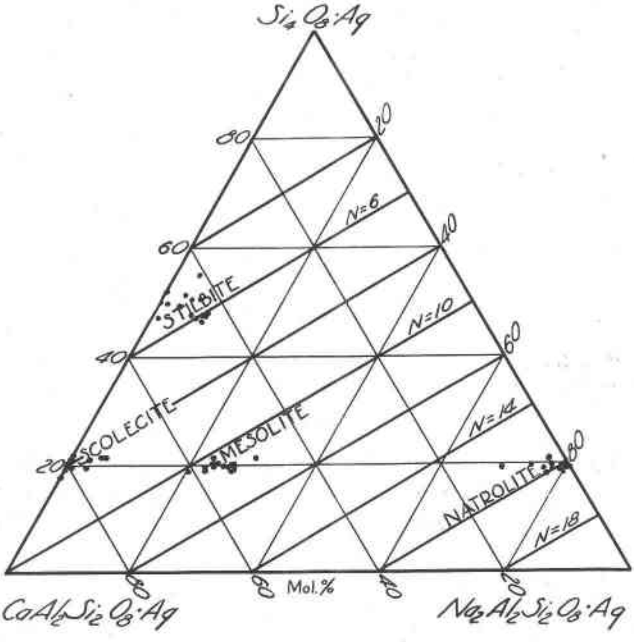

FIG. 7. Composition of scolecite, mesolite, natrolite, and stilbite.

The variations in composition of thomsonite are shown in Fig. 5, as well as those of chabazite and gmelinite. The wide scattering of points in Fig. 6 expresses the apparently lawless way phillipsite varies in composition, but all the points may be explained as due to the feldspar type of variation (with $N=10$), plus (secondary?) variation under valence control. Scolecite, mesolite, and natrolite are nearly fixed in composition, as shown in Fig. 7; stilbite varies only a little more than the others.

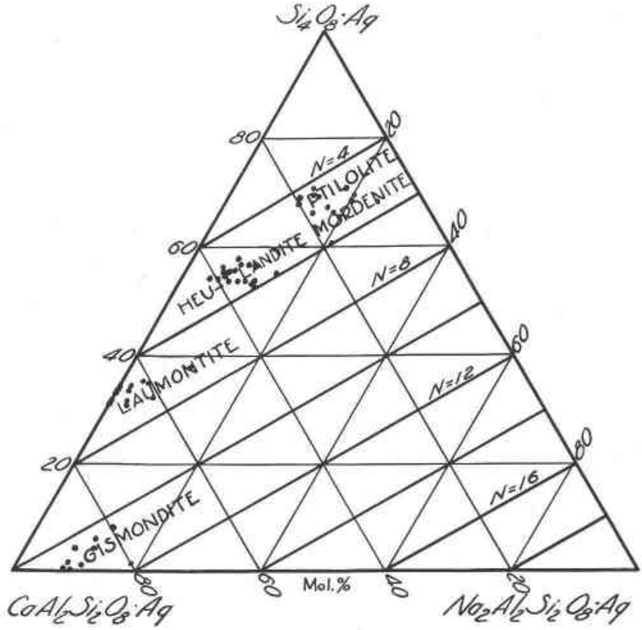

FIG. 8. Variations of composition in gismondite, laumontite, heulandite, mordenite, and ptilolite.

Laumontite and gismondite vary a little more, as shown in Fig. 8, which also shows the relation between heulandite, mordenite and ptilolite; heulandite and mordenite seem to form a (discontinuous?) series.

It is a surprise to the writer to discover in this way that some zeolites are seventy per cent. silica[5] (Si_4O_8) with only thirty per cent. of molecules

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[5] To find the point representing any analysis of a zeolite on any one of these triangular diagrams it is only necessary to use: (a) the per cent. of Na_2O molecules in the total Na_2O+CaO molecules, and (b) the per cent. of Si_4O_8 which may be obtained from:

$$\%\ Si_4O_8=\frac{1/4(SiO_2-2Al_2O_3)100}{1/4(SiO_2-2Al_2O_3)+Al_2O_3}.$$

Analyses in which Al_2O_3 molecules differ materially from Na_2O+CaO molecules are probably incorrect and should not be used.

which have the minimum tenor of silica in zeolites. In this connection it may be worth while to state that the writer does not consider any of the molecules used on these triangular diagrams to be end-members of any zeolite, though gismondite has an end-member molecule which is not very different from $CaAl_2Si_2O_8 \cdot Aq$.

Variations of optical properties corresponding with these variations in composition in zeolites are not easily defined, partly because the optical properties depend upon both types of variation in composition, and also upon the state of hydration, which is not always complete. Nevertheless, the relations between variations in optic properties and variations in composition (of the feldspar type) in thomsonite are illustrated in Fig. 9.

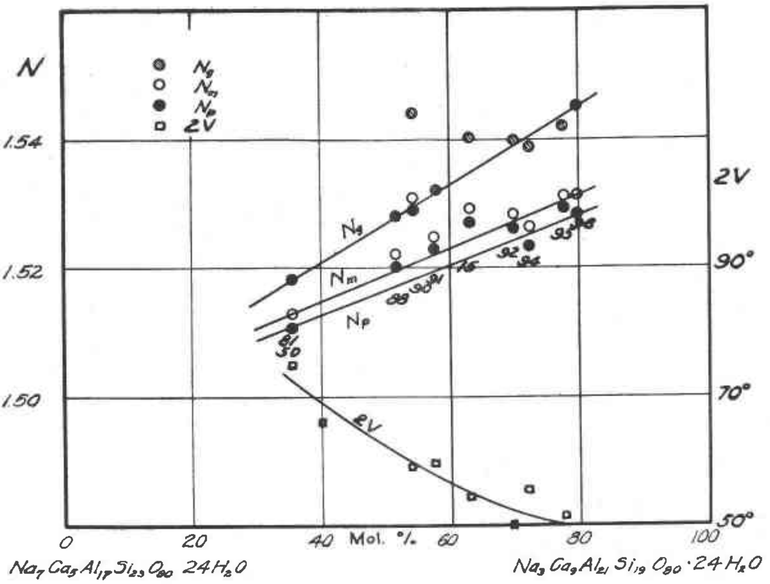

FIG. 9. Variations in composition and optic properties in thomsonite. Based on data of M. H. Hey: *Mineral. Mag.*, vol. **23,** p. 51, 1932, and others.

REFERENCES FOR ANALYSES

FIG. 1. Thomsonite numbers 9, 12, 15, 18, 26–28, 31, 36–42, 44, 46, 49–53, 56, 57, 61, 66 and 67 are Doelter's[1] numbers and 69 to 74 are listed on p. 93, *Am. Mineral.*, vol. **10,** 1925.

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77. Sextant Rapids, Ont. Walker, T. L.: *Univ. Toronto Geol. Ser.*, vol. **32,** p. 5, 1932.

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78. Grant Co., Ore. Hewett, D. F., *et. al.: Proc. U. S. Nat. Mus.*, vol. **73,** 1928, Art. 16.
79. Valle di Vin. Gennaro, Va.: *Atti Accad. Sci. Torino*, vol. **64**, p. 133, 1929.
80. Monte Rosa. Gennaro, Va.: *loc. cit.* Also *Min. Abst.*, vol. **4,** p. 376, 1930.
81. Table Mt., Colo. Hey, M. H.: *Mineral. Mag.*, vol. **23,** p. 51, 1932.
82. Nolsö, Faroe Isl. Hey, M. H.: *loc. cit.*
83. Goble, Ore. Hey, M. H.: *loc. cit.*
84. Nolsö, Faroe Isl. Hey, M. H.: *loc. cit.*
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91. Bozen, Tyrol. Hey, M. H.: *loc. cit.*
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94. Monte Somma. Hey, M. H.: *loc. cit.*
95. Old Kilpatrick. Hey, M. H.: *loc. cit.*
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97, 98. Disco Isl., Greenland. Gaertner, H. R., and Machatschki, F.: *Cent. Min.*, A, p. 365, **1927.**

Chabazite numbers 4, 5, 27, 32, 37, 39, 46, 52, 57, 77–79, 87, 89 and 96–99 are Doelter's numbers.

100. Boise Co., Idaho. Shannon, E. V.: *U. S. Nat. Mus., Bull.*, **131,** p. 357, 1926.

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110, 111. Csódi-Berg, Hungary. Reichert, R. and Erdelyi, J.: *Tsch. Min. Pet. Mit.*, vol. **46,** p. 237, 1935.

Gmelinite numbers 1, 2, 3, 7, 9–11, 13 and 15 are Doelter's numbers:

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101–103. White Head, Ireland. Smith, G. F. H., Ashcroft, F. N. and Prior, G. T.: *Mineral. Mag.*, vol. **17,** p. 274, 1916.

Fig. 2. Phillipsite numbers 2, 3, 7, 8, 10, 16–19, 23–27, 38 and 40–43 are Doelter's numbers.

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47. Leipa, Bohemia. Koenigsberger, J. and Müller, W. J.: *N. Jahrb. Bl. Bd.*, **44,** p. 402, 1921.

Stilbite numbers 12, 26–28, 32, 46, 72 and 76 are Doelter's numbers.

80. Partridge Isl., N. S. Parsons, A. L.: *Univ. Toronto Stud., Geol. Ser.*, **14,** p. 68, 1922.
81. Long Point, N. S. Parsons, A. L.: *loc. cit.*
82. Morden, N. S. Parsons, A. L.: *loc. cit.*
85. Gooseberry, W. Austral. Simpson, E. S.: *Min. Abst.*, vol. **5,** p. 94, 1932.
86. Piedmont. Resegotti, G.: *Min. Abst.*, vol. **5,** p. 83, 1932.
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FIG. 3. Gismondite numbers 3 to 10 are Doelter's numbers.

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Scolecite numbers 9, 16, 24, 25, 27–29, 39 and 40 are Doelter's numbers.

41. Digby Gut, N. S. Walker, T. L.: *Univ. Toronto Geol. Ser.*, **14**, p. 67, 1922.
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44. Miage, Italy. Bianchi, A. and Cavinato, A.: *Min. Abst.*, vol. **4**, p. 470, 1930.
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47. Maderanertal, Switz. Cavinato, A.: *loc. cit.*
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Mesolite numbers 10, 11, 25, 26 and 28 are Doelter's numbers.

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45. Iceland, Hey, M. H.: *loc. cit.*
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78. Salesl. Hey, M. H.: *loc. cit.*
80. De Beers Mine. Hey, M. H.: *loc. cit.*
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Laumontite numbers 3, 4, 6, 10, 14, 26, 39, 40, 46, 47 and 53 are Doelter's numbers.

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    This is the same as mordenite No. 3.

Mordenite numbers 3 and 4 are Doelter's numbers.

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Ptilolite numbers 1, 2, 3 and 5 are Doelter's numbers.

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