$CH_3COOC_2H_5Cl_3$ and $CH_3COOC_2H_5Br_3$ being formed. This regularity is not shown in the case of the halogen acid compounds.

COLLECTED RESULTS.

| Compounds. | M. P. |
|---|---|
| $(CH_3HO)_3(HCl)_2$ | $-64°$ |
| $(CH_3CHO)_2(HCl)_3$ | $-18°$ |
| $(CH_3COOH)_2(HCl)_3$ | $-53°$ |
| $(CH_3COOC_2H_5)(HCl)_2$ | $-75°$ |
| $(CH_3CHO)_2(HBr)_3$ | $-15°$ |
| $(CH_3COOC_2H_5)_2(HBr)_3$ | $-40°$ |
| $(CH_3CHO)_3(HI)_2$ | $-32°$ |
| $CH_3COOC_2H_5HI$ | $-23°$ |

No attempt has been made to indicate the constitutions of these bodies, which may be done by making the oxygen a tetrad. That these compounds differ in many respects from the so-called molecular combinations (salts with water of crystallization etc.), I shall attempt to show in another paper.

McGILL UNIVERSITY, March, 1906.

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## THE CONSTITUTION OF CERTAIN NATURAL SILICATES.[1]

BY H. C. McNEIL.

THE representation of natural silicates as substitution products of simple silicic acids, was begun by Professor Clarke about 1886 and has been developed continuously ever since. A formula to be satisfactory is expected to accord, with all known facts of the genesis, alterations, artificial syntheses and transformations, as well as physical and chemical properties of the mineral. The chief lines of laboratory work have been fractional analyses by several methods, and varied substitution reactions.

The graphical representations of Butureanu,[2] Vernadsky,[3] and Simmonds,[4] may be mentioned as the more recent attempts in this line.

The present investigation was carried out in the Chemical Laboratory of the United States Geological Survey, under the supervision of Professor Clarke, in the development of his theory

[2] Bull. soc. sci. fis. Bucuresci, 1896, 60-73, 117-124, 129-139, 254-279.

[3] Z. Kryst. Min. 34, 37-66 (1901).

[4] J. Chem. Soc. 1903, 1449-1469, and Ibid. 1904, 681-685.

of the constitution of the natural silicates. In one part of the work a simple method was sought for the breaking down of the molecule in fractions, and thus, if possible, to arrive at some conclusions as to its structure. In the second part substitutions within the molecule were studied.

Much of the material used was that already prepared and analyzed in the Survey laboratory. When such material was not available a sample in sufficiently large amount was finely ground and a careful analysis made. The experiments were then carried out on that particular sample. In the first part of the work a sodium carbonate solution, consisting of 100 cc. of water and 25 grams of sodium carbonate, was adopted as one reagent. The experiments were carried out by boiling about a half gram of the prepared mineral in this solution in a covered platinum dish, water being added as it was lost by evaporation. The silica that went into solution was determined by acidifying with hydrochloric acid and evaporating in the usual way. In other experiments 30 cc. of hydrochloric acid consisting of 25 cc. of fully concentrated acid and 5 of water were used. In a covered platinum crucible this would not change bulk appreciably in the longest digestions on the steam-bath. The digestion of the mineral was concluded by evaporating off the hydrochloric acid on the steam-bath. The residue was then treated with hot water, acidified with hydrochloric acid, and the dissolved material determined.

These reagents have been used considerably for the purpose of determining the amounts of silica and alumina liberated under certain conditions, and it was thought that by repeated treatment alternately, some insight into the molecular arrangement might be obtained. The minerals studied were treated with these reagents in a variety of ways and through varying periods of time, in the natural state, after dehydration at low temperatures, and after blasting.

*Talc.*—A series of twenty-nine experiments was carried out on a sample of talc on the supposition that it was pyrophyllite and rapidly brought to a close when its true nature was determined. The results confirm the observation of Clarke and Schneider[1] that on sharp blasting talc is broken down and yields one-fourth of its silica in a form soluble in a solution of sodium carbonate. The treatment with the sodium carbonate solution must be

[1] Bull. U. S. Geol. Survey, No. 78, 13-15.

rather thorough.  Digestion on the steam-bath is not sufficient. Gentle boiling for three hours gave satisfactory results.  The part insoluble in sodium carbonate solution is broken down as a whole by the hydrochloric acid used, and not some part of it removed, the effect being so great as to argue against the metasilicate formula for it, that being characterized by great stability toward hydrochloric acid.  The results in general are best represented by considering talc to contain an ortho- and a trisilicate radicle, which latter on blasting is transformed into a $Si_2O_5$ group.  This interpretation is in as good accord with alteration data as any other and was proposed as a possibility by Professor Clarke.[1]

*Kaolin.*—Thirty experiments were carried out on a sample of kaolin from Aikin, S. C., which, according to the analysis of Mr. Steiger,[2] contained 44.94 per cent. $SiO_2$; 39.18 per cent. $Al_2O_3$; and 13.85 per cent. water yielded above 100° C.

A half-gram sample boiled with sodium carbonate lost 1.64 per cent. $SiO_2$.  On blasting and treating with the carbonate solution it gave up 2.60 per cent., and when dehydrated at a barely red heat 3.50 per cent. of silica was obtained on three hours' boiling.  To the hydrochlroic acid the kaolin lost 2.97 per cent. $Al_2O_3$.  After blasting, only 1 per cent. of $Al_2O_3$ was obtained on twenty hours' digestion and smaller amounts for a shorter time. On heating barely to redness one hour the loss was 13.51 per cent., and the dehydrated residue yielded 38.79 per cent. $Al_2O_3$ to the acid reagent.

The effect of sodium carbonate solution on kaolin is small. However, the blasted residue, which by treatment with the acid gave only 1 per cent. of $Al_2O_3$, lost 7 per cent. of $SiO_2$ on boiling in the alkali.  Similar results were obtained on repetition with other samples.  A blasted sample, after treatment with the carbonate solution to which it gave up 1.39 per cent. $SiO_2$, yielded 8.81 per cent. $Al_2O_3$ to the acid.
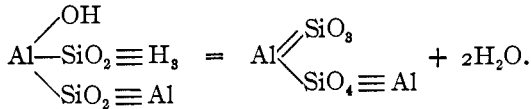
The increase in the amount of material dissolved by one reagent when following a treatment by the other is very noticeable.  There is no evidence that the composition of the residue changes, for alumina or silica is in excess, depending on whether the last treatment was with carbonate solution or acid.

Experiments with alumina and freshly prepared silica, mixed

[1] Bull. U. S. Geol. Survey, No. 125.

[2] Ibid. No. 228, p. 355.

and blasted together in the proportion found in kaolin, gave almost no solubility of the silica, and solubility of the alumina almost three times as great as with the kaolin. The formation of $Al_2Si_2O_7$ on igniting kaolin is favored, therefore, rather than the formation of a mixture of $Al_2O_3$ and $SiO_2$. The formation of such a compound is easily explained on the supposition that kaolin is an orthosilicate of the constitution proposed by Professor Clarke to accord with its genesis.[1]

$$Al{\overset{\displaystyle /OH}{\underset{\displaystyle \backslash SiO_2 \equiv Al}{-SiO_2 \equiv H_3}}} = Al{\overset{\displaystyle /SiO_3}{\underset{\displaystyle \backslash SiO_4 \equiv Al}{}}} + 2H_2O.$$

Experiment shows that the residue when dehydrated at a low temperature, is completely decomposed by hydrochloric acid, but if blasted, it is but slightly attacked. A possible explanation is that on ignition the residue polymerizes. The explanation of Vernadsky, who assumes that the water in kaolin is held half by the alumina and half by the silica, and only that held by the alumina is driven off at low redness, leaving a partially hydrated molecule decomposable by hydrochloric acid, is proven incorrect, for the kaolin is practically dehydrated at low redness but is almost entirely decomposed by the acid treatment following.

Some experiments of Thugutt[1] have indicated that one-third of the aluminum in kaolin differs from the rest. Indications were found in this work pointing in the same direction, but in an experiment carried out to test this point, the rate of solution runs at a maximum until over one-third of the alumina is dissolved, when there is a decline in the rate, which continues to the end of the experiment, as might be expected if working with a substance of simple constitution. Other experiments bearing on this point fall into line with this observation. All the evidence in this series of experiments favors the formula cited above.

*Halloysite.*—Halloysite being entirely decomposed by hydrochloric acid, only the product of ignition could be studied by the method used in this investigation. Seven experiments upon a sample from Nevada, nine upon a sample from Texas, and fifteen upon a sample from Kentucky indicate that, on blasting, the compound $Al_2Si_2O_7$ is formed as in the case of kaolin. This

[1] Bull. U. S. Geol. Survey, No. 125, pp. 31–32.
[2] Neues Jahrb. Min., Beilage, Band 9, 592–598.

residue is appreciably more soluble in hydrochloric acid than when derived from kaolin. The formula for kaolin with one added molecule of water satisfies our present knowledge of halloysite. The difference in the effect of acid on kaolin and halloysite may be referred to this water of crystallization, for which there is no adequate theory.

*Pyrophyllite.*—Seventeen experiments with pyrophyllite showed extreme stability toward the reagents used, though by repeated digestions alternately with acid and alkali it was slowly disintegrated. Blasting had little influence. The carbonate solution showed somewhat greater effect than the acid. Pyrophyllite may be regarded as a true acid metasilicate.

## ZEOLITES.

The second part of the work consisted in making substitutions of various metals, using members of the zeolite group for the experiments, as described hereafter. This work follows the same general lines as experiments carried on in the Chemical Laboratory of the Geological Survey for several years by Mr. Steiger, on the same and other minerals. In his experiments sealed tubes have been used, and ammonium, silver, and thallium substitutions, chiefly, were studied. The substitutions herein described were effected by fusion in a platinum crucible at atmospheric pressure.

The formulations were derived by dividing the percentages in the analysis by the molecular weight of the constituent in question, the result thus obtained being used without change.

*Analcite.*—The material used in these experiments was an analyzed sample from Table Mountain, Colorado, upon which work had already been done by Mr. Steiger. It contained, according to his analysis,[1] $SiO_2$ 55.72 per cent., $Al_2O_3$ 23.06 per cent., $Na_2O$ 12.46 per cent., $H_2O$ 8.39 per cent., and CaO 0.17 per cent. Ignoring the water and combining the monoxide bases, this analcite may be formulated: $R'_{208}Al_{226}Si_{482}O_{1364}$. This may be regarded as made up of a commingling of $SiO_4$ groups with $Si_3O_8$ groups in the proportion of 99 : 121. Combining these, the formula becomes $R'_{208}Al_{226}X_{220}$, where X stands for the silica radicle in general.

Two grams of analcite and 12 grams of pure barium chloride were fused in a platinum crucible for thirty minutes. An infusible skeleton floated in suspension in the mass. On washing

[1] Bull. U. S. Geol. Survey, No. 207, 11.

the cooled melt, a flocculent residue could be distinguished from a glassy or gritty one. The latter was ground in an agate mortar, washed until barium ceased to be found in the wash-water, dried at 107°, and analyzed.

Analysis A and corresponding formulation derived as with the original analcite.

| Analysis. Per cent. | Formulation. |
|---|---|
| $SiO_2$ ................................ 40.00 | $Ba_{261}Al_{356}Si_{622}G_{2039}$. |
| $Al_2O_3$ ............................. 18.16 | $SiO_4:Si_3O_8::286:112$. |
| BaO............................... 40.00 | $Ba_{261}Al_{356}X_{398}$. |
| $Na_2O$ ............................. 0.08 | |
| $H_2O$............................... 1.65 | |
| Total..................... 99.89 | |

The flocculent material was not in sufficient quantity to furnish a satisfactory analysis.

In succeeding experiments, increasing quantities of barium chloride were used, up to 25 grams. With the increase in the amount of the barium chloride a better fusion was obtained and a lower temperature made possible. The glassy product diminished or disappeared while the flocculent material was much more abundant. A typical analysis of this is given.

| Analysis. Per cent. | Formulation. |
|---|---|
| $SiO_2$........ .................... 45.61 | $Ba_{204}Al_{406}Si_{755}O_{2323}$. |
| $Al_2O_3$........... .............. 20.71 | $SiO_4:Si_3O_8::230:176$. |
| BaO................... 31.36 | $Ba_{204}Al_{406}X_{406}$. |
| $Na_2O$........................ Not determined. | |
| $H_2O$............................. 1.78 | |
| Total..................... 99.46 | |

The filtrate from washing the above product yielded 0.2116 gram of silica or 19 per cent. of the total silica in the analcite used, and 0.1042 gram of alumina or 22.6 per cent. of the total alumina.

The first object of the experiments, the substitution of barium for sodium, has been accomplished perfectly. Accompanying this change there has been a breaking down of the analcite to a considerable extent, as shown by the variations in the formulas and the change in the proportions of $SiO_4$ to $Si_3O_8$. The silica and alumina thus liberated are dissolved by the barium chloride in somewhat near the same proportions, apparently, so that their presence, while rendering the results less concordant than is to be

desired, does not obscure the general similarity of the barium product to the original analcite, as shown by the approximation to the proportion Ba:Al:X as $1:2:2$ in the general formulas, corresponding to $R':Al:X$ as $2:2:2$ in analcite. Since the products of substitution are readily decomposed by hydrochloric acid, and to some extent by the carbonate solution, it is not possible to remove the freed alumina and silica and thus have a pure residue for analysis. The glassy and flocculent products show that we are dealing with mixtures, also.

To test the solubility of silica in fused barium chloride, a gram of freshly prepared silica was blasted and subjected to treatment with fused barium chloride for thirty minutes. On cooling and digesting with water, 9.73 per cent. of the silica was found in the filtrate.

A repetition with 10 grams of barium chloride yielded 9.45 per cent. of silica. With powdered quartz in 10 grams of barium chloride 7.71 per cent. was dissolved. When only 10 grams of barium chloride were used, the addition of the silica necessitated an increase of the temperature almost to the limit of the blast-lamp to keep the mass in a state of fusion. The residue was glassy but on digestion in water it left behind pure silica, the clear filtrates yielding the amounts above stated.

Alumina is not soluble in fused barium chloride, even the air-dried hydroxide, unignited, failing to give results. But the moist hydroxide made from metallic aluminum in sufficient amount to equal 1 gram of alumina, mixed with 10 grams of barium chloride and slowly heated to fusion and so maintained for thirty minutes, gave 11.15 per cent. of the alumina in the filtrate. This unexpected solubility of silica and alumina deserves further investigation.

Where large amounts of barium chloride were used in the analcite experiments perhaps the silica liberated in the destruction of the molecule was largely dissolved, and the alumina only a little less so. In the preparation of the products such as analyzed in A the barium chloride was not in sufficient amount to give a good fusion, but the mass remained pasty. The excess of barium in these products may have been caused by mixtures formed under those circumstances. With a large excess of barium chloride and as low a temperature as possible barely to maintain the salt in fusion, it may be possible to obtain pure products, and make the interpretation of the results possible.

Experiments with strontium chloride show that strontium displaces sodium in analcite completely. The accompanying decomposition is even greater than with barium chloride but the residue obtained still shows the same general type.
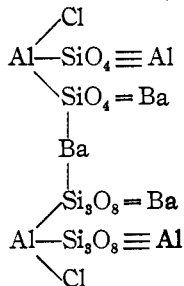
*Chabazite.*—The chabazite used was a sample from Wassons Bluff, Nova Scotia, used in former experiments in the Survey Chemical Laboratory. The analysis given is by Mr. Steiger:[1] $SiO_2$, 50.78 per cent.; $Al_2O_3$, 17.18 per cent.; CaO, 7.84 per cent.; $Na_2O$, 1.28 per cent.; $K_2O$, 0.73 per cent.; $H_2O$, 21.85 per cent.; $Fe_2O_3$, 0.40 per cent. The formula for this chabazite, if the alkalis are combined, becomes: $R'_{66}Ca_{140}Al_{336}Si_{843}O_{2843}$; combining bases as calcium, $Ca_{173}Al_{336}Si_{843}O_{2843}$; $SiO_4 : Si_3O_8 :: 252 : 86$; $Ca_{173}Al_{336}X_{338}$.

⁻Two grams of chabazite, mixed with 20 grams of barium chloride and the mass kept in quiet fusion as with analcite, gave similar phenomena. The filtrate yielded 20.3 per cent. of the total silica and 11.96 per cent. of the total alumina in the fusion, or $Al_2O_3 : SiO_2 :: 1 : 8\frac{1}{2}$. Analysis B and the formulation are given.

| | A. Per cent. | B. Per cent. | Formulation. |
|---|---|---|---|
| $SiO_2$ | 40.09 | 39.68 | $Ba_{264}Al_{320}Si_{859}O_{1985}.Cl_{153}$. |
| $Al_2O_3$ | 17.00 | 16.31 | $SiO_4 : Si_3O_3 :: 163 : 171$. |
| BaO | 38.33 | 40.37 | $Ba_{264}Al_{320}X_{334}.Cl_{153}$. |
| Cl | 5.91 | 5.44 | |
| Less $O = Cl$ | 1.63 | 1.24 | |
| Total | 100.00 | 100.56 | |

This product is represented by the formula given below, which is of the general chabazite form with chlorine replacing a group $Si_8O_8 \equiv H_2(AlO_2H_2)$, and corresponds to the composition given as the calculated in A. A closer approximation to the analysis could hardly be expected under the circumstances of its production.

Formula for (A).

$$
\begin{array}{c}
Cl \\
\diagup \\
Al{-}SiO_4 \equiv Al \\
\diagdown \\
SiO_4 = Ba \\
| \\
Ba \\
| \\
\diagup Si_8O_8 = Ba \\
Al{-}Si_8O_8 \equiv Al \\
\diagdown \\
Cl
\end{array}
$$

[1] Bull. U. S. Geol. Survey, No. 207, p. 32.

Another preparation confirmed the above.

The substitution of barium for calcium being found so complete, sodium substitutions were next attempted.

Twenty grams of sodium chloride were fused and 2 grams of chabazite added and kept in fusion thirty minutes. A brisk reaction ensued and a glassy skeleton soon formed that remained unchanged. The product was washed until chlorine-free. No silica or aluminum was found in the filtrate, but 6.70 per cent. of the calcium oxide was obtained, reckoned on the original chabazite. The residue gently ignited gave the following analysis and formula:

|  | Analysis. Per cent. | Formulation. |
|---|---|---|
| $SiO_2$ | 55.40 | $Na_{338}Ca_{24}Al_{394}Si_{920}O_{2640}.Cl_{188}.$ |
| $Al_2O_3$ | 20.16 | $SiO_4 : Si_3O_8 :: 140 : 260.$ |
| CaO | 1.36 | $R'_{608}Al_{394}X_{400}.$ |
| $Na_2O$ | 17.33 | |
| Cl | 6.69 | |
| Less | 1.51 | $O = Cl.$ |
| Total | 99.43 | |

It is noticeable that with sodium the substitution is not so complete as it is with barium. Using a formula of the same type as for the barium chabazite, and computing the calcium to sodium, this may be represented as a mixture in the proportion of two to one of

$$Al{<}^{Cl}_{Si_3O_8 \equiv Na_3}{-}Si_3O_8 \equiv Al \qquad and \qquad Al{<}^{Cl}_{SiO_4 \equiv Na_3}{-}SiO_4 \equiv Al .$$
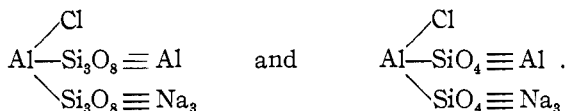
The composition for this is shown in A and the analysis calculated to 100 per cent. and bases as sodium in B.

|  | A. Per cent. | B. Per cent. |
|---|---|---|
| $SiO_2$ | 55.72 | 55.58 |
| $Al_2O_3$ | 20.30 | 20.24 |
| $Na_2O$ | 18.51 | 18.98 |
| Cl | 7.06 | 6.71 |
| Less $O = Cl$ | 1.59 | 1.52 |
| Total | 100.00 | 100.00 |

*Stilbite.*—The sample of stilbite used was from that already prepared and used in experiments carried out recently by Mr. Steiger.[1]
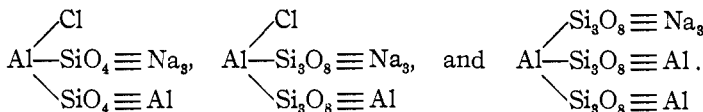
[1] Bull. U. S. Geol. Survey, No. 207, p. 29.

Analysis gives: $SiO_2$, 55.41 per cent.; $Al_2O_3$, 16.85 per cent.; CaO, 7.78 per cent.; $Na_2O$, 1.23 per cent.; and $H_2O$, 19.01 per cent. Neglecting the water and calculating to 100 per cent. the formulation becomes: $Na_{48}Ca_{170}Al_{410}Si_{1130}O_{3069}$. Combining sodium and calcium gives: $Ca_{194}Al_{410}Si_{1130}O_{3169}$; $SiO_4:Si_3O_8::44:363$; $Ca_{194}Al_{410}X_{407}$.

Twenty grams of sodium chloride and 2 grams of stilbite, fused together, gave exactly the same phenomena as chabazite. Analysis was made on the thoroughly washed mass, which was glassy in appearance. In a repetition of the above experiment the same results were obtained. An analysis is given.

|  | Analysis.<br>Per cent. | Formulation. |
|---|---|---|
| $SiO_2$ | 65.58 | $Na_{418}Al_{396}Si_{1089}O_{2981}\cdot Cl_{49}$. |
| $Al_2O_3$ | 20.21 | $SiO_4:Si_3O_8::39:350$. |
| CaO | 0.79 | $Na_{418}Al_{396}X_{389}$. |
| $Na_2O$ | 12.10 | |
| Cl | 1.76 | |
| Less O = Cl | 0.40 | |
| Total | 100.04 | |

Accounting for the sodium in the same way as in the sodium chabazite, the sodium stilbite may be regarded as a mixture in the proportions of $1:1:4$ of

$$Al\overset{\diagup Cl}{\underset{\diagdown SiO_4\equiv Al}{-SiO_4\equiv Na_3,}} \quad Al\overset{\diagup Cl}{\underset{\diagdown Si_3O_8\equiv Al}{-Si_3O_8\equiv Na_3,}} \quad \text{and} \quad Al\overset{\diagup Si_3O_8\equiv Na_3}{\underset{\diagdown Si_3O_8\equiv Al}{-Si_3O_8\equiv Al}}.$$

The percentage composition of such a mixture is shown in A, and the average of the analyses, calculated to 100 per cent., and the monoxide bases reckoned as $Na_2O$ is shown in B.

|  | A.<br>Per cent. | B.<br>Per cent. |
|---|---|---|
| $SiO_2$ | 64.88 | 65.00 |
| $Al_2O_3$ | 20.05 | 20.03 |
| $Na_2O$ | 13.72 | 13.64 |
| Cl | 1.74 | 1.72 |
| Less O = Cl | 0.39 | 0.39 |
| Total | 100.00 | 100.00 |

With sodium the substitution is not complete, as it is with barium and strontium, though more nearly so than in chabazite. The breaking down of the mineral is little, however, and the alumina and silica formed by such decomposition, if it occurs,

are not dissolved and removed by the sodium chloride as was the case with the barium and strontium chlorides. The agreement of the analyses with each other and with the theoretical is therefore satisfactory.

*Thomsonite.*—Like the preceding, the material used was from a sample analyzed and used in similar work by Mr. Steiger.[1] His analysis gives: $SiO_2$, 41.13 per cent.; $Al_2O_3$, 29.58 per cent.; CaO, 11.58 per cent.; $Na_2O$, 5.31 per cent.; $H_2O$, 13.13 per cent.; total, 100.40 per cent.
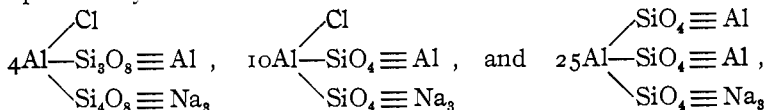
Neglecting the water and calculating to 100 per cent. the formulation becomes: $Na_{196}Ca_{230}Al_{664}Si_{783}O_{2890}$. Counting all the bases as sodium it becomes: $Na_{656}Al_{664}Si_{783}O_{2890}$; $SiO_4 : Si_3O_8 :: 602 : 60$; $Na_{656}Al_{664}X_{662}$.

Twenty grams of sodium chloride and 2 grams of thomsonite were fused together, as in the experiments with chabazite and stilbite, with the same results, except that the product of the reaction could not be fused into one mass at the temperature of melted sodium chloride, as was the case with chabazite and stilbite. The product was ground in an agate mortar and washed with great thoroughness. 8.11 per cent. of calcium oxide was found in the wash-water.

A second experiment repeated the first except that the product was ground unusually fine and washed with extreme thoroughness. The results were entirely similar. An analysis and formulation follows.

| Analysis. Per cent. | Formulation. |
|---|---|
| $SiO_2$.......................... 43.60 | $Na_{596}Ca_{50}Al_{650}Si_{724}O_{2729}.Cl_{84}$. |
| $Al_2O_3$......................... 33.18 | $Na_{696}Al_{650}Si_{724}O_{2729}.Cl_{84}$. |
| CaO........................... 2.81 | $SiO_4 : Si_3O_8 :: 631 : 31$. |
| $Na_2O$ ........................ 18.51 | $Na_{696}Al_{650}X_{662}$. |
| Cl ............................ 2.97 | |
| Less O = Cl............... 0.67 | |
| Total ...................100.00 | |

Representing the results with thomsonite on a basis similar to that used for chabazite and stilbite, they may be graphically expressed by

$$4Al{\overset{\displaystyle /Cl}{\underset{\displaystyle \backslash Si_4O_8 \equiv Na_3}{-Si_3O_8 \equiv Al}}} , \quad 10Al{\overset{\displaystyle /Cl}{\underset{\displaystyle \backslash SiO_4 \equiv Na_3}{-SiO_4 \equiv Al}}} , \quad and \quad 25Al{\overset{\displaystyle /SiO_4 \equiv Al}{\underset{\displaystyle \backslash SiO_4 \equiv Na_3}{-SiO_4 \equiv Al}}} ,$$
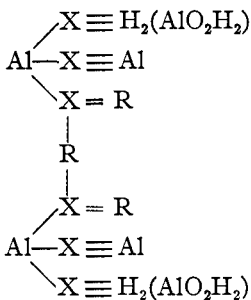
[1] Bull. U. S. Geol. Survey, No. 207, p. 34.

which corresponds to A.   The average of the analyses, computed to 100 per cent. and calcium oxide calculated to sodium oxide, is shown in B.

|  | A.<br>Per cent. | B.<br>Per cent. |
|---|---|---|
| $SiO_2$ | 43.53 | 43.76 |
| $Al_2O_3$ | 32.02 | 32.67 |
| $Na_2O$ | 22.11 | 21.26 |
| Cl | 3.03 | 2.98 |
| Less $O = Cl$ | 0.69 | 0.67 |
| Total | 100.00 | 100.00 |

This formulation best represents the known facts, and places chabazite, stilbite and thomsonite in the same class of zeolites, based on a generalized formula of the type given below, in which X represents chiefly the $SiO_4$ group in thomsonite, principally $Si_3O_8$ in stilbite, and a more nearly equal commingling of the two in chabazite.

$$
\begin{array}{l}
\quad\quad\diagup X \equiv H_2(AlO_2H_2) \\
Al\!-\!X \equiv Al \\
\quad\quad\diagdown X = R \\
\quad\quad\quad | \\
\quad\quad\quad R \\
\quad\quad\quad | \\
\quad\quad\diagup X = R \\
Al\!-\!X \equiv Al \\
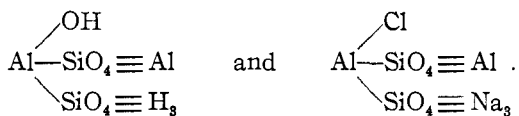\quad\quad\diagdown X \equiv H_2(AlO_2H_2)
\end{array}
$$

Generalized formula for thomsonite, stilbite and chabazite.

The results of Mr. Steiger,[1] where silver nitrate or thallium nitrate was used and the $N_2O_5$ group was retained similarly to the chlorine, admit of the same interpretation as the one used here for the chlorine compounds. Other interpretations are possible for single cases but none found can be applied so generally.

A comparison of this general formula, with that of the chlorine derivative under chabazite, indicates that the basic aluminum is the point of attack for chlorine or $N_2O_5$. On dehydration, presumably, this aluminum atom has its three valences satisfied by the acid like the other aluminum atoms. Experiments with these zeolites carefully dehydrated before treatment with the fused chloride ought to give valuable results.   It is hoped that presently work along this line may be taken up, together with an attempt

[1] Bull. U. S. Geol. Survey, No. 262.

to synthesize by substitutions on kaolin, the sodium-chlorine derivative which is not known. Its relation to kaolin is shown by the formulas:

$$\begin{array}{ccc} \mathrm{Al} \overset{\textstyle / \mathrm{OH}}{\underset{\textstyle \backslash \mathrm{SiO_4} \equiv \mathrm{H_3}}{\mathrm{-SiO_4} \equiv \mathrm{Al}}} & \text{and} & \mathrm{Al} \overset{\textstyle / \mathrm{Cl}}{\underset{\textstyle \backslash \mathrm{SiO_4} \equiv \mathrm{Na_3}}{\mathrm{-SiO_4} \equiv \mathrm{Al}}} . \end{array}$$

## SUMMARY.

A method of fractional analysis has been devised and carried out on four minerals, both with and without previous ignition, in which the material abstracted and the residue left have been studied. This has given some data as to the structure. As a large number of minerals comes to be subjected to this treatment, and as the range of reagents possible to be used is widened, it promises to be a valuable aid in determining constitution.

The work on substitutions has shown that the metals are readily substituted, one for the other, even under the simplest conditions of heating in an open crucible. A type of formula accounting for the retention of chlorine, has been developed for chabazite, stilbite and thomsonite.

Incidentally, the surprising solubility of silica in fused barium chloride and of alumina under certain conditions has been noted and demonstrated.

I wish here to express my heartiest appreciation of the facilities provided, and to acknowledge my great obligation to Professor Clarke for his kindly interest and many invaluable suggestions during the progress of the work.

GEORGE WASHINGTON UNIVERSITY, 1905.

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## FERRICYANIDES OF MERCURY.

BY GUSTAVE FERNEKES.

IN A recent number of this Journal,[1] I described a compound, $K_2HgFe(CN)_6$, which is obtained as a precipitate by the action of mercuric chloride on potassium ferrocyanide. When a solution of potassium ferrocyanide is added to a solution of mercurous nitrate, a precipitate is also obtained. Furthermore, potassium ferricyanide gives precipitates with solutions of both mercuric

[1] This Journal, 28, 87.