ART. III.—*The Action of Ammonium Chloride upon certain Silicates*; by F. W. CLARKE and GEORGE STEIGER.

IN our previous communications* upon the ammonium chloride reaction, we have shown that different silicates are very differently affected by the reagent. From analcite, leucite, natrolite and scolecite we obtained new salts, in which the alkali or lime of the original mineral had been replaced by ammonium. On the other hand, prehnite was practically unattacked, while the pectolite molecule was quite thoroughly broken down, with liberation of much free silica. We now submit the results obtained with several additional silicates; results which serve to emphasize our former conclusions.

Our mode of operation has been precisely the same as before. Each mineral, in fine powder, was intimately mixed with four times its weight of dry ammonium chloride, and the mixture was then heated for about five or six hours to 350° in a sealed combustion tube. After cooling, the mixture was leached out with water, and the air-dried insoluble residue was analyzed. Determinations of free silica were effected by boiling the mineral, or its derivative, for fifteen minutes with a solution of sodium carbonate containing 250 grams to the liter. From the solution so obtained the silica was recovered by acidulation with hydrochloric acid and evaporation to dryness. In each case all of the experiments were made upon one uniform sample of material, so that the data for any one species are strictly comparable. So much premised, we may go on to consider the results of our investigations.

Stilbite.

The specimen selected for study was a nearly white, typical example from Wasson's Bluff, Nova Scotia. The analysis and the fractional water determinations were as follows:

Analysis.		Fractional water,	
SiO ₂	55.41	At 100°	3.60
Al ₂ O ₃	16.85	“ 180°	6.46
Fe ₂ O ₃	.18	“ 250°	3.80
MgO.....	.05	“ 350°	2.10
CaO.....	7.78	Low redness	2.95
Na ₂ O.....	1.23	Full “	.06
H ₂ O.....	19.01	Over blast	.04
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100.51		19.01	

* This Journal (4), ix, pp. 117, 345; February and May, 1900.

On boiling with sodium carbonate, 1.37 per cent of silica went into solution. After ignition, only 1.03 per cent was obtained. No silica, therefore, is split off when stilbite is ignited. If the mineral were a hydrous acid metasilicate, $H_4CaAl_2Si_6O_{18} \cdot 4H_2O$, as has been assumed by some authorities, one-third of the silica should have been set free. Hence the metasilicate formula is to be regarded as unsatisfactory. The evidence here presented counts for something against it.

Two samples of the ammonium chloride derivative were prepared. In leaching with water the insoluble residue was washed until the washings gave no reaction for chlorine. The chlorine shown in the subjoined analyses is, therefore, present in an insoluble form, and not as adhering ammonium chloride. Dried at 50° , the two products gave the following composition:

	A	B
SiO ₂	60.80	60.67
Al ₂ O ₃	18.36	18.25
CaO	1.86	1.46
Na ₂ O	.08	.15
NH ₃	5.12	5.13
H ₂ O	12.96	13.91
Cl	1.31	1.04
	<hr/>	<hr/>
	100.49	100.61
Less O	.29	.23
	<hr/>	<hr/>
	100.20	100.38

Sample B was further examined as to the presence of soluble silica, and 1.52 per cent was found. After ignition, only 1.62 per cent went into solution. These results conform to those obtained with the original stilbite, and tend to show that the ammonium derivative is a compound of the same order. In the case of the unignited substance the residue remaining after the removal of soluble silica was thoroughly washed, and then examined for alkali. It was found to contain 9.30 per cent of soda, which shows that the ammonium salt had been transformed back into the corresponding sodium compound.

From the foregoing facts it is clear that stilbite, like the zeolites previously studied, is converted by the action of ammonium chloride into an ammonium salt. That is, sodium and calcium are removed as chlorides, ammonium taking their place to form ammonium-stilbite. The reaction, however, is less complete than it was in the cases of analcite and natrolite, but whether this is due to a greater stability of the stilbite molecule, or only to a different degree of fineness in the powder upon which the operations were performed, we cannot

say. Neither have we any explanation to offer of the retention of chlorine by the ammonium derivative. Although the amount of chlorine is small, it needs to be accounted for.

If we discuss the composition of the stilbite and of its ammonium derivative, the relations between them become very clear. Neglecting the water as "zeolitic," to use Friedel's phrase, and, therefore, as not a part of the chemical molecule, and also rejecting the 1.37 per cent of soluble silica as probably an impurity, the ratios derived from the analysis give this empirical formula for the mineral:

This corresponds to a mixture of ortho- and trisilicates in which $\text{Si}_3\text{O}_8 : \text{SiO}_4 :: 286 : 43$; and uniting these radicles under the indiscriminate symbol X , we have, as a more general expression,

or, combining monoxide bases,

which is essentially $\text{R}''\text{Al}_2\text{X}_2$. Since the SiO_4 groups are practically equal in number to the sodium atoms, the stilbite is probably a mixture, very nearly, of NaAlSiO_4 and $\text{CaAl}_2(\text{Si}_3\text{O}_8)_2$ in the ratio of one to seven. This is in accordance with the well-known theory of Fresenius as to the constitution of the phillipsite group, to which stilbite belongs. Stilbite is mainly a hydrous calcium albite, commingled with varying amounts of corresponding orthosilicates of soda and lime.

For the ammonium derivative similar relations hold. Taking analysis "B" for discussion, rejecting soluble silica and chlorine as impurities, and neglecting all water except that which belongs to the supposable ammonium oxide, the ratios give this formula:

Uniting sodium and calcium with ammonium this becomes

or, more generally,

The derivative, therefore, is a compound of the same order as the original stilbite, with the ratio of 1 : 7 still holding between the ortho- and trisilicate groups. This conclusion, however, ignores the presence of chlorine, and is, therefore, inexact to some extent. We are not dealing with ideally pure compounds.

Heulandite.

Pure, white heulandite from Beruflörd, Iceland, was the material taken for investigation. Upon boiling with sodium carbonate, 1.73 per cent of silica went into solution. From previously ignited heulandite only 1.14 per cent was extracted. No silica, therefore, was liberated upon ignition, and a hydrous metasilicate formula for the mineral seems to be improbable. Only one lot of the ammonium chloride derivative was prepared, and its composition, together with that of the heulandite, is given below.

	Heulandite.	Ammonium salt.
SiO ₂	57.10	61.24
Al ₂ O ₃	16.82	18.00
MgO	.07	----
CaO	6.95	2.56
SrO	.46	----
Na ₂ O	1.25	} .60
K ₂ O	.42	
NH ₃	----	4.42
H ₂ O at 100°	3.61	} 13.63
H ₂ O above 100°	13.00	
	<hr/> 99.68	<hr/> 100.45

Here again we have the same kind of transformation as before, but rather less complete than in the case of stilbite. That the ammonium taken up is equivalent to the bases removed, is shown by a study of the ratios. Ignoring water and the soluble silica, the heulandite ratios are as follows:

or, uniting bases,

Again simplifying, this becomes

or very nearly 1 : 2 : 2, as in stilbite.

Similarly discussed, the ammonium salt gives the ratios

equivalent to

In both cases the orthosilicate molecules are few, and the compounds approximate to trisilicates very closely.

Chabazite.

Characteristic flesh-colored crystals from Wasson's Bluff, Nova Scotia. The analysis and fractional water determinations are as follows:

Analysis.		Fractional water.	
SiO ₂	50.78	At 100°	5.22
Al ₂ O ₃	17.18	" 180°	5.70
Fe ₂ O ₃	.40	" 250°	3.92
MgO	.04	" 350°	2.36
CaO	7.84	Low redness	4.51
Na ₂ O	1.28	Full redness	.13
K ₂ O	.73	Over blast	.01
H ₂ O	21.85		
			<hr/> 21.85
	100.10		

The unignited mineral, upon boiling with sodium carbonate, gave 0.86 per cent of soluble silica. After ignition only 0.53 per cent was soluble. Here again no silica is liberated by calcination, and metasilicate formulæ may be disregarded.

Two samples of the ammonium chloride derivative were prepared, which after thorough washing were dried at 40° to 50°. As in the case of stilbite, small quantities of chlorine appear in the compound, not removable by washing. The amount of change effected is also somewhat less than with stilbite, and about the same as with heulandite. The analyses of the two samples are subjoined, with the remaining alkali all reckoned as soda.

	A	B
SiO ₂	55.88	56.09
Al ₂ O ₃	19.15	19.49
CaO	2.25	2.01
Na ₂ O(K ₂ O)	.35	.24
NH ₃	4.64	4.83
H ₂ O	16.57	16.01
Cl	.95	1.35
	<hr/> 99.79	<hr/> 100.02
Less O	.21	.30
	<hr/> 99.58	<hr/> 99.72

In B, 1.50 per cent of soluble silica was found. After ignition, this was reduced to 1.12 per cent. No liberation of silica accompanies the splitting off of water and ammonia.

Upon studying the molecular ratios for chabazite and its derivative, relations appear precisely like those found for stilbite and heulandite. For chabazite itself, rejecting water and the 0.86 per cent of soluble silica, we have

or, consolidating soda with lime,

One step further and this becomes

$$\text{Ca}_{170} \text{Al}_{340} \text{X}_{340} = 1 : 2 : 2.$$

Treating derivative "B" in the same way, and ignoring chlorine as an unexplained impurity, the analysis gives

or, consolidating bases as before,

$$\text{R}'_{362} \text{Al}_{382} \text{X}_{378} = 1 : 1 : 1 \text{ nearly.}$$

The assumption of commingled ortho- and trisilicate molecules conforms to Streng's theory of the constitution of chabazite.

Thomsonite.

The compact-fibrous variety from Table Mountain, near Golden, Colorado. Analytical data as follows:

Analysis.		Fractional water.	
SiO ₂	41.13	At 100°	1.01
Al ₂ O ₃	29.58	" 180°	1.44
CaO	11.25	" 250°	1.05
Na ₂ O	5.31	" 350°	3.90
H ₂ O	13.13	Low redness	5.65
		Over blast	.08
	<hr/> 100.40		<hr/> 13.13

Before ignition the mineral yielded 0.45 per cent of silica to sodium carbonate solution. After ignition, 0.68 per cent was soluble. The difference is trifling.

Two samples of the ammonium chloride derivative were prepared. In "A" the heating was only to 300°, in "B" to 350°. Analyses of the leached products gave the following results:

	A	B
SiO ₂	42.41	42.65
Al ₂ O ₃	30.50	31.34
CaO	10.00	9.23
Na ₂ O	2.63	2.48
NH ₃	2.45	2.67
H ₂ O	11.96	11.81
	<hr/> 99.95	<hr/> 100.18

In "A," 1.80 per cent of soluble silica was found.

In this case the amount of change is very much less than with the zeolites previously examined. Little lime was removed, and only about half of the soda. Both samples were prepared with six hours of heating in the sealed tube, and it

seemed to be desirable to determine whether a more prolonged treatment would produce any greater effect. Accordingly a third lot of thomsonite was mixed with ammonium chloride, and heated in a sealed tube to 350° for 24 hours. The leached product contained 3.40 per cent of ammonia, a distinct increase over the other findings; although the amount of transformation into an ammonium salt was still only moderate.

We have already seen that stilbite, heulandite and chabazite approximate more or less nearly to trisilicates in their composition. Thomsonite, however, is essentially an orthosilicate, with variable admixtures of trisilicate molecules. In the example under consideration, ignoring water and soluble silica, the molecular ratios give this formula:

or, condensing,

Here the acid radicles are ten-elevenths orthosilicate. Ammonium derivative "A," similarly computed, gives first—

or, uniting univalent bases with line,

the fundamental ratios being practically unchanged.

It will be observed that in all of these computations of formulæ we have assumed that all the water is "zeolitic"; that is, independent of the true chemical molecules. This question, however, needs to be separately investigated for each individual species. While the assumption is valid for some of these minerals, it is not necessarily valid for all. The real chemical differences between the zeolites are yet to be determined; our work merely proves that ammonium compounds are formed, completely in some cases, partially in others. The research should be extended to cover all the zeolites; but this task we must leave to other investigators. Silicates belonging to quite different groups must now claim our attention.

Ilvaite.

This rare mineral was found by Mr. Waldemar Lindgren at the Golconda Mine, South Mountain, Owyhee County, Idaho. It occurs in jet black masses and occasional rough crystals, imbedded in quartz or calcite, and intimately associated with two other minerals which appear to be garnet and tremolite. Traces of pyrite also appear. The specific gravity of the ilvaite, as determined by Dr. Hillebrand, is 4.059 at 31°.

Upon grinding the powdered mineral with ammonium chloride in an agate mortar, a distinct smell of ammonia was noticeable. Three tubes of the mixture were heated to 350° , and one exploded because of the liberation of gas within. Upon opening the second and third tubes, a strong outrush of ammonia was observed. When the contents of these tubes were leached with water, large quantities of ferrous chloride went into solution; which, rapidly oxidizing, formed a deposit of brownish hydroxide, and interfered seriously with filtration. The greater part of the lime in the ilvaite was dissolved also. The washed residue, containing much ferric hydroxide, was partially analyzed, and enough data were obtained to show that a general breaking down of the ilvaite molecule had been effected. Apparently, also, small quantities of an ammonium derivative had been formed; but this point is uncertain. The original mineral was analyzed by Dr. W. F. Hillebrand; and his analysis, contrasted with that of the leached residue, is given below.

	Ilvaite (Hillebrand).	Residue (Steiger).
SiO ₂	29.16	43.01
Al ₂ O ₃	.52	} 40.08
Fe ₂ O ₃	20.40	
FeO	29.14	8.75
MnO	5.15	.85
CaO	13.02	2.25
MgO	.15	undet.
Na ₂ O	.08	undet.
NH ₃	---	.88
H ₂ O at 105°	.15	undet.
H ₂ O above 105°	2.64	undet.
Cl	---	small amount.
	<hr/> 100.41	<hr/> 95.82

In the leached residue from the third tube 21.37 per cent of soluble silica was found; silica which had been liberated during the reaction between the ilvaite and the ammonium chloride. In short, ilvaite behaves towards the reagent much like pectolite, and the product is a mixture of uncertain character. The evident instability of the ilvaite molecule may account for its rarity as a mineral species. Only exceptional conditions would favor its formation.

Riebeckite?

The results obtained with ilvaite made it desirable to study, for comparison, some other silicates of iron. Among these the mineral from St. Peter's Dome, near Pike's Peak, Colo-

rado, originally described by Koenig as arfvedsonite, but identified by Lacroix as near riebeckite, happened to be available. It was treated with ammonium chloride in the usual way, and no presence of liberated gas was noticed when the tube was opened. On leaching the product with water, ferrous chloride went into solution, and ferric hydroxide with some manganic hydroxide were deposited. In the leached mass 6.90 per cent of soluble silica was found, and in the wash water from the leaching there were 6.76 per cent of soda. According to Koenig's analysis the mineral contains 8.33 per cent of soda, so that a large portion of the total amount had been extracted. There was also, evidently, a considerable breaking down of the molecule, but no definite ammonium derivative had been formed. This is shown by the following analysis of the leached residue, which is contrasted with Koenig's published analysis* of the original mineral, in order to indicate the amount of change. In the third column of figures we give the amount of each constituent which could be dissolved out from the residue by treatment with hydrochloric acid.

	Riebeckite (Koenig).	Residue (Steiger).	Soluble portion.
SiO ₂	49.83	67.54	
TiO ₂	1.43	----	
ZrO ₂	.75	----	
Fe ₂ O ₃	14.87	21.28	15.74
FeO	18.86	4.94	4.94
MnO	1.75	.64	.64
MgO	.41	none	
CaO	----	trace	
Na ₂ O	8.33	} 1.04	
K ₂ O	1.44		
NH ₃	----	.53	.53
H ₂ O	.20 (ign.)	3.33	
Cl	----	trace	
	<hr/> 97.87	<hr/> 99.30	

The residue is evidently a mixture of free silica and ferric hydrate with probably at least two silicates, one soluble, the other insoluble in hydrochloric acid. The reaction itself is noteworthy because of the fact that the original mineral is but slightly attacked when boiled with strong hydrochloric acid. The other minerals so far studied by us are all easily decomposable by acids, while this one is quite refractory. The energetic character of the ammonium chloride reaction is thus strongly emphasized.

* Dana's System of Mineralogy, 6th ed., p. 400.

Aegirite.

Material from the well known locality at Magnet Cove, Arkansas. Not absolutely pure, but somewhat contaminated by ferric hydroxide. This impurity is evident in a discussion of the ratios furnished by the analysis, but is not serious. It does not affect the problems under consideration. By heating with ammonium chloride the mineral was only slightly changed. In the leach water from the product there were 1.66 per cent $(\text{AlFe})_2\text{O}_3$, 0.51 CaO, and 1.18 Na_2O . Analyses as follows: A of the aegirite, B of the air dried, leached residue.

	A	B
SiO_2	50.45	51.83
Al_2O_3	2.76	} 25.24
Fe_2O_3	23.42	
FeO	5.26	5.69
MnO	.10	----
MgO	1.48	1.58
CaO	5.92	5.74
Na_2O	9.84	} 9.07
K_2O	.24	
NH_3	----	.26
H_2O at 100°	.15	} .90
H_2O above 100°	.40	
	100.02	100.31

Of the silica in the residue 4.42 per cent was soluble in sodium carbonate solution. An ammonium derivative was not formed.

From these data we see that the three iron silicates are very differently attacked by ammonium chloride; ilvaite very strongly, riebeckite moderately, and aegirite but feebly. The aegirite is the most stable, and at the same time the commonest of the three. A comparison of the aegirite analysis with that made by J. Lawrence Smith of material from the same region, shows notable differences. The mineral evidently varies in composition; the variation depending upon the relative amounts of the two silicate molecules $\text{FeNaSi}_2\text{O}_6$ and R''SiO_3 . Two samples taken from different parts of the same rock area are not necessarily identical in composition.

Serpentine.

In 1890 Clarke and Schneider published an investigation* relative to the action of gaseous hydrochloric acid upon various minerals. Among these were the three species serpentine,

* Bulletin 78, U. S. Geol. Survey, p. 11.

leuchtenbergite, and phlogopite, and the remainders of the original samples were fortunately at our disposal. The analyses made by Schneider are, therefore, directly comparable with the new data secured by us.

The serpentine, from Newburyport, Massachusetts, was but moderately attacked upon heating with ammonium chloride. Upon leaching the contents of the sealed tube with water, 0.18 per cent of silica and 5.23 of magnesia went into solution. The washed residue and the serpentine had the following composition.

	Serpentine (Schneider).	Residue (Steiger).
SiO ₂	41.47	45.42
Fe ₂ O ₃ , Al ₂ O ₃	1.73	.88
MgO	41.70	39.54
FeO	.09	---
NH ₃	---	.09
H ₂ O	15.06	14.01
	<hr/> 100.05	<hr/> 99.94

The leached residue contained 1.06 per cent of soluble silica. The amount of change effected in the mineral was evidently small, and no ammonium compound was produced.

Leuchtenbergite.

From the standard locality near Slatoust in the Urals. When the contents of the sealed tube were leached with water, there passed into solution 0.19 per cent of alumina, plus iron, 2.10 of magnesia, and 2.03 of lime. The residue was not completely analyzed, but the few determinations made contrast with Schneider's results as follows:

	Leuchtenbergite.	Residue (Steiger).
SiO ₂	32.27	32.82
Al ₂ O ₃	16.05	
Fe ₂ O ₃	4.26	
FeO	.28	
MgO	29.75	
CaO	6.21	4.67
NH ₃	---	.25
H ₂ O	11.47	12.11
	<hr/> 100.29	

No definite ammonium compound was formed, and the amount of decomposition was small. As the lime shown by the analysis is at least partly due to the presence of garnet as an impurity in the mineral, it will be interesting to determine the effect producible by ammonium chloride upon that species.

Phlogopite.

From Burgess, Canada. The contents of the sealed tube, after heating, showed little appearance of change. The leach water contained magnesia. Analysis as follows:

	Phlogopite (Schneider).	Residue (Steiger).
SiO ₂	39.66	45.03
TiO ₂	.56	----
Al ₂ O ₃	17.00	} 15.07
Fe ₂ O ₃	.27	
FeO	.20	----
BaO	.62	----
MgO	26.49	24.94
Na ₂ O	.60	.94
K ₂ O	9.97	8.69
NH ₃	----	.21
H ₂ O	2.99	5.01
F	2.24	----
	<hr/>	<hr/>
	100.60	99.89
Less O	.94	
	<hr/>	
	99.66	

The residue, on boiling with sodium carbonate, gave 0.40 per cent of soluble silica. From these data it appears that phlogopite is somewhat attacked by ammonium chloride, but not strongly. No ammonium derivative is formed.

As opportunity offers, this investigation will be carried further, and the reaction will be applied to other mineral species.

Laboratory U. S. Geological Survey, Oct. 12, 1901.