

ART. XXXII.—*The Action of Ammonium Chloride upon Natrolite, Scolecite, Prehnite and Pectolite*; by F. W. CLARKE and GEORGE STEIGER.

IN our last paper upon the ammonium chloride reaction,* we showed that analcite and leucite, when heated to 350° with this reagent in a sealed tube, both yielded the same compound, ammonium leucite, $\text{NH}_4\text{AlSi}_2\text{O}_6$. We also showed that the reaction was not limited to these minerals, but that it was fairly general in character; and that with other species analogous results could be obtained. We now have data relative to four more minerals, and these exhibit a range of variation which well illustrates the availability of the method for investigations into the chemical constitution of silicates. Three of the species now studied have previously been regarded by one of us as analogous in structure, provided that all or part of their *water* can be interpreted as constitutional; and the formulæ assigned were as follows:

Scolecite	$\text{Al}_2(\text{SiO}_4)_3\text{CaH}_4\cdot\text{H}_2\text{O}$
Natrolite	$\text{Al}_2(\text{SiO}_4)_3\text{Na}_2\text{H}_4$
Prehnite.....	$\text{Al}_2(\text{SiO}_4)_3\text{Ca}_2\text{H}_2$

Two of these formulæ must now be abandoned, because of the experimental evidence which we have obtained. We may first study the three species individually.

Natrolite.

In our former paper we reported a crude, preliminary experiment made upon impure, yellowish natrolite from Aussig in Bohemia. After heating with ammonium chloride in a sealed tube and subsequent leaching with water, 17.56 per cent of soda was extracted, and in the residue 8.29 per cent of ammonia was found. Natrolite, therefore, was a suitable mineral for further investigation; and our expectations regarding it have been fully confirmed.

The material available for our new experiments came from the well known locality at Bergen Hill, New Jersey, and consisted of a mass of slender needles densely matted together. Part of the uniform, ground sample was analyzed, with fractional determinations of the water, and part was used for the sealed tube experiments, precisely as in the research upon analcite and leucite. Three of these experiments were made; and in each case the natrolite was mixed by grinding in an agate

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mortar with four times its weight of dry ammonium chloride, after which it was heated to 350° in the sealed tube. Even during the grinding a slight reaction took place, and a distinct smell of ammonia was given off by the mixture. With pectolite the same smell was perceived. The three experiments may be summarized as follows:

- A. Heated 11 hours. Upon leaching, 14.89 per cent of soda and 1.20 of lime were extracted. In the residue 9.26 per cent of ammonia was found.
- B. Heated 9 hours. Leach not examined. 9.26 of ammonia in residue. The complete analysis of the residue is given farther on.
- C. Heated 3 hours. 14.09 per cent of soda and 0.20 of lime were extracted. The residue contained 8.87 per cent of ammonia. In this instance the heating was relatively brief, in order to learn whether its duration could be advantageously lessened. The reaction was evidently less complete than in experiments A and B.

In the subjoined table we give first the analysis of the natrolite itself, and then that of the leached residue from experiment B. In the latter we found that 0.86 per cent of silica was soluble in sodium carbonate solution; and that soda and lime remained corresponding to 4.61 per cent of the original mineral. Deducting these impurities, together with the 0.42 per cent of hygroscopic water, and recalculating to 100 per cent, we get the *reduced* composition of the residue. In the last column is given the calculated composition of an anhydrous ammonium-natrolite, $(\text{NH}_4)_2\text{Al}_2\text{Si}_3\text{O}_{10}$. This compound has evidently been formed to an extent represented by over 94 per cent of the leached natrolite residue. The agreement between theory and even the unreduced analysis is practically conclusive on this point.

	Natrolite found.	Residue found.	Residue reduced.	$(\text{NH}_4)_2\text{Al}_2\text{Si}_3\text{O}_{10}$ calculated.
SiO_2	46.62	53.71	53.86	54.06
Al_2O_3	26.04	29.94	30.52	30.43
CaO	1.48	.34	----	----
K_2O	none	----	----	----
Na_2O	15.67	.37	----	----
NH_3	----	9.26	9.85	10.14
H_2O at 100°39	.42	----	----
H_2O above 100° ..	10.18	5.94	5.77	5.37
	100.38	99.98	100.00	100.00

It may not be superfluous to note that the water given in the last two columns represents the difference between ammonia and the hypothetical ammonium oxide which has replaced soda.

Two other experiments upon natrolite remain to be noticed. First, the fresh mineral was boiled for 15 minutes with a 25 per cent sodium carbonate solution; 0.72 per cent of silica dissolved. Similar treatment of ignited natrolite took out 0.62 per cent. No silica is split off by ignition. Ammonium-natrolite before ignition yielded 0.85 per cent of soluble silica, and after ignition 0.86 per cent. Here again no silica had been split off from the molecule, and practically none was liberated by the action of the ammonium chloride upon the natrolite. A simple, direct substitution of ammonium for sodium had occurred.

Scolecite.

On account of the well-recognized analogy between natrolite and scolecite, the latter mineral seemed to be peculiarly worthy of examination. The specimen at our disposal was a mass of stout, radiating needles, which was collected by one of us at Whale Cove, on the island of Grand Manan, New Brunswick. Scolecite, we believe, has not hitherto been recorded from this locality; and on this account alone the material deserved attention.

Three sealed tube experiments were carried out, essentially as in the case of natrolite, as follows:

- A. Heated 10 hours at 350°. 13.74 per cent of lime and 0.35 of soda were taken out. The residue contained 8.78 per cent of ammonia.
- B. Heated 10 hours at 370°. 12.97 of lime and 0.22 of soda were extracted. 8.48 per cent of ammonia in the residue. On account of the excessive temperature of this experiment, some reversion of the converted material had taken place.
- C. Heated 5 hours at 340°–350°. Leach not studied. 8.91 per cent of ammonia in residue.

Analyses of the scolecite and of residues B and C are given below. The less perfect transformation in the case of B is evident.

	Scolecite.	Residue B.	Residue C.
SiO ₂	45.86	53.39	53.69
Al ₂ O ₃	25.78	30.51	30.50
CaO	13.92	.62	.42
Na ₂ O41	undet.	.29
NH ₃	---	8.48	8.91
H ₂ O at 100°40	.74	.12
H ₂ O above 100°	13.65	6.28	6.52
	<hr/> 100.02	<hr/> 100.02	<hr/> 100.45

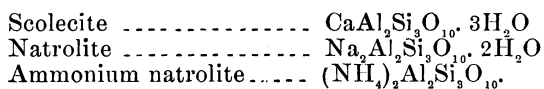
The product of the reaction is plainly the same as that obtained from natrolite, and the identity in type of the two

species is perfectly clear. This fact is further emphasized by an experiment upon the solubility of silica. The fresh scolecite gave up 0.36 per cent of silica to sodium carbonate solution, and the ignited mineral yielded only 0.50 per cent. Again, natrolite and scolecite behave in the same way.

Upon both minerals fractional determinations of the water were made, and the amount lost at each temperature was noted. The results, expressed in percentages of the original minerals, were as follows:

Temperature.	Water lost.	
	Natrolite.	Scolecite.
100°	·39	·40
180°	·40	·52
250°	·37	4·76
350°	8·51	·55
Incipient redness...	·72	7·72
Full redness	·12	·04
Over blast	·06	·06
	10·57	14·05

Scolecite contains one more molecule of water than natrolite, and that amount, one-third of its total, seems to go off at a lower temperature than the other two molecules. Otherwise the two series of experiments are probably not far apart, and they indicate that the water is in neither case constitutional. The same conclusion is suggested by the existence of the anhydrous ammonium compound, the three formulæ being as follows:



The parallelism is complete; and all three compounds are evidently salts of an acid $\text{H}_8\text{Si}_3\text{O}_{10}$, which is probably orthotrisilicic acid, $\text{Si}_3\text{O}_2(\text{OH})_8$. The second anhydride of this acid, $\text{H}_4\text{Si}_3\text{O}_8$, would be the ordinary trisilicic acid of orthoclase and albite; a relation which is certainly suggestive. We do not, however, care to enter upon the question of chemical structure in this paper, and we therefore leave the subject for fuller consideration at some future time. It is clear, however, that orthosilicate formulæ for natrolite and scolecite must be discarded.

Prehnite.

The prehnite taken for examination was an old specimen from Paterson, New Jersey. The analysis, with fractional water determinations, is given below.

Analysis.		Fractional water.	
SiO ₂	42.31	At 100°	.21
Al ₂ O ₃	19.95	At 180°	.18
Fe ₂ O ₃	6.20	At 250°	.10
FeO	none	At 350°	.11
CaO	26.63	Incipient red heat	.28
H ₂ O	5.02	Full red heat	4.05
	<hr/>	Over blast	<hr/> .09
	100.11	Total	5.02

With sodium carbonate solution, 0.38 per cent of silica was extracted from the fresh mineral. From the ignited prehnite, 1.22 per cent was taken out. Very little silica, therefore, is liberated by ignition.

Two determinations were made of the action of ammonium chloride, as follows:

- A. Heated 8 hours. On leaching with water, 1.31 per cent of lime and 0.17 of alumina dissolved.
- B. Heated 12 hours. 1.41 per cent of lime was extracted, and in the washed residue 0.22 per cent of ammonia was found.

Prehnite, therefore, differs widely from natrolite and scolecite in its behavior with ammonium chloride. Very little action takes place, even upon long heating to 350° in a sealed tube, and practically no ammonia is absorbed. The water is more firmly held than was the case with the other two minerals, and is almost certainly to be regarded as constitutional. The orthosilicate formula for prehnite is unaffected by these results, and may stand as fairly probable. Prehnite cannot be correlated with natrolite and scolecite on any basis of similar chemical structure.

Pectolite.

In the first paper of this series* we described a number of experiments upon pectolite, in which we showed that it was almost undoubtedly a metasilicate; but the action of ammonium chloride upon it was neglected, as having been studied already by Schneider and Clarke.† In their experiments upon pectolite from Bergen Hill, which was nearly identical in composition with our sample, a triple heating in an open crucible with ammonium chloride removed 20.50 per cent of lime, 6.95 of soda, and 0.54 of manganous oxide; or about two-thirds of the total amount of bases present. In our last paper we reported a preliminary experiment by the sealed tube method, and found that 20.72 per cent of lime and 6.46 of

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† Bulletin No. 113, U. S. Geological Survey, p. 34.

soda were taken out, while 1.44 of ammonia was retained by the residue. Here again two-thirds, approximately, of the bases, had been converted into chlorides by the reaction. The open crucible and the sealed tube gave essentially the same results, although the retention of ammonia was not noticed by Schneider and Clarke.

In order to obtain further light upon pectolite we continued our experiments with the sealed tube method, and have obtained very variable results. All of the heatings with ammonium chloride were conducted at 350°, and the pectolite used was from the same Bergen Hill specimen which served us for our previous work. Our data are as follows; including for convenience of comparison the preliminary experiment which was cited above.

- A. Heated 6 hours. On leaching, 20.72 per cent of lime, 6.46 soda, and 0.11 alumina dissolved. The residue contained 1.44 per cent of ammonia.
- B. Heated 6 hours. 20.10 per cent lime and 5.80 of soda extracted. 1.45 per cent ammonia in the residue. The residue was also examined for silica soluble in 25 per cent sodium carbonate solution (on 15 minutes boiling), and 43.38 per cent was found.
- C. Heated 6 hours. Soluble portion neglected. The residue contained 2.23 per cent of ammonia and 61.79 per cent of soluble silica. The full analysis of this residue is given later.
- D. Heated 10 hours. A complex breaking up of the pectolite took place, and leaching with water extracted the following percentages :

SiO ₂	5.43
Al ₂ O ₃22
CaO	28.20
MnO23
Na ₂ O	8.29

The residue from this leaching contained 39.63 of soluble silica, but ammonia was not determined.

These results are so irregular that definite conclusions can hardly be drawn from them. A and B agree fairly with each other, and also with the earlier work of Schneider and Clarke. C contains more ammonia, but differs widely from B as to the amount of soluble silica in the residue. D, which represents a long heating, indicates a more complete reaction than was observed in either of the other cases.

An ammonium compound, however, is evidently formed during the reaction, although its precise nature cannot be determined from the evidence now in hand. Something may be inferred from the following figures, which are to be summarized thus: First, we reproduce from our earlier paper

the analysis of the pectolite itself. Secondly, we give the analysis of the insoluble residue obtained in experiment C. The third column of figures is obtained by subtracting from the second column 61.79 of soluble silica and 1.18 of hygroscopic water, and recalculating the remainder to 100 per cent. The fourth column contains the molecular ratios calculated from the third.

	Pectolite.	Residue found.	Residue reduced.	Ratios.
SiO ₂	53.34	75.98	37.74	.629
Al ₂ O ₃33	.08	.19	.002
CaO.....	33.23	9.56	25.43	.454
MnO.....	.45	.24	.63	.009
Na ₂ O.....	9.11	1.84	4.89	.079
NH ₃	----	2.23	5.93	.349
H ₂ O at 100°.....	.27	1.18	----	
H ₂ O above 100°.....	2.70	9.47	25.19	1.399
CO ₂67	----	----	
	<hr/> 100.10	<hr/> 100.58	<hr/> 100.00	

These ratios roughly suggest the formation of a salt approximating in composition to the formula $R'_2Ca_2Si_3O_6 \cdot 6H_2O$, in which R' is about two-thirds ammonium and one-third sodium. Pectolite itself has the formula $NaHCa_2Si_3O_6$; so that the existence of a hydrous ammonium pectolite is indicated; a conclusion which is probable, but not proved. The reaction between pectolite and ammonium chloride is possibly simple at first, but followed by or entangled with secondary changes which obscure the results. The experiments are interesting, however, as showing how widely pectolite differs from the other minerals which we have studied, as regards the ammonium chloride reaction. The general investigation is to be continued, and we hope to take up next the more important lime-soda zeolites.

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