ART. XXVII.—*Experiments relative to the Constitution of Pectolite, Pyrophyllite, Calamine, and Analcite*; by F. W. CLARKE and GEORGE STEIGER.

IN a series of investigations by Clarke and Schneider which were carried out in the laboratory of the United States Geological Survey between 1889 and 1892,* a number of reactions were examined which shed some light upon the constitution of several natural silicates. The work then begun was unfortunately interrupted for several years; but it is now resumed, with the hope that it may be pushed considerably further.

Two of the reactions studied by Clarke and Schneider were of peculiar interest. First, in the case of talc, it was found that one-fourth of the silica could be liberated by ignition; and that the fraction thus set free was measurable by solution in aqueous sodium carbonate. This reaction suggests that other acid metasilicates may behave in a similar way, and that we perhaps have a means of discrimination between such salts and other compounds which simulate them. In other words, an acid metasilicate may be experimentally distinguished from a pseudo-metasilicate by the way in which it splits up when ignited. Evidence bearing upon this supposition will be found in the present paper.

The second of the reactions just referred to is that between dry ammonium chloride, at its temperature of dissociation, and various silicates.† This involves, in part at least, the action of dry gaseous hydrochloric acid upon the compounds which are studied; and different minerals are very differently attacked. Some are almost completely decomposed, others are affected but slightly; and here again there seems to be a method of diagnosis which deserves further attention. Both reactions suggest the main purpose of the investigation; which is, the fractional analysis of silicates by means of various reagents, in order to gain evidence bearing upon their chemical structure. The evidence at least is of value, whether the interpretation of it be right or wrong. Each fact helps to the ultimate solution of the central problem, the problem of constitution.

Pectolite.

The pectolite which was chosen for examination was the well-known radiated variety from Bergen Hill, N. J. The mineral was in long white needles, and apparently quite pure;

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* This Journal, III, vol. xl, pp. 303, 405, 452; vol. xlii, p. 242; vol. xliii, p. 378.

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

but the analysis shows that it contained some carbonate as an impurity. Enough of the material was ground up to furnish a uniform sample for the entire series of experiments, and the work properly began with a complete analysis. The results obtained are as follows:

	Analysis.
SiO_2	53·34
Al_2O_3	·33
CaO	33·23
MnO	·45
Na_2O	9·11
Total H_2O	2·97
CO_2	·67
	100·10

	Fractional water.
Water at 105°	0·27
" " 180°	0·16
" " 300°	0·22
" " redness	2·32
	2·97

All of the water was given off at a barely visible red-heat; and the figures show that practically all of it is constitutional; a fact which perhaps hardly needed reverification. The analysis gives the accepted formula for pectolite,

$$HNaCa_2Si_3O_9.$$

Does this represent, as is commonly assumed, a true metasilicate? If it does, we should expect that ignition would split off silica proportional to the acid hydrogen, or one-sixth of the total amount. To answer this question several portions of the pectolite were sharply ignited, to complete dehydration, and then boiled each for fifteen minutes with a solution of sodium carbonate containing 250 grams to the liter. In the extract so obtained the silica was determined; and three experiments gave the following percentages:

	8·96
	8·67
	8·42
Mean,	8·68

One-sixth of the total silica is 8·89 per cent; and the experiments, therefore, justify the original expectation. The belief that pectolite is a metasilicate is effectively confirmed.

Upon the unignited pectolite the sodium carbonate solution has a slow decomposing action, both silica and bases being withdrawn. In two experiments fifteen minutes of boiling extracted 2·07 and 2·55 per cent of silica, and by a treatment lasting four days 4·80 per cent was taken out. With water alone similar results were obtained; the action being so rapid, although relatively slight, that pectolite, moistened, gives an immediate and deep coloration with phenol phthalein. By boiling the powdered pectolite with distilled water alone, 1·65 per cent of silica was brought into solution, and the ignited mineral, similarly treated for fifteen minutes, gave 1·78 per cent. The extraction in these cases is really an extraction of alkaline silicate; as the two following experiments prove. In A the unignited pectolite was boiled for fourteen hours with distilled water; and in B the mineral after ignition was subjected to like treatment for four hours. The dissolved matter in each case was determined, with the subjoined results:

Extracted.	A.	B.
SiO_2	2·98	3·03
CaO	·30	·10
Na_2O	·81	1·50
	4·09	4·63

In A, no simple ratio appears; but in B the extracted silicate approximates very nearly to the salt $Na_2Si_2O_5$. In each instance the ratios vary widely from those of the original mineral, showing that actual decomposition and not a solution of the pectolite as such has occurred.

In the experiments upon pectolite the heating with dry ammonium chloride was omitted, for the data are already given in the original paper by Schneider and Clarke. In their experiments the mineral was thrice heated with ten times its weight of the reagent to above 350°, and then leached out with water. In the solution 20·50 per cent of lime and 6·95 of soda were found, with part of the manganese; showing that a very considerable decomposition had taken place. Possibly, by repeated treatments with ammonium chloride a complete decomposition might be effected; but this question is one upon which it seemed unnecessary to spend further time.

Pyrophyllite.

The empirical formula for pyrophyllite, $AlHSi_2O_6$ is apparently that of an acid metasilicate, and the mineral is therefore peculiarly available for fractional analysis. The compact variety from Deep River, N. C., was taken for examination, and a uniform sample was prepared. Analysis gave the following results:

SiO_2	64·73
TiO_2	·73
Al_2O_3	29·16
Fe_2O_3	·49
MgO	trace
Ignition	5·35
	100·46

If now, pyrophyllite is an acid metasilicate it should break up on ignition in accordance with the equation

$$2AlHSi_2O_6 = Al_2Si_3O_9 + SiO_2 + H_2O.$$

That is, one-fourth of the silica, or 16·18 per cent, should be liberated. The mineral itself is very slightly attacked by boiling with the sodium carbonate solution, and in an experiment of this kind only 0·72 per cent of silica was dissolved. Upon ignition under varying circumstances the following data were obtained :

Ignited ten minutes over a Bunsen burner, and then extracted with sodium carbonate solution, 1·51 per cent of SiO_2 dissolved.

Ignited fifteen minutes over a Bunsen burner, 1·89 per cent became soluble.

Ignited ten minutes over a Bunsen burner and then fifteen minutes over the blast, 2·84 per cent of silica was liberated.

These results are of a different order from those given by pectolite and talc, and raise the question whether pyrophyllite, despite its ratios, is a metasilicate at all. So far as the evidence goes, it may with propriety be regarded as a basic salt of the acid $H_2Si_2O_5$, and its formula then becomes

$$Si_2O_5 = Al-OH.$$

This formula is at least as probable as the metasilicate expression, which latter rests upon assumption alone. Still other formulæ, but of greater complexity, are possible; but until we know more of the genesis and chemical relationships of pyrophyllite, speculation concerning them would be unprofitable.

By heating with dry ammonium chloride, pyrophyllite is very slightly attacked. In two experiments it lost in weight 6·17 and 6·30 per cent respectively. The excess of loss over water is due, as we have proved, to the volatilization of a little ferric and aluminic chloride. The residue of the mineral after this treatment contained no chlorine, so that no chlorhydrin-like body had been formed. The formation of such a compound, the replacement of hydroxyl by chlorine, would, if it could be effected, be a valuable datum towards determining the actual constitution of the species.

Calamine.

The simplest constitutional formula for calamine, the one which is generally accepted, represents it as a basic metasilicate, $SiO_3=(ZnOH)_2$. In this the hydrogen is all combined in one way, and so, too, is the zinc. In all other possible formulæ, simple or complex, the hydrogen as well as the zinc must be represented as present in at least two modes of combination; a condition of which, if it exists, some evidence should be attainable. Our experiments upon calamine have had this point in view; and we have sought to ascertain whether water or zinc could be split off in separately recognizable fractions. Our results, in the main, have been negative, and tend towards the support of the usual formula; but the data are not conclusive, although they seem to be worthy of record.

The beautiful, white calamine from Franklin, N. J., was selected for study, and gave the subjoined composition:

	Analysis.
SiO_2	24·15
Al_2O_3, Fe_2O_3	·19
ZnO	67·55
CaO	·12
H_2O	7·95
	99·96

	Fractional water.
At 100°	·27
" 180°	·22
" 250°	·75
" 300°	·88
Incipient red heat	4·46
Full red heat	1·37
	7·95

Here no clear and definite fractionation of the water is recognizable, at least of such a character as to suggest any other than the ordinary formula for calamine.

Upon boiling powdered calamine with water, practically nothing went into solution, but by boiling with the solution of sodium carbonate, 0·25 per cent of silica was dissolved. After ignition at a red heat, only 0·14 per cent of silica became soluble in sodium carbonate, and after blasting, only 0·24. In these experiments a very little zinc was dissolved also; but there was no evidence that any breaking up of the mineral into distinguishable fractions had occurred. In a hot ten per cent solution of caustic soda both the fresh and the ignited calamine dissolve almost completely; but boiling with aqueous ammonia seems to leave the mineral practically unattacked. All experiments aiming to extract a definite fraction of zinc while leaving a similar fraction behind, resulted negatively.

By heating with dry ammonium chloride, calamine is vigorously attacked, and gains in weight by absorption of chlorine. In two experiments the mineral was intimately mixed with three times its weight of powdered salammoniac, and heated in an air-bath for several hours to a temperature somewhat over 400°. A large part of the residue was soluble in water, and the percentage of this portion, together with the percentage increase in weight, is given below.

	I.	II.
Gain in weight	27·60	25·78
Soluble in water	53·23	67·13

A conversion of calamine into the chlorhydrin, $SiO_3(ZnCl)_2$ would involve a gain in weight of 15·34 per cent. Complete conversion into $2ZnCl_2+SiO_2$ implies an increase of 38·14 per cent. The figures given lie between these two; and are indefinite also for the reason that there was volatilization of zinc chloride.

In two more experiments the calamine, mingled with three times and four times its weight of ammonium chloride respectively, was heated for an hour and a half to bright redness in a combustion tube. The zinc chloride which was formed, volatilized, and was collected by suitable means for determination. It corresponded to 59·6 and 59·0 per cent of the original mineral, calculated as zinc oxide; which indicates a nearly complete decomposition of the calamine into $2ZnCl_2+SiO_2$. The residue was mainly silica, with a small part of the zinc, about half of the silica being soluble in sodium carbonate solution. Here again no definite fractionation of the mineral could be observed.

Finally the action of dry hydrogen sulphide upon calamine was investigated. The mineral was heated to redness in a current of the gas, and gained perceptibly in weight. The percentage data, reckoned on the original calamine, were as follows, in two experiments:

	I.	II.
Gain in weight	6·00	6·43
SiO_2 soluble in Na_2CO_3	16·45	20·95
Sulphur in residue	----	24·12

Complete conversion of calamine into $2ZnS+SiO_2$ implies a gain in weight of 5·80 per cent; and it is therefore evident from the figures of the second experiment that the limit of change was approached very nearly. The 24·12 of sulphur taken up is quite close to the 26·53 per cent which is required by theory. About eight-ninths of the calamine had undergone complete transformation. Again, no definite fractionation was detected.

The hydrogen sulphide reaction was examined still further with reference to the temperature at which it becomes effective. Even in the cold, calamine is slightly attacked by the gas, but its action is unimportant until the temperature of 400° is approximated. Then it becomes vigorous and the reaction goes on rapidly. A few experiments with willemite showed that it also was attacked by hydrogen sulphide, but less vigorously than calamine.

Analcite.

Analcite, from many points of view, is a species of peculiar interest, and of late years it has received a great deal of attention. Its formula may be written in various ways, especially as regards the interpretation of its one molecule of water; but evidence too often has yielded before pre-conceived opinion. Additional evidence is now available, partly from the experiments of Friedel, and partly from the data obtained during the present investigation.

The analcite examined by us was in well-developed crystals from Wasson's Bluff in Nova Scotia. A uniform sample was prepared, as usual, and the analysis, given below, is contrasted with the theoretical composition required by the accepted empirical formula $NaAlSi_2O_6 . H_2O$.

	Found.	Calculated.
SiO_2	57·06	54·55
Al_2O_3	21·48	23·18
Fe_2O_3	·13	
CaO	·16	
Na_2O	12·20	14·09
H_2O at 100°	·58	
" over 100°	8·38	8·18
	99·99	100·00

Fractions of water.	
At 100°	·58
" 180°	1·16
" 260°	3·64
" 300°	1·57
Low redness	1·90
Full redness	·11
Blast	none
	8·96

The fractional water determinations were made by heating in an air-bath to constant weight at each temperature up to 300°, and finally over the direct flame. The first fraction, at 100°, is evidently hygroscopic or extraneous water, which can be disregarded. The remainder of the water, 8·38 per cent, belongs to the species. The significance of the analytical figures will be considered later.

Upon boiling the powdered analcite with sodium carbonate solution, 250 grams to the liter as in all the preceding experiments, 0·73 per cent of silica was extracted. After ignition the mineral in two determinations yielded 1·46 and 1·38 per cent respectively. The splitting off of silica is therefore very slight; and one of the formulæ proposed by Doelter,* $Na_2Al_2Si_2O_8+2H_2SiO_3$ may be set aside as improbable. Metasilicic acid or an acid metasilicate can hardly be present in analcite; although the possibility of a neutral metasilicate, as indicated by the empirical formula, is not excluded. By Doelter's formula one-half of the silica ought to be removable.

Upon heating analcite with dry ammonium chloride, results of a remarkable character were obtained. Sodium chloride

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* Neues Jahrb., 1890, i, 133.

was formed, which could be leached out by water and measured; while ammonia, free from chlorine, was retained by the residue to a notable and surprisingly stable degree. The experiments in detail were as follows:

A. Analcite, mixed with four times its weight of ammonium chloride, was heated for four hours to 350°. There was a gain in weight of 2·18 per cent, and 6·10 per cent of soda, or one-half of the total amount, was converted into NaCl, which was leached out by water, examined as to its purity, and weighed. In the residue 1·20 per cent of silica was extractable by sodium carbonate, showing that no more splitting off had occurred than was previously observed. The gain in weight, as will be seen from subsequent experiments, is due to the fact that all of the NH_4Cl had not been driven off; or else that more water was retained.

B. Analcite was ground up with four times its weight of NH_4Cl, heated for several hours, reground with another four-fold portion of chloride, and heated to 350° for 21 hours. Gain in weight, 0·08 per cent. 5·57 per cent of soda was extracted as chloride.

C. Analcite heated to 350° for 8 hours, with four times its weight of NH_4Cl. Loss of weight, 0·10 per cent.

D. Six grams of mineral and 28 of chloride, mixed by thorough grinding, was heated to 350° for 14 hours; then was reground with 28 grams of fresh NH_4Cl and heated for 35 hours. Loss of weight, 0·13 per cent. 5·07 per cent of soda was extracted as chloride; plus 0·14 of ammonium chloride unexpelled. 2·03 per cent of silica was rendered soluble in sodium carbonate.

So far, three facts are noticeable. First, the weight of the mineral after treatment is almost exactly the same as before; showing that gains and losses have balanced each other. Secondly, little silica has been split off. Thirdly, approximately, but not rigorously, one-half of the soda has been converted into NaCl. In A, it was exactly half; in the other experiments, a little less than half. Furthermore, in the sodium chloride dissolved out there is only a very little ammonium chloride, amounting at most to 0·14 per cent, calculated upon the weight of the original mineral.

In the residue of the analcite after extraction of sodium chloride, abundant ammonia can be detected, with either no chlorine or at most a doubtful trace. If, however, the unleached mineral, still retaining its sodium chloride, be heated strongly, say from 400° up to redness, NH_4Cl is regenerated and given off. Its absence, as such, both from the leach and the residue was repeatedly proved. The ammonia and water retained by the analcite after heating to 350° with ammonium chloride were several times determined; and the following percentages, still reckoned on the original mineral, were found:

	NH_3.	H_2O.
In B	2·03	2·25
" C	2·19	2·00
" D	2·36	1·89
" "	2·35	....
" "	2·06	....
Mean	2·20	2·04

Correcting the ammonia for the 0·14 of NH_4Cl found in D, the mean value becomes 2·15. This permanent ammonia is not given off upon warming the material with caustic soda solution; and is therefore not present as a salt. The determinations of it were made by three distinct methods, and there is no possible doubt as to its presence and character.

The composition of the analcite after the treatment with ammonium chloride may now be considered, with the subjoined combination of the data. The NaCl in A, 11·50 per cent, was in material which had gained 2·18 per cent, and is subject to a correction which reduces the figure to 11·26. In B, C, and D the corresponding correction is so small that it may be neglected. The last column gives the composition of the leached residue, recalculated to 100 per cent, after deduction of NaCl and the soluble silica. The letters refer back to the several experiments, and the little iron is included with the alumina.

	A.	B.	C.	D.	Average.	Residue.
Sol SiO_2 ..	1·20	....	....	2·03	1·61	....
Insol. SiO_2				54·96	54·96	62·59
Al_2O_3				21·37	21·37	24·34
CaO				·16	·16	·18
NaCl	11·26	10·50	....	9·57	10·44	....
Na_2O				7·12	7·12	8·11
NH_3	....	2·03	2·19	2·21	2·15	2·46
H_2O	....	2·25	2·00	1·89	2·04	2·32
				99·31	99·85	100·00

The analcite residue, like the original mineral, is completely decomposible by aqueous hydrochloric acid. It may be a mixture; but it seems more probable that it is a definite compound; for it approximates in composition to the formula

$$H_2Na_2Al_4Si_8O_{24} \,.\, NH_3.$$

This represents a quadrupled analcite formula, in which half of the sodium is replaced by hydrogen, and with NH_3 in place of $4H_2O$. The analytical comparison is as follows:

	Found.	Calculated.
SiO_2	62·59	61·46
Al_2O_3	24·34	26·12
CaO	·18	----
Na_2O	8·11	7·94
H_2O	2·32	2·30
NH_3	2·46	2·18
	100·00	100·00

The agreement is not close, but it is close enough to be suggestive, and to indicate the character of the reaction which has taken place. It needs, however, verification by additional experiments upon other preparations, and upon analcite from other sources. In this connection it may be well to reiterate that the substance was prepared by very long heating at 350°, and is therefore stable at that temperature.

An interesting feature of these experiments is their harmony with the researches of G. Friedel,* who has shown that the water of zeolites may be replaced by ammonia and other substances, without change of the crystalline structure. In the case of analcite, ammonia was taken up to the extent of 2·04 per cent; or almost exactly the amount found in our analcite residue. The great difference between Friedel's method of experimentation and ours, renders the agreement all the more striking; and sustains our belief that the mineral and the residue are compounds of the same general order. We hope to continue our experiments and to extend our investigation to other zeolites.

If, now, analcite and its derivative, our analcite residue, are analogous compounds, the relation between them is expressed by these formulæ:

Analcite .... $Na_4Al_4Si_8O_{24} . 4H_2O$.
Analcite residue .... $H_2Na_2Al_4Si_8O_{24} . NH_3$.

That is, the minimum molecular weight assignable to analcite is represented by four times its empirical formula. Other interpretations of the evidence are possible, but this appears to be the simplest. The water of analcite, as Friedel has shown, must be regarded as water only, not as hydroxyl; for it can be expelled by heat without destruction of the crystalline nucleus, the anhydrous salt, and is taken up again from moist air.

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* Bull. Soc. Min., xix, 94, 1896.

But whatever its mode of union may be, the amount of water corresponds to the simple molecular ratio which is indicated in the formula of the species. One molecule of analcite holds a certain definite number of water molecules; and Friedel's observations are not incompatible with the idea that these are retained with varying degrees of tenacity. This idea is suggested by the various series of fractionation experiments which have been made from time to time, by independent workers, even though the data are not by any means concordant. Thus Lepierre* found that half the water of analcite was driven off at or below 300°, the other half above 440°. In our own experiments three-fourths were expelled at 300°, the remaining fourth being held up to a much higher, but undetermined temperature. In both series the water fractions are representable by fourths; but Friedel's experiments† indicate a continuity of loss in weight of quite a dissimilar order. Friedel holds that all of the water fractionations heretofore made upon analcite are fallacious, and that no definite fractions can be identified, a conclusion strongly supported by his own data, even though the proof is not absolutely positive. The most that can be said is, that the weight of evidence, so far, is in favor of Friedel's contention, but that additional investigation is necessary in order to reconcile all discrepancies. The full significance of the water in analcite remains unknown.

In order to discuss the constitution of analcite, let us recur to the analysis of the mineral itself. It is at once evident from the comparison made on a preceding page that our sample of the mineral varies notably in composition from the requirements of theory. The silica is two and one-half per cent too high, while alumina and soda are correspondingly low. No probable impurity and no presumable errors of manipulation can amount for so great a divergence. If we consult other analyses, as we find them tabulated in manuals like those of Dana and of Hintze, we shall find other cases resembling this, and also examples of variation in the opposite direction, with silica low and an apparent excess of bases. Most analcite gives quite sharply the metasilicate ratios required by the accepted formula; but the variations from it are large enough, common enough and regular enough to command attention. The analyses are not all covered by the recognized theory; and the apparent irregularities are not fortuitous, but are systematic in character.

One explanation of the seeming anomalies is simple and clear. If analcite, instead of being a metasilicate, is really a

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* Bull. Soc. Chim. (3), xv, 561, 1896.

† Bull. Soc. Min., xix, 363, 1896.

mixture of ortho- and trisilicate, then all of the analyses become intelligible. In most cases the two salts are commingled in the normal ratio of one to one; but in our analcite the trisilicate predominates, while in some other samples the ortho-salt is in excess. All reduce alike to the simple expression

$$NaAlX . H_2O,$$

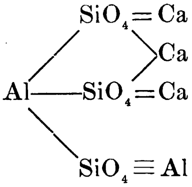
in which X represents $nSiO_4+mSi_3O_8$; a formula which agrees with evidence from various other sources.

For example, analcite may be derived in nature either from albite, $AlNaSi_3O_8$, or nephelite, $AlNaSiO_4$, and on the other hand alterations of it into feldspars have been observed. Its closest analogue, leucite, has yielded pseudomorphs of orthoclase and elæolite; while leucite and analcite are mutually convertible each into the other.' The evidence of this character, the evidence of relationship between analcite and other species, is varied and abundant; and the simplest conclusion to be drawn from it is that which has been given. Every alteration, every derivation, every variation in the composition of analcite, points to the same belief. The consistency of the data cannot well be denied.

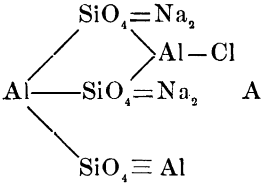
In the case of a normal analcite, that is, one which conforms to the usual empirical formula, the expression which best represents these relations is

$$Al_4Na_4(SiO_4)_2\ (Si_3O_8)_2\ .\ 4H_2O;$$

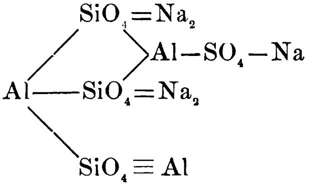
and this accords with the minimum molecular weight as determined by the study of our ammoniated residue. Structurally, this is comparable with the formulæ of garnet, zunyite, sodalite, nosite and leucite; all of which are also isometric in crystallization. The more important of the symbols are as follows:



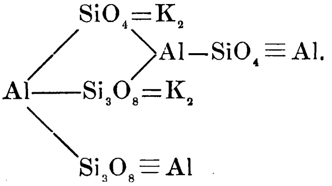
Garnet.



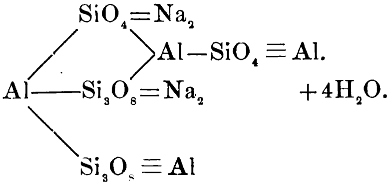
Sodalite.



Nosite.



Leucite.



Analcite.

That is, analcite and leucite become members of the garnet-sodalite group of minerals, and their relations to nephelite, albite, prehnite, natrolite, etc., natural and artificial, are perfectly clear. In analcite there may be admixtures of strictly analogous ortho- or trisilicate molecules; but these remain to be separately discovered.

Now these formulæ are not ultimate verities to be blindly accepted. They are simply expressions which represent composition and a wide range of established relationships, and which serve a distinct purpose in the correlation of our knowledge. Properly used, with due recognition of their limitations, they are helpful, and suggest possibilities of research; misused, they may become mischievous. They now satisfy all known conditions; and that is a sufficient warrant for their existence.

U. S. Geological Survey, July 1, 1899.