

ART. III.—*On Solid Solution in Minerals with Special Reference to Nephelite*; by H. W. FOOTE and W. M. BRADLEY.

It is a fact well known to mineralogists that there are certain minerals to which no satisfactory chemical formulæ can be assigned which agree with the results of analysis. The reason for this in many cases, particularly where the mineral is rare and little investigated, is probably that the material is impure, containing included foreign matter, or else the analysis is incorrect. There appear to be cases, however, where the material has been so carefully selected that foreign matter could not be present except in traces, and where analyses have been made with the greatest care and still the formula cannot be definitely assigned. A case of this kind is that of the mineral nephelite, to which the formulæ NaAlSiO_4 and $\text{Na}_3\text{Al}_2\text{Si}_2\text{O}_{10}$, besides others more complicated have been given. An examination of several good analyses of this mineral will show that the analytical data do not support any one formula, but that there are considerable variations from it which are greater than can be accounted for by the ordinary errors of analysis.

In general the composition of a mineral as obtained in analysis varies from the composition of the ideal pure compound for two reasons, aside from errors of analysis. Either there is (a) isomorphous replacement of one element or radical by another, or (b) there are mechanical impurities present. Where there is merely isomorphous replacement, the formula of the pure compound can be derived from the analysis by the ordinary methods of calculation, which need not be considered here. The presence of mechanical impurities can usually be determined by other means, for instance, by the use of heavy solutions or by microscopic examination. We wish to call attention to another influence which must probably be taken into account in cases like that of nephelite. It appears to us necessary to assume that in certain cases a substance on crystallizing forms a solid homogeneous solution with foreign matter which cannot be assumed to be isomorphous with any constituent, and which is not to be regarded as a mechanical mixture. It can be compared to the solution of salt in water, in which the salt takes on the appearance and form of the water without taking any part in the formula of the water. A case of this kind in minerals would not be a mechanical admixture of the foreign substance, comparable to the suspension of a solid in water, but would form a homogeneous mass with the rest of

the mineral comparable to the salt solution. If such an impurity were present in appreciable amount, it is obvious that the formula of the pure compound could not be calculated correctly from the analysis. This type of solid solution must be clearly distinguished from isomorphous replacement, which is also commonly considered as solid solution. In the latter case, the formula of the compound can be derived directly from the analysis, as previously mentioned.

Before considering the application of these statements to nephelite, we wish to mention a simple case of solid solution which is known in artificial crystals. It has been shown by Roozeboom* that when ammonium chloride crystallizes from a solution containing ferric chloride, the crystals deposited are colored and may contain as much as seven per cent of ferric chloride. Here there can be no question of isomorphous replacement, and on the other hand the ferric chloride is not mechanically enclosed by the ammonium chloride. The latter point is proved partly by the fact that the crystals appear perfectly homogeneous, and it is proved much more definitely by the fact that the solubility of such crystals varies with their composition. If a mechanical mixture were present, the solubility would not vary with the composition of the mixed crystals, but there would be a definite solubility at a given temperature independent of the composition. The colored crystals are to be regarded as one homogeneous phase in which the ferric chloride is held in solid solution by the ammonium chloride. Similar occurrences have been noted in artificial minerals with a good deal of probability. Day and Shepherd† have observed an artificial calcium metasilicate crystallizing with tridymite which differs slightly in optical properties from the pure silicate. The variation appears to be due to the presence of silica taken up in solid solution by the metasilicate. The same metasilicate is also capable apparently of absorbing a considerable amount of the orthosilicate and still appear homogeneous. Again, Shepherd and Rankin‡ have shown that artificial corundum may take up a limited amount of sillimanite (or silica) in solid solution and also a small quantity of calcium oxide. We believe such cases also exist in certain minerals such as nephelite.

Several years ago, the late Prof. S. L. Penfield suggested to one of us (Bradley) that the reason for the variation in the composition of nephelite might be due to the presence of mechanical impurities and that if material of undoubted purity

* *Zeitschr. f. phys. Chem.*, x, 145, 1892.

† *This Journal* (4), xxii, 265, 1906.

‡ *This Journal* (4), xxviii, 293, 1909.

could be obtained so far as mechanical admixture was concerned an analysis would show the correct formula of the mineral. A sample of nephelite from Eikaholmen, Norway, was chosen for analysis and freed from other minerals by use of acetylene tetrabromide. The sample used in analysis floated when the specific gravity of the liquid was 2.638 and sank when it was lowered to 2.632, so that variation in the density of the mineral was not more than .006. The resulting nephelite contained a minute amount of albite which was insoluble in hydrochloric acid, but the quantity was so small that it could be neglected. The material obtained was, we believe, as pure as it is possible to obtain nephelite by mechanical means, since observations under the microscope showed the sample to be of excellent quality and practically homogeneous.

Two complete analyses and two other partial ones were made on this material with the greatest care (by Bradley). Only brief mention seems necessary of the methods employed in the chemical analysis. Silica was determined in the usual way, after dissolving the mineral in hydrochloric acid and by testing its purity traces of alumina were recovered. Alumina was precipitated as hydroxide and this was dissolved, reprecipitated and weighed in the usual manner. The small percentage of iron was determined volumetrically with potassium permanganate. A Smith's fusion was made for the alkalis. The results in detail with the ratios obtained are given below.

TABLE I.
Analyses of Nephelite (Bradley).

I Nephelite from Eikaholmen, Norway.						
	1	2	3	4	Average	Ratio
SiO ₂	44.59	44.31	44.37	44.59	44.46	.736
Al ₂ O ₃	33.29	33.02	33.41	32.71	33.11	.324
Fe ₂ O ₃	.96	.96	.96	.96*	.96	.006
K ₂ O	5.62	5.62	----	5.59	5.61	.060
Na ₂ O	16.59	16.31	----	16.06	16.32	.263
H ₂ O	.38	.38*	----	.38*	.38	
	101.43	100.60		100.29	100.84	

The above analyses were not published at the time they were made, as the formula derived from them was complex, and the results could not be regarded as establishing the formula.

* Taken from anal. I.

The composition of nephelite was further investigated the following year by Morozewicz,* who also gives an excellent review of the literature on the subject. The author gives analyses of six different nephelites which were apparently made with the greatest care on carefully purified material. By his method of analysis, he was able to free his material from even a trace of albite. The results and the ratios derived are given below.

TABLE II.

Analyses of Nephelite (Morozewicz).

II			III		
Nephelite (Elæolite) from Mariupol. Porphyritic Crystals.			Nephelite (Elæolite) from Mariupol. Coarse and granular.		
		Ratio			Ratio
SiO ₂	43·65 }	2·21	SiO ₂	43·46 }	2·21
TiO ₂	·10 }		TiO ₂	·07 }	
Al ₂ O ₃	33·12 }	1·00	Al ₂ O ₃	32·82 }	1·00
Fe ₂ O ₃	0·48 }		Fe ₂ O ₃	0·75 }	
CaO.....	0·49 }	0·99	CaO.....	0·31 }	0·99
K ₂ O.....	5·69 }		K ₂ O.....	5·55 }	
Na ₂ O.....	15·91 }		Na ₂ O.....	16·12 }	
H ₂ O.....	0·74 }		H ₂ O.....	0·89 }	
	<hr/>			<hr/>	
	100·18			99·97	
IV			V		
Nephelite (Elæolite) Mariupol. Reddish Crystals.			Nephelite (Elæolite) from Miask.		
		Ratio			Ratio
SiO ₂	43·55 }	2·21	SiO ₂	42·71 }	2·12
TiO ₂	·03 }		TiO ₂	0·04 }	
Al ₂ O ₃	32·96 }	1·00	Al ₂ O ₃	33·83 }	1·00
Fe ₂ O ₃	0·66 }		Fe ₂ O ₃	0·40 }	
CaO.....	0·25 }	1·00	CaO.....	0·32 }	1·00
K ₂ O.....	6·09 }		K ₂ O.....	5·86 }	
Na ₂ O.....	16·00 }		Na ₂ O.....	16·46 }	
H ₂ O.....	0·33 }		H ₂ O.....	0·18 }	
			MgO.....	trace	
			Impurities ..	0·06	
	<hr/>			<hr/>	
	99·86			99·86	

* Bull. Acad. Sciences Cracovie, 958, 1907.

VI			VII		
Nephelite from Vesuvius.			Nephelite from Vesuvius. Different specimen from VI.		
		Ratio			Ratio
SiO ₂ -----	42·53	2·11	SiO ₂ -----	43·24	2·15
TiO ₂ -----	0·01		TiO ₂ -----	trace	
Al ₂ O ₃ -----	33·92	1·00	Al ₂ O ₃ -----	33·75	1·00
Fe ₂ O ₃ -----	0·30		Fe ₂ O ₃ -----	0·50	
CaO-----	1·97	1·02	CaO-----	2·20	1·03
MgO-----	0·07		MgO-----	0·24	
K ₂ O-----	5·82		K ₂ O-----	4·34	
Na ₂ O-----	15·12		Na ₂ O-----	15·66	
H ₂ O-----	0·13		H ₂ O-----	0·23	
Impurities---	0·24				
<hr/> 100·11			<hr/> 100·26		

We consider the seven analyses given above to be the best which have been made on nephelite. A considerable number of other analyses have been made, however, and we give below a summary of the ratios obtained from the analyses given in Dana's Mineralogy, page 425. The numbers are the same as in the Mineralogy.

TABLE III.

Ratios obtained from Analyses of Nephelite given in Dana's Mineralogy.

	SiO ₂	Al ₂ O ₃ etc.	Na ₂ O etc.
No. 1.	2·21	1·00	1·00
2.	2·25	"	·99
3.	2·17	"	1·00
4.	2·29	"	·95
5.	2·20	"	·91
6.	2·24	"	1·04
7.	2·18	"	1·02
8.	2·24	"	1·01
9.	2·31	"	·97
10.	2·60	"	1·16
11.	2·24	"	1·05
12.	2·06	"	·94
13.	2·14	"	·93
14.	2·29	"	·97
15.	2·19	"	·98

The summary of the ratios obtained in the seven analyses first given is as follows:

TABLE IV.

Summary of Ratios from Analyses by Bradley and Morozewicz.

No.	SiO ₂	Al ₂ O ₃ etc.	Na ₂ O etc.
I.	2·23	1·00	0·98
II.	2·21	"	0·99
III.	2·21	"	0·99
IV.	2·21	"	1·00
V.	2·12	"	1·00
VI.	2·11	"	1·02
VII.	2·15	"	1·03

In this table the ratio of Na₂O:Al₂O₃ is as nearly 1:1 as could be desired. There can be no question that soda and alumina are present in this proportion. The ratio for silica varies from 2·11 to 2·23, and this variation is greater than can be accounted for either from errors of analysis, or from the presence of impurities. For instance, analysis No. I contains more than two per cent excess of silica if the ratios were to be the same as in No. VI. There is no case known, we believe, where silica can be considered as replacing isomorphously either alumina or soda, and if it did in this case, the ratio between these two would not be simple. The same general conclusion as regards composition may be drawn from the ratios derived from older analyses given in Table III, though many of the analyses are probably not as good as the more recent ones.

Morozewicz* has shown that the nephelites may be considered as consisting of two series of compounds, a normal series and a basic one. The normal series should be represented by the formula $K_2Na_nAl_{n+2}Si_{n+3}O_{4n+10}$, in which $n=8, 9, 10$, and 11 , and the basic series by the formula $K_4Na_{18}Al_{23}O_{90}$. By this series of variable formulæ, the variation in composition can be expressed. This method of representing the composition is open to the serious objection that a chemical compound, so far as we know, does not vary in type. Isomorphous replacement, for instance, varies the composition, but the type of compound remains the same.

If nephelite be considered a solid solution, the case becomes very different. A solution may be defined as a homogeneous mixture of substances which cannot be separated by mechanical means and whose composition varies continuously within certain limits. This definition distinguishes a solution from a suspension on the one hand and from a chemical compound on the other. It characterizes a solution of a salt in water, and a solid solution of ferric chloride in ammonium chloride and we

* Loc. cit.

can see no reason why nephelite should not be treated in the same class. This method of considering the composition of nephelite has the advantage of being much more simple than using a series of complicated formulæ, and it appears to us to agree with the facts. It need hardly be said that a chemical formula could be assigned to any solution but a different one would have to be used for each change in concentration of the solution, just as Moroscewicz uses a different formula for each nephelite.

From what has been said, we think it fair to consider that nephelite as it occurs in nature is not a pure compound but a solid solution analogous to the solid solution of ferric chloride in ammonium chloride. It then becomes of interest to consider the probable formula of the pure compound which forms the basis of nephelite. This appears to be the orthosilicate NaAlSiO_4 . This formula is supported in two ways: (1) Nephelite has the same crystalline form as encryptite LiAlSiO_4 and kaliophilite KAlSiO_4 , which are in the same group, making it very probable that the type of formula is the same in all three cases. (2) Artificial nephelites have been prepared by Doelter* which have the same general characteristics as natural nephelite and vary in composition from the formula NaAlSiO_4 to compounds containing potash and an excess of silica corresponding to the mineral.

Perhaps the point should be emphasized that nothing whatever is known about the actual condition of the dissolved silica, whether it is present as dissolved albite or silica or leucite or in any other form, just as very little is known about the condition of dissolved substances in liquids as to whether they are combined with the solvent. It is certain, however, that the dissolved silica does not have the properties of either ordinary quartz or albite, since it is soluble in hydrochloric acid. In the same way, the properties of a dissolved salt are entirely different from the properties of the solid.

The excess of silica which can be taken up by nephelite to form a saturated solution can apparently be determined from the data given by Morozewicz and ourselves. Where albite is found intimately mixed with nephelite it is evident that the nephelite must be saturated with silica and the excess of the latter has formed albite.

In this case, therefore, the nephelite should have a constant ratio of silica to alumina, and these nephelites should contain the maximum amount of silica that can be taken up. The influence of temperature in determining the composition of the saturated solution can apparently be neglected. In our

*Zeitschr. f. Kryst., ix, 321, 1884.

own specimen, albite was associated with the nephelite, and Morozewicz states that albite was present in the specimens containing the nephelites of analyses II and III and microcline-micropertthite, which would have a similar effect, in analysis IV. The ratio for silica in these four cases is 2.23, 2.21, 2.21 and 2.21, which is as nearly constant as could be desired. In analysis V, where the ratio for silica is only 2.12, the mineral is stated to be exceptionally pure, with biotite crystals on the outside. In VI or VII, where the ratios are 2.11 and 2.15, sanidine was present which might have the effect of albite, tending to raise the ratio to the saturation point, but in just these two cases (from Vesuvius) the nephelite appears to be a later growth on the sanidine and not intimately mixed with it. In these cases, then, where albite or its equivalent was not formed with nephelite, the ratio of silica to alumina shows that the nephelite has not taken up the maximum amount of silica. The most basic rock containing nephelite with which we are acquainted is an iolite described by Hackman.* This rock contains essentially pyroxene and nephelite with smaller amounts of titanite, apatite and ivaarite. There is no albite, quartz or feldspar present. The nephelite in this rock had the following composition and ratios:

		Ratio
SiO ₂	43.98	2.13
Al ₂ O ₃	34.93	1.00
CaO	0.36	0.94
Na ₂ O	16.76	
K ₂ O	3.83	
	<hr/> 99.86	

Here, again, the silica is below what we may call the "saturation ratio" of 2.21.

It would be of considerable interest if nephelites could be found which closely approximated the formula NaAlSiO₄. From what has been said above, such an occurrence could only be expected where crystallization had taken place from a magma so deficient in silica that albite did not form.

In conclusion, the authors consider that the arguments advanced in the present article may be applicable to other minerals. Work has already been begun on the mineral pyrrhotite with the hope that similar deductions may be applied to this mineral.

Chemical and Mineralogical Laboratories of the Sheffield Scientific School of Yale University.

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* Bull. de la Commis. Geol. de Finlande, 1900, p. 9.