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Art. XII.—*The Sodium-Potassium Nephelites;* by N. L. Bowen.

Introduction.

Among rock-forming minerals, especially those of the interesting alkaline rocks, nephelite takes a prominent place and for this reason has attracted considerable study on the part of mineralogists and petrologists. This study has revealed in nephelite considerable chemical complexity the explanation of which has been and, to some extent, still is a matter of controversy. The simple compound $NaAlSiO_4$ is now rather generally regarded as the fundamental molecule of nephelite, but the composition of the natural mineral always departs from this markedly, showing a large content of potash, often considerable lime, and a variable excess of silica above the orthosilicate ratio. A study of the fundamental compound and of the lime content of nephelite has already been made at this laboratory.* The present paper describes the continuance of this work in the study of the potash-bearing nephelites or the binary system, $NaAlSiO_4$–$KAlSiO_4$.

The End Members.

$NaAlSiO_4$.—The compound $NaAlSiO_4$ can be prepared by sintering together Na_2CO_3, Al_2O_3 and SiO_2 in the proper proportions at a low temperature (about 800°) to prevent loss of soda. Sintering must be repeated several times with intermediate grindings and then the whole may be raised above the melting temperature. The product is a clear homogeneous glass of the appropriate composition.† This glass crystallizes at low temperatures to the hexagonal form, nephelite, and at high temperatures to the triclinic (?) form, carnegieite. The inversion temperature of 1248° ± 5 obtained in the earlier work was confirmed during the present investigation, as was also the melting temperature of carnegiete, 1526°.

Pure sodium nephelite is hexagonal and negative. The refractive indices are $\omega = 1{\cdot}537 \pm {\cdot}002$; $\epsilon = 1{\cdot}533 \pm {\cdot}002$. The density is 2·619 at 21°.

Carnegieite always shows a complicated polysynthetic twinning. There are often two intersecting sets of lamellæ suggesting the microcline twinning and again three sets giving an hexagonal aspect. It has been considered triclinic, though it could be, perhaps, orthorhombic or monoclinic. The refractive

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* N. L. Bowen, this Journal, xxxiii, 551, 1912.

† The reasons for this procedure are given in the former paper, this Journal, xxxiii, 552, 1912.

indices are $\gamma = 1{\cdot}514 \pm {\cdot}002$, $\alpha = 1{\cdot}509 \pm {\cdot}002$. It is biaxial, with negative optical character and $2V = 12°–15°$. The density is 2·513 at 21°.

Glass of composition $NaAlSiO_4$ has a refractive index $1{\cdot}510 \pm {\cdot}002$.

$KAlSiO_4$.—The preparation of the pure potash compound is not so readily accomplished. The same precautions of sintering at a low temperature before raising above the melting point are not adequate in this case to prevent volatilization of the alkali, partly because the potash is much more volatile than soda and partly because of the high melting-temperature of the potash compound. In raising the charge to this temperature which is somewhat above the melting-point of platinum, considerable potash is lost. The pure compound cannot, then, be prepared in the dry way simply by mixing the components and melting them, though its preparation by this method has been claimed. Especially should one not attempt to prepare it by fusion in a platinum crucible, for the crucible melts and runs away when the sintered charge is still intact. In a poorly mixed charge melting can be obtained at comparatively low temperatures, silica and potash fluxing together and leaving much alumina undissolved, but this is not melting of kaliophilite. Nevertheless one can obtain a product with only a moderate deficiency in potash by sintering at a low temperature as described and then rapidly raising to the melting temperature in an iridium furnace. The glass so obtained is apparently not very different in viscosity from the nephelite glass and crystallizes about as readily when not too rapidly cooled. In this way one obtains crystals which correspond in properties with the natural mineral kaliophilite, always, however, with a little foreign material since the composition does not lie exactly at the compound $KAlSiO_4$.

The artificial kaliophilite so obtained is hexagonal and negative, $\omega = 1{\cdot}532 \pm {\cdot}002$, $\epsilon = 1{\cdot}527 \pm 002$. The prism and base are predominant with only an occasional truncation of the edge by a pyramidal face. One sees, then, the hexagonal basal sections and quadratic prismatic sections precisely as in nephelite.

With the aid of potassium tungstate as a flux good crystals of kaliophilite were prepared at about 1300°. The largest of these were somewhat contaminated with the flux and showed higher indices of refraction than those given above, but the smallest crystals were found to agree exactly in all their properties.

Small crystals of kaliophilite were prepared hydrothermally by Morey in this laboratory. Kahlbaum's potassium aluminate and potassium silicate were used. These were placed with water in a gold crucible in a steel bomb after the usual method.* The temperature was kept at 600° and the pressure of water vapor at about 1000 atmospheres for 24 hours.

An analysis of the kaliophilite crystals obtained is stated below.

	I	II
SiO_2	38·0	38·07
Al_2O_3	32·0	32·21
K_2O	29·8	29·72
H_2O	·12	....
	99·9	100·00

I. Artificial kaliophilite. Analyst N. L. Bowen.
II. Theoretical composition, $KAlSiO_4$.

The optical properties were exactly as given above.

Formation of leucite.—In attempting to prepare kaliophilite by heating glass of composition $KAlSiO_4$ at about 800° with potassium tungstate occasional crystals of kaliophilite were obtained but the great bulk of the product was a material of weak double refraction and conspicuous polysynthetic twinning. The refractive index was 1·509. This value, together with the polysynthetic twinning, gave the impression, at first, that a form of the potash compound corresponding with carnegieite had been obtained. These properties agree, however, with those of leucite and an occasional crystal suggested the typical icositetrahedron of that mineral though the majority of them were in branching forms. The amount of material was insufficient for analysis so a small portion was converted to glass in the oxy-hydrogen flame and the refractive index of the glass determined. The index was found to be about 1·490 and to correspond with that of glass made by melting leucite from Vesuvius whereas the index of glass of composition $KAlSiO_4$ is 1·508. The crystals were thus proved to be leucite and not a new form of $KAlSiO_4$. At 800° with potassium tungstate as a flux, then, $KAlSiO_4$ glass is largely converted to leucite crystals whereas at 1300° it crystallizes as kaliophilite.

Orthorhombic form of $KAlSiO_4$.—In the charges heated in the iridium furnace occasional crystals were seen with polysynthetic twinning. These were thought to be kaliophilite twinned on a pyramidal face because the indices were sensibly those of kaliophilite. In the later work on intermediate mixtures it was found that those rich in kaliophilite always showed this twinned form when quenched from high temperatures. These better crystals were found to be biaxial. The crystals are usually interpenetration twins giving an hexagonal section

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* G. W. Morey, Jour. Am. Chem. Soc., xxxvi, 217, 1914.

divided into six sextants that extinguish together in opposite pairs. Occasionally polysynthetic twinning similar to that in albite is shown, but this appears to follow the same law as the previous case with the same prism face acting repeatedly as composition face instead of adjacent faces as in the case of penetration twins.

Crystals of this orthorhombic form were made by fusing together silica, alumina and potassium fluoride over a Bunsen burner after the method of Duboine.* The twinning was not so frequently developed as in the crystals obtained at high temperatures but occasionally appeared in typical form. The refractive indices are $\gamma = 1·536$, $\alpha = 1·528$, 2V = 39 ± 3° negative.

The product obtained by this method is not strictly pure but contains an amount of foreign material estimated under the microscope to be about 5 per cent. This consists of isotropic octahedra whose refractive index is about 1·540. The correspondence with the compound $K_2Al_2SiO_6$ as described by Weyberg† is complete.

Analysis of this mixture resulted as follows:

SiO_2	36·7	38·07
Al_2O_3	32·8	32·21
K_2O	30·3	29·72
	99·8	100·00

I Product obtained from fusion with KF. Analyst N. L. Bowen.

II $KAlSiO_4$, theoretical composition.

It will be noted that the analyzed material is low in silica and high in alumina and potash and calculation shows that it corresponds with a mixture of 93 per cent $KAlSiO_4$ with 7 per cent $K_2Al_2SiO_6$. The analysis and the microscopic examination together may therefore be regarded as definitely proving that the foreign material is $K_2Al_2SiO_6$ present to the extent of about 5–7 per cent and that the twinned material corresponds with kaliophilite in composition.

Glass of composition $KAlSiO_4$ (approximately) has a refractive index for sodium light of 1·508 ± ·002.

A number of supposed other forms of $KAlSiO_4$ have been encountered by various investigators, but the material was always poorly crystallized and the measured properties were hardly sufficient to individualize them as species. No crystalline forms of $KAlSiO_4$ other than the two described were encountered during the course of the present work. The

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* Bull. Soc. Min. Fr., xv, 191, 1892.

† "In Canada-balsam sehr schwer sichtbar," Weyberg, Centralblatt Min. 1908, p. 329.

alteration product obtained by Stephenson is very similar to if not identical with the twinned form of $KAlSiO_4$.*

Intermediate Mixtures.

By mixing the alkaline carbonates, silica and alumina, in the proper proportion, sintering and then fusing, the intermediate mixtures containing up to 40 per cent of the potash compound were made satisfactorily. In mixtures richer in potash, however, the temperature which must be reached to obtain a homogeneous melt is higher so that a little alkali is lost. The loss increases as the potash end is approached. An attempt was made to avoid this difficulty by using kaliophilite made hydrothermally by Morey, and nephelite made in the ordinary way as the ingredients of the mixtures. Even with this method the same loss of potash was encountered in those mixtures whose melting required a high temperature. The results from the potash-rich mixtures are, therefore, to some extent unsatisfactory. This loss of potash is not, however, so serious as to obscure the relationships involved, though it does interfere with the accurate fixing of temperatures.

A study of equilibrium in these mixtures was made in the ordinary way by the method of quenching. Besides the loss of potash noted above certain difficulties were encountered in the optical determinations which are, perhaps, worthy of note. The hexagonal forms of the two components nephelite and kaliophilite are so nearly identical in properties that when obtained as small crystals embedded in glass, as they are in quenchings, it is impossible to determine whether the crystals are kaliophilite or nephelite or of an intermediate composition. As a rule in such a case one can obtain a clue to the composition of the crystals by determining the composition of the glass, but in the present instance the extreme glasses and all intermediate glasses have nearly the same refractive indices and the composition cannot, therefore, be determined by such a method. To determine optically the question of solid solution between the components, and its limits, one crystallizes a glass of intermediate composition and examines the product to see whether it is homogeneous or not. In the present system, however, one cannot determine whether the fine-grained product so obtained consists of homogeneous mix-crystals or whether kaliophilite and nephelite are present as distinct phases.

Studies of equilibrium are often made in systems of various kinds with little observation of the phases themselves. The work is almost entirely a measurement of the temperatures at which changes of phase take place in various compositions, the change being recorded, say, thermally or dilatometrically. When these temperatures are plotted against composition it is

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* Jour. Geol. xxiv, 197, 1916.

usually possible to deduce a complete equilibrium diagram. Dependence had to be placed on this method to a considerable extent in the present case. The temperatures at which beginning of melting and inversion and completion of melting and inversion take place were measured by the quenching method. These, when plotted against composition, give a complete equilibrium diagram from which the composition of the crystalline phases can be determined even though this cannot be done by optical means. Even in these determinations difficulties were encountered as a result of the near agreement of the refractive index of all the glasses with that of carnegieite. Thus when one takes crystalline nephelite-like material and holds it at successively higher temperatures, a temperature is finally reached at which a small trace of interstitial material of low refraction is formed but one is at a loss to decide whether it is carnegieite or glass. By raising the temperature the size of the interstitial patches can be increased until their nature is determinable. Unfortunately, however, one cannot be sure that small patches which were carnegieite have not, with the rise of temperature, been changed to patches of glass, indeed there are some mixtures in which this does take place within a narrow range of temperature.

Then again there is the difficulty of determining the temperature at which carnegieite mix-crystals begin to melt, for the first trace of glass cannot be found under the microscope on account of the correspondence of refraction in glass and carnegieite. The microscope will detect the glass only when enough has been formed to give definite isotropic patches. It was found, however, that the first appearance of glass could best be determined macroscopically in this case. Before the formation of glass the material is a white, opaque, sintered cake but on the formation of glass the interstices become filled with it, and since the index matches that of the crystals the charge becomes transparent and to all appearances entirely glassy even when under the microscope no unmistakable glass can be detected. Some difficulty is experienced, too, in determining the temperature at which final solution of carnegieite takes place. Rare crystals of carnegieite in glass are easily overlooked, for they appear merely as indefinite birefringent patches without distinguishable outline against the glass.

These difficulties were finally solved, especially as a result of the assembling and correlation of all the results, but during the course of the investigation they were often very discouraging.

Results of Quenching Experiments.

The results of the quenching experiments may now be given in tabular form. (Table I.)

TABLE I.

Beginning of inversion of nephelite to carnegieite.

Composition Ne	Kp*	Initial condition	Temperature	Time	Result
95	5	crystalline	1276	1 hr.	hexagonal form persists unchanged
"	"	"	1282	"	trace of carnegieite formed
90	10	"	1302	"	hexagonal form unchanged
"	"	"	1306	"	trace of carnegieite
85	15	"	1322	"	hexagonal form unchanged
"	"	"	1327	"	trace of carnegieite
80	20	"	1345	"	hexagonal form unchanged
"	"	"	1350	"	trace of carnegieite
75	25	"	1366	"	hexagonal form unchanged
"	"	"	1370	"	trace of carnegieite
70	30	"	1384	"	hexagonal form unchanged
"	"	"	1388	"	trace of carnegieite

Completion of inversion of nephelite to carnegieite.

95	5	crystalline	1335	2 hrs.	a little nephelite
"	"	"	1340	1/2 hr.	all carnegieite
90	10	"	1370	2 hrs.	a little nephelite persists
"	"	"	1375	1/2 hr.	all carnegieite
85	15	"	1392	2 hrs.	a little nephelite persists
"	"	"	1397	1/2 hr.	all carnegieite

Beginning of melting of carnegieite.

95	5	crystalline	1448	1 hr.	all carnegieite
"	"	"	1452	"	a little glass formed
90	10	"	1420	"	all carnegieite
"	"	"	1424	"	a little glass formed

Completion of melting of carnegieite.

95	5	crystalline	1506	1/2 hr.	glass and carnegieite
"	"	"	1510	"	glass only
90	10	"	1485	"	glass and carnegieite
"	"	"	1489	"	glass only
85	15	"	1463	"	glass and carnegieite
"	"	"	1467	"	glass only
80	20	"	1436	"	glass and carnegieite
"	"	"	1440	"	glass only
75	25	"	1413	"	glass and carnegieite
"	"	"	1417	"	glass only

* Ne = $NaAlSiO_4$, Kp = $KAlSiO_4$.

Eutectic temperature and composition.

Composition		Initial condition	Temperature	Time	Result
Ne	Kp				
80	20	crystalline	1402	1 hr.	nephelite and carnegieite
“	“	“	1406	“	carnegieite and glass
75	25	“	1402	“	nephelite and carnegieite
“	“	“	1406	“	carnegieite and glass
72·5	27·5	“	1402	“	nephelite and carnegieite
“	“	“	1406	“	glass only
70	30	“	1402	“	nephelite and carnegieite
“	“	“	1406	“	nephelite and glass
65	35	“	1402	“	nephelite only
“	“	“	1406	“	glass and nephelite

Beginning of melting of mix-crystals.

50	50	crystalline	1435	1/2 hr.	crystals and glass stringers
“	“	“	1445	“	marked increase of glass
40	60	“	1480	“	crystals and glass stringers
“	“	“	1490	“	marked increase of glass
30	70	“	1540	“	crystals and glass stringers
“	“	“	1550	“	marked increase of glass

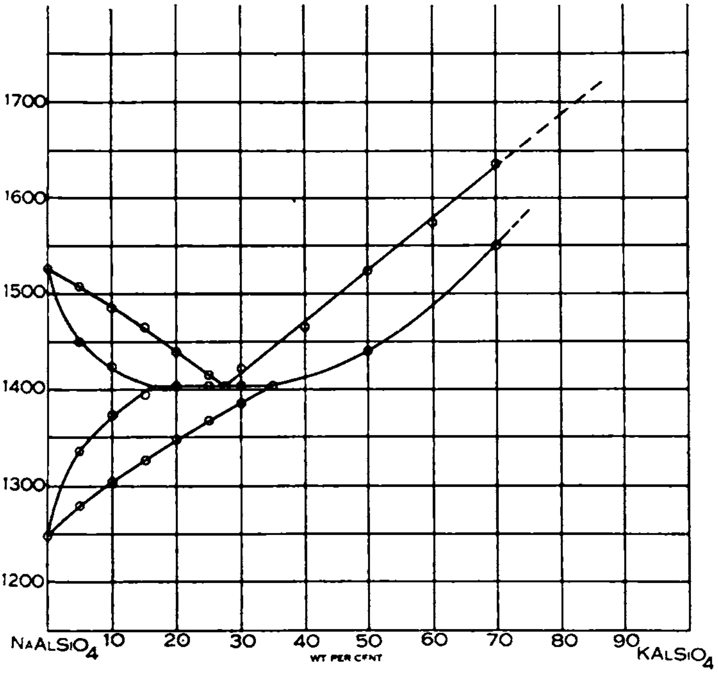
Completion of melting of mix-crystals.

70	30	crystalline	1420	1/2 hr.	glass and crystals
“	“	“	1424	“	glass only
60	40	“	1463	“	glass and crystals
“	“	“	1467	“	glass only
50	50	“	1520	“	glass and crystals
“	“	“	1524	“	glass only
40	60	“	1570	“	glass and crystals
“	“	“	1574	“	glass only
30	70	“	1629	“	glass and crystals
“	“	“	1633	“	glass only

Discussion of Results.

The mixtures containing 50 per cent or more of $KAlSiO_4$ always show a little glass even when quenched from temperatures below the eutectic. This behavior is the result of the deviation from true composition to which reference has already been made. Concerning the method of determining the temperature of beginning of melting in such material a word of explanation is, perhaps, necessary. The glass formed at moderate temperatures occurs throughout the crystalline grains as shreds which are revealed only after close scrutiny under the microscope. These shreds do not increase very materially in amount as the temperature is raised and appear, moreover, to be of a highly viscous, presumably siliceous, glass which occasions no sintering of the powdered charge. On raising the temperature further, however, a point is finally reached at which rapid increase of glass takes place for only a few degrees rise of temperature. This glass has, moreover, quite different properties. It evidently flows comparatively freely and fills all the interstices of the powdered charge which becomes, even to the naked eye, obviously semi-vitreous. This temperature at which rapid increase of glass is first observed is regarded as the true temperature of beginning of melting.

Fig. 1.



The method involves the personal equation to some extent. The temperature is probably somewhat lower than that which the true composition would show. Nevertheless there can be no question that the true curve would have a steep slope and approximate in position the determined curve shown in fig. 1.

The temperature of completion of melting of these somewhat impure mixtures is easily determined in the ordinary manner. On account of deviation of the mixtures from the true composition the various points are somewhat too low, no doubt. The effect of a small amount of impurity in lowering the temperature of beginning of melting may be very great if the impurity has a low melting point, whence the small amounts of glass found in these mixtures at moderate temperatures. The effect on the temperature of completion of melting, the so-called melting point, is, however, a more or less direct function of the amount of impurity. Since the deviation from true composition is small the position of the curve as far as it has been determined is believed to be substantially correct.

The equilibrium diagram is of a peculiar type, though among those deduced by Roozeboom as possible in a system involving solid solution and inversion.* Between the potash compound and carnegieite there is a eutectic, but with nephelite a complete series of solid solutions is formed. As was noted formerly, solid solution cannot be definitely proved by optical means but such is the only possible interpretation of the thermal results. There is a continuous rise in the inversion temperature of nephelite as far as 35 per cent $KAlSiO_4$ amounting in all to more than 150°. Such a change of inversion temperature can be accomplished only through solid solution. At 35 per cent $KAlSiO_4$ the inversion curve gives place to a melting curve which shows a continuous rise in temperature of beginning of melting. If the possibility is entertained that an hiatus may exist in the series in those mixtures close to kaliophilite whose beginning of melting cannot be accurately fixed, then it may be pointed out that there should be a corresponding break in the liquidus. There is, however, no break in the liquidus at least up to about 1580°. In the neighborhood of this latter temperature there probably is a break, but this is occasioned not by the appearance of kaliophilite as a separate phase but by the appearance of the orthorhombic form of $KAlSiO_4$. Solid solution as far as about 70 per cent $KAlSiO_4$ is established, therefore, beyond all question, while none of the evidence furnishes any reason for doubting complete solid solution.

It may seem at first thought that the evidence of the natural minerals is against complete solid solution. We have, for example, nephelite with upwards of 32 per cent $KAlSiO_4$ in solid solution but none with a greater amount. Then at the other end we have a maximum of 10 per cent of $NaAlSiO_4$ in kaliophilite. The interval is unbridged among known natural minerals, but this does not mean that no such minerals are possible. Nephelites which contain, say 20 to 30 per cent $KAlSiO_4$, are never found in contact with kaliophilite in such a manner as to indicate approximately simultaneous formation. Only such an association would prove that the nephelite was incapable of taking up more $KAlSiO_4$. For these reasons we

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* Zs. phys. Chem., xxx, p. 426, 1899.

must conclude that the moderate amount of $KAlSiO_4$ usually found entering into nephelite is the result of a deficiency of supply rather than of any inability on the part of nephelite to take up greater quantities in solid solution.

Crystallization of a Typical Mixture.

The phenomena observed during the cooling of a mixture in which perfect equilibrium is attained are, perhaps, of sufficient interest to be described in detail. A mixture of 80 per cent $NaAlSiO_4$ and 20 per cent $KAlSiO_4$ begins to crystallize at 1438° with separation of crystals of carnegieite containing 6 per cent $KAlSiO_4$ (see fig. 1). As the temperature falls the liquid changes in composition towards the eutectic and the carnegieite crystals increase in amount and become richer in potash content. At the eutectic temperature, 1404°, they contain about 16 per cent $KAlSiO_4$ and are then joined by hexagonal crystals (nephelite) containing 35 per cent $KAlSiO_4$. The temperature remains constant until all the liquid has disappeared. Then as the temperature falls carnegieite immediately begins to invert to nephelite and both change in composition, becoming richer in soda, until at 1348° all the carnegieite has changed to nephelite which now has the composition $NaAlSiO_4$ 80 per cent, $KAlSiO_4$ 20 per cent.

Relation between the hexagonal aud orthorhombic forms of $KAlSiO_4$.—Both forms of $KAlSiO_4$ can be obtained at low temperatures. Kaliophilite has been obtained hydrothermally by Morey and several others at temperatures in the neighborhood of 500°. The orthorhombic form was prepared in a similar manner by Lemberg.* Both forms can likewise be obtained with the aid of various fluxes at moderate temperatures. Nevertheless a number of facts point to the stability of kaliophilite only at low temperatures and of the orthorhombic form only at high temperatures with the inversion temperature somewhere in the neighborhood of 1540°. In the present mixtures when working without fluxes the orthorhombic form was obtained only in mixtures containing 70 per cent or more of $KAlSiO_4$ and in these only at high temperatures. Moreover, ordinary, uniaxial kaliophilite formed by crystallizing glass made in the iridium furnace, is converted at 1550° into excellent twinned crystals of the orthorhombic form. The change is here facilitated by the formation of a little liquid as a result of the deviation of the material from the true composition. Pure kaliophilite made by Morey suffers a change at about the same temperature or a little lower, 1540°. In this case no liquid is formed and for that reason the crystals are not as typically developed, but the quadratic section of kalio-

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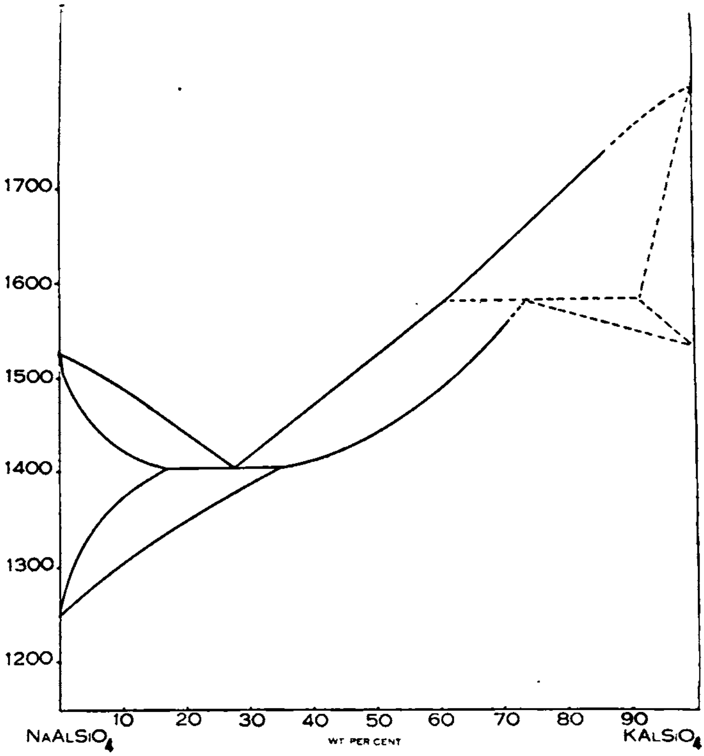
* See Z. Weyberg, Centralblatt Min., p. 401, 1908.

philite with its parallel extinction is broken up into two or more areas which are in twinned relation with each other and whose extinction has no relation to the elongation. At about 1540°, therefore, or possibly somewhat lower, the hexagonal kaliophilite is converted into the orthorhombic form. The formation of the orthorhombic form at low temperatures with fluxes is not at all incompatible with its stability at high temperatures only, for many such forms can be so obtained, notable examples being the forms of silica.* The writer has not, however, been able to convert the orthorhombic form into the hexagonal form, but this does not necessarily preclude an enantiotropic relation between them, for it is not uncommon to experience great difficulty in converting the high temperature form into its low temperature equivalent.

Fig. 2.



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* C. N. Fenner, this Journal (4), xxxvi, 339, 1013.

The orthorhombic variety is encountered in the mixture with 20 per cent $NaAlSiO_4$ only at a considerably higher temperature, 1580°. The inversion point is, therefore, raised, which means that the low temperature, hexagonal form takes more $NaAlSiO_4$ into solid solution than does the high temperature form. This is precisely as one would expect it to be, since the hexagonal form is so like the corresponding form of $NaAlSiO_4$, and, indeed, forms with it an unbroken series of mix-crystals.

On the basis of these results fig. 2 is presented as representing a partly hypothetical but very probable equilibrium diagram of the complete system. Some of the curves are shown in broken lines because they are less well supported by ascertained facts than the others, though they are believed to offer the only possible interpretation of the results obtained.

The Composition of Natural Nephelite.

It is now established beyond question that natural nephelites are of variable composition. That the molecules $NaAlSiO_4$ and $KAlSiO_4$ are fundamental constituents of nephelite may be regarded as definitely decided by the present investigation.

Concerning the excess silica in nephelite above the orthosilicate ratio there is still some controversy. Most investigators believe that $NaAlSiO_4$ and $KAlSiO_4$ are fundamental and that the variable excess of silica is to be ascribed to the presence in variable amount of a more silicious molecule. The suggestion that this molecule is $NaAlSi_3O_8$ was first made, apparently, by Clarke[*] and later stated in terms of the more modern solid solution theory by Schaller[†] and the writer.[‡] Thugutt,[§] however, would still assign a definite formula to nephelite and assumes that it is

$$8Na_2Al_2Si_3O_{10}.4Na_2Al_2O_4.3K_2Al_2Si_3O_{10}$$

and that any deviation from this formula is the result of an admixture of products of its own decomposition. He therein ignores the fact that the later students of the composition of nephelite have taken the greatest precautions in selecting only absolutely fresh material for analysis.[‖] He likewise fails to consider the fact that one can prepare nephelite showing the same variability by dry fusion, under conditions absolutely precluding the possibility of aqueous decomposition.[¶] No consideration is given,

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[*] F. W. Clarke, U. S. Geol. Survey Bull. 125, 18, 1895.

[†] Jour. Wash. Acad. Sci., i, 109, 1911.

[‡] This Journal (4), xxxiii, 49, 1912.

[§] C. R. Soc. Sci. Varsovie, VI Année. Fasc. 9, 862, 1913.

[‖] Morozewicz, Bull. Acad. Sci. Cracovie, 958, 1907.

[¶] Wallace, Zs. anorg. Chem., lxiii, 1, 1909; and Bowen, this Journal (4), xxxiii, 50, 1912.

moreover, to the fact that $NaAlSiO_4$ and mixtures of it with $KAlSiO_4$ can be prepared in a form identical with nephelite and, indeed, occur so in nature in the so-called pseudonephelite, whereas the molecules chosen by Thugutt do not occur in forms at all suggesting nephelite.

Several objections have been raised to the suggestion that the albite molecule, $NaAlSi_3O_8$, is the siliceous molecule present in nephelite. Thugutt points out that albite has never been isolated from nephelite, which is perfectly true, but neither has albite been isolated from labradorite. The suggestion of Foote and Bradley that the question of the condition of the excess silica should be left open* is safe, to be sure, but there are nevertheless good reasons for preferring the albite molecule.

It was formerly considered, if a triclinic mineral was taken into solution by an hexagonal mineral, that the triclinic mineral must be dimorphous, must have an hexagonal modification. But this idea is now known to be contrary to well-ascertained facts. We may take the case of anorthite in solid solution in nephelite, which extends as far as 35 per cent anorthite, yet anorthite has no hexagonal modification. It seems to the writer, in the light of recent studies of the actual atomic structure of crystals, to be more reasonable to assume that the anorthite atomic pattern, though of triclinic symmetry, is nevertheless sufficiently close to the hexagonal symmetry of nephelite or sufficiently amenable to modification that, under the influence of the fields of force existing within a nephelite crystal, it is capable of being so modified as to conform with the hexagonal pattern, though not in unlimited amounts. Is it surprising, then, that the albite atomic pattern should be capable of precisely the same modification by a nephelite crystal, up to a certain limit, when we consider the fact that albite and anorthite are so nearly alike in pattern that they form an unbroken series of mix-crystals?

Or if we look at the question from the point of view of phase equilibria and remember that albite and anorthite in any system form not two phases but the single phase, plagioclase, then it becomes quite inappropriate to speak of the solubility in nephelite of anorthite and of albite except as limiting values of the solubilities of the phase, plagioclase. Any nephelite forming in a magma together with plagioclase must, of necessity, dissolve the amount of both anorthite and albite (i. e. of the phase plagioclase) that is required by the conditions prevailing, sufficient opportunity for equilibrium to become established being assumed.

It may be said, then, that theoretical considerations afford

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* This Journal (4), xxxiii, 439, 1912.

the strongest additional reasons for stating the composition of nephelite in terms of the molecules $NaAlSiO_4$, $KAlSiO_4$, $CaAl_2Si_2O_8$ and $NaAlSi_3O_8$. These appear, moreover, to be entirely adequate for the purpose, apart from the small iron content. In the following are tabulated the percentages by weight of the above four constituents in some typical nephelites. For various reasons the sums of these constituents are not 100, an important one being that H_2O seems to replace the alkaline oxides to a moderate extent in some nephelites.

	I	II	III	IV	V	VI	VII	VIII	IX
Ne......	65·0	63·0	56.0	70·0	68·0	64·5	73·5	70·0	9·5
Kp......	13·0	12·0	32·0	19·0	19·0	18·5	13·0	12·0	89·0
An......	1·5	15·0	12·0	0·0	2·5	4·0	2·0	4·0	1·5
Ab......	9·5	2·0	0·0	10·0	9·5	5·0	6·0	11·0	0·0

I. Nephelite from Wausau, Wis. Weidman, Geology of North Central Wisconsin, Wisconsin Survey Bull., xvi, 1907, p. 317. Analysis I.

II. Same. Analysis II.

III. "Pseudonephelite" Zambonini, Zs. Kryst., lii, 606, 1913.

IV. Nephelite from Eikaholmen, Norway. Foote and Bradley, this Journal, xxxi, 27, 1911.

V. Nephelite from Mariupol. Morozewicz, Bull. Acad. Sciences Cracovie, 958, 1907.

VI. Nephelite from Coimbatore, India. Mem. Geol. Surv. Ind., xxx, pt. 3, 187, 1901.

VII. Nephelite from Kuusamo. Hackman after Ramsay, Bull. de la Commis. Geol. de Finlande No. 11, 9, 1911.

VIII. Nephelite from Monte Ferru, Washington and Merwin, Jour. Wash. Acad. Sci., v, 391, 1915.

IX. Kaliophilite from Vesuvius. Zambonini, Mineralogia Vesuviana Appendix, p. 23.

Dependable analyses of nephelite are apparently not very numerous and no very definite general conclusions can be drawn from them. Nephelite III shows no albite, i. e. has no excess silica above the orthosilicate ratio, and II has very little,* showing that excess silica is not essential. When the albite is high the anorthite tends to be low (I, IV, V and VIII) and when the anorthite is high the albite tends to be low (II and III). The suggestion is that the members of the former group were formed from solutions containing sodic

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*Some of the albite of II occurs as minute inclusions. Weidman, Wis. Survey Bull. XVI, p. 318. It might be assumed, therefore, that the nephelite should be saturated with albite and that the analysis is faulty. It is possible, however, to imagine conditions under which saturation would not occur even with albite inclusions.

plagioclase and those of the latter group from solutions of calcic plagioclase, but it is impossible to be sure that this is true from the data at hand. The nephelites average upwards of 12 per cent plagioclase in solid solution.

The peculiar twinned nephelite described by Esch, from Etinde volcano, West Africa, seems to correspond definitely with the orthorhombic form of the potassium-rich nephelites.* Esch observed slightly inclined extinction and therefore considers his mineral triclinic, but the correspondence is too great in other respects to render it likely that his form is distinct from the artificial form. It is to be noted that the nephelinites described by him, though dominantly soda-rich, are sometimes rather rich in potash as well, running to leucitites. Possibly, then, some of the nephelite is potash-rich and closely related to the artificial varieties showing the same twinning. It was suggested in a former paper that Esch's mineral might be carnegieite with its properties modified by solid solution, but this suggestion now seems quite unjustified.†

General Considerations.

The mineral nephelite proves to be of rather complex constitution, a common feature of a number of rock-forming minerals. The micas, pyroxenes and amphiboles exhibit this characteristic in even more marked form; indeed their constitution has not yet been satisfactorily explained. The difficulty is the result of the binding up, within one crystalline phase or mineral, of several of the components‡ of the magma. While the complexity of the individual crystalline phases is greatly increased their number is correspondingly decreased and, in some respects, a simplification of the process of crystallization results. This fact is the key to the problem of the "gesteinsserie." It is the crystallization from the magma of these minerals of continuously varying composition which results in the formation from a single magma of a series of rock-types showing that consanguinity which is found to characterize the petrographic province.

Nephelite syenite is undoubtedly the most important of the alkaline rocks. Alkalic feldspar is a prominent constituent and through it nephelite syenite is related to sub-alkaline types. The suggestion has been offered in another paper that the nephelite syenites are intimately related to the mica-bearing sub-alkaline rocks, biotite granites.§ They are considered to

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* Sitzb. Berl. Akad., xviii, 400, 1901.

† N. L. Bowen, this Journal (4), xxxiii, 572, 1912.

‡ Components in the specialized phase rule sense, not synonymous with constituents.

§ The Later Stages of the Evolution of the Igneous Rocks, Jour. Geol. Supplement vol. xxiii, 55, 1915.

be probably a residuum from the granite magma, especially rich in volatile components. From the present work we obtain definite proof of a fact long suspected, viz. the existence in nephelite of the molecule $KAlSiO_4$. This commonly occurs in amounts of 15 per cent or more and is the same molecule that plays a fundamental rôle in the formation of the micas. At the same time it is not to be expected that any definite solution of the relation between two such rocks will be accomplished experimentally except in aqueous systems. The methods of attacking such systems, combining high temperatures and high pressures, have been worked out by Morey* and his investigations will be extended to more complex systems with a view to the solution of this and related problems.

The existence in nephelite of an average of more than 10 per cent plagioclase is of importance in connection with such rocks as iolite and nephelinite. Though free from plagioclase as a separate mineral, it is plain that one cannot consider the crystallization of the magma except as a part of a plagioclase-bearing system. This system would include likewise the plagioclase rocks with which nephelinite is normally associated and consideration of the crystallization of such a system serves to emphasize the relationship of the types.

The inversion temperature of nephelite does not prove to be very useful for the determination of the temperatures of formation of minerals. The pure compound $NaAlSiO_4$ inverts at 1248° but all the materials that it takes into solid solution occasion a sharp rise in the temperature of inversion. In order to appear in the carnegieite form, separation would have to take place at least as high as 1325°-1350°. The non-occurrence of carnegieite may, therefore, be considered as proof, if any be needed, that the separation of nephelite from magmas has always taken place at temperatures below those named.

The occurrence of the pseudo-hexagonal, twinned form of nephelite in the nephelinite described by Esch is not to be considered as evidence that separation took place at high temperatures. It is true that this form is believed to be a high temperature form of potassium-rich nephelites or kaliophilites but, unlike carnegieite, it can form at low temperatures also. Moreover it will persist at these temperatures just as the forms of silica, tridymite and cristobalite do.

Summary.

The present paper gives the results of an experimental investigation of the binary system $NaAlSiO_4$-$KAlSiO_4$. The soda compound occurs in two enantiotropic forms, nephelite

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* Jour. Am. Chem. Soc., xxxvi, 215, 1914.

and carnegieite, with an inversion point at 1248°. The high temperature form, carnegieite, melts at 1526°. The potash compound shows two forms, kaliophilite, isomorphous with nephelite, and an orthorhombic form with twinning analogous to that in aragonite. The orthorhombic form is apparently stable at temperatures above 1540° and melts in the neighborhood of 1800°.

The potash compound has a eutectic with carnegieite at 1404°. With nephelite it forms an unbroken series of solid solutions. It is concluded, therefore, that $NaAlSiO_4$ and $KAlSiO_4$ are the fundamental molecules of natural nephelites. But, in addition to these, nephelites contain variable amounts of plagioclase in solid solution, the plagioclase varying from albite to anorthite, the latter accounting for the lime content and the former for the excess silica of the natural mineral. The composition of nephelite should, therefore, be expressed in terms of the four molecules $NaAlSiO_4$, $KAlSiO_4$, $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$. Reference is made to the petrogenetic importance of the occurrence of the last two molecules, viz. plagioclase, in nephelites.

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D. C., December 4, 1916.