MINERALOGICAL MAGAZINE

JOURNAL OF THE MINERALOGICAL SOCIETY

Vol. 32 June 1959 No. 245

Nepheline solid solutions

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[Taken as read 2 April 1959.]

Summary. Published chemical analyses demonstrate that the nepheline formula should be written $K_xNa_yCa_z\square_{8-(x+y+z)}Al_{x+y+2z}Si_{16-(x+y+2z)}O_{32}$, where $\square$ stands for vacant sites. X-ray data are presented for the nepheline phase in four binary systems: Ne–$CaAl_2O_4$, Ne–An, Ne–Ab, Ne–Kp. Only in two of these systems do the cell-dimensions change with composition. In the first one, the cell-volume V increases linearly with increasing calcium content; in the last one, two singularities in the curve of V against x divide the phase $Na_{8-x}K_xAl_8Si_8O_{32}$ into three subphases: subpotassic ($0 < x < 0{\cdot}25$), mediopotassic ($0{\cdot}25 < x < 2{\cdot}00$), and perpotassic ($2{\cdot}00 < x < 4{\cdot}73$). Only in the subpotassic range are both high- and low-temperature forms found. Twenty-eight natural nephelines, for which chemical analyses and X-ray data are available in the literature, show that only the potassium content affects cell-dimensions. Although all analysed natural nephelines fall outside the subpotassic range, the re-examination of a Monte Somma specimen studied by Bannister (1931) reveals a few euhedral crystals of subpotassic nepheline in a mediopotassic phase.

NEPHELINE is an interesting example of a mineral that forms more than one type of solid solution, a fact which the formula as it is usually written, $(Na,K)AlSiO_4$, does not bring out. Even before the crystal structure of nepheline had been determined, Bannister (1931) pointed out that the number of oxygen atoms per cell is 32, and that the number of silicon and aluminium atoms must equal 16 if nepheline is a framework structure. The formula obtained from chemical analysis can be written essentially[1] as $K_xNa_yCa_zAl_nSi_mO_{32}$, with $x = K+\Delta K$, $y = Na+\Delta Na$, ..., &c., where K, Na, ..., are the exact numbers of potassium, sodium, ..., atoms per cell and ΔK, ΔNa, ..., are the corresponding errors of the analysis.

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[1] Neglecting small amounts of other cations whose role is discussed below.

TABLE I. Cell contents and X-ray data of natural nephelines $(\mathrm{K, Na, Ca, Mg, Fe^{2+}, Mn, Ti}, \square)_8(\mathrm{Si, Al, Fe^{3+}})_{16}\mathrm{O}_{32}$.

For each specimen the following data are listed: numbers of cations per cell (as obtained from the chemical analysis, i.e., K+ stands for x = K+ΔK, Na+ for y = Na+ΔNa, Ca+ for z = Ca+ΔCa, &c.); number of vacant sites □ (taken as the difference between 8 and the observed total number of cations per cell); numbers of tetrahedrally co-ordinated atoms per cell (as for cations, Al+ stands for Al+ΔAl, &c.); $\Sigma = (\mathrm{Al+Fe^{3+}+Si})+(\Delta\mathrm{Al}+\Delta\mathrm{Fe^{3+}}+\Delta\mathrm{Si})$, i.e. observed total number of tetrahedral atoms; $\Delta = \Delta\mathrm{Al}+\Delta\mathrm{Fe^{3+}}+\Delta\mathrm{Si}$; cell edges a and c (Å. units), $a \pm 0{\cdot}05\%$, $c \pm 0{\cdot}1\%$; $V_{\mathrm{obs.}}$, cell-volume (Å.^{3}) found by X-rays; $\mathrm{K_{pr.}}$ = K predicted from cell-volume (fig. 3); $\partial\mathrm{K} = \mathrm{K_{obs.}}-\mathrm{K_{pr.}}$; $V_{\mathrm{pr.}}$, cell-volume predicted from K content (fig. 3); $\partial V = V_{\mathrm{obs.}}-V_{\mathrm{pr.}}$; $D_{\mathrm{calc.}}$ and $D_{\mathrm{obs.}}$, calculated and observed densities (g./cm.^{3}).

Nos. 1, 4, 7, 9, 13 are M. Hey's nos. I, II, V, VI, VII, respectively (Bannister, 1931). No. 15 is N. Saito's Shinjozan (Miyashiro and Miyashiro, 1954). The remaining analyses (Smith and Sahama, 1954) are identified as follows: Nos. 2, 3, 5, 11, 14, 16, 18 are J. H. Scoon's nos. 63197, 34475, 34480, 238, 273, 276, E2, respectively. Nos. 6, 10, 19, 20, 21, 23, 24, 25, 27, 28 are P. Ojanperä's FEAE nos. 198, 170, 90, 49, 89, 88, 87, 86, 92, 93, respectively. Nos. 8 and 26 are H. B. Wilk's FEAE-134 and C9956. No. 12 is E. G. Zies' Gooderham. No. 17 is M. Lehijärvi's Ivoara. No. 22 is R. B. Ellestad's R-118.

No.	1.	2.	3.	4.	5.	6.	7.	8.	9.
K+	0·76	0·90	0·94	0·97	1·15	1·24	1·25	1·28	1·29
Na+	6·00	6·43	6·31	5·59	6·28	5·96	5·97	5·84	5·53
Ca+	0·51	0·15	0·28	0·38	0·16	0·07	0·25	0·00	0·44
Mg+	—	0·00	0·02	—	0·01	0·00	—	0·02	—
$\mathrm{Fe^{2+}}$+	—	—	—	—	—	0·05	—	0·04	—
Mn+	—	—	0·00	—	0·00	0·00	—	0·00	—
Ti+	—	0·00	0·00	—	0·00	0·01	—	0·00	—
□	0·73	0·52	0·45	1·06	0·40	0·67	0·53	0·82	0·74
Al+	7·69	7·26	7·64	7·70	7·60	7·33	7·58	7·44	7·89
$\mathrm{Fe^{3+}}$+	—	0·08	0·02	—	0·07	0·14	—	0·08	—
Si+	8·29	8·59	8·29	8·39	8·30	8·53	8·38	8·55	8·16
Σ	15·98	15·93	15·95	16·09	15·97	16·00	15·96	16·07	16·05
Δ	−0·02	−0·07	−0·05	+0·09	−0·03	0·00	−0·04	+0·07	+0·05
a	9·997	9·981	9·987	9·972	9·988	9·990	9·982	9·990	9·982
c	8·348	8·361	8·368	8·378	8·374	8·373	8·378	8·381	8·363
$V_{\mathrm{obs.}}$	722·5	721·4	722·8	721·5	723·5	723·7	723·0	724·4	721·7
$\mathrm{K_{pr.}}$	1·00	0·82	1·05	0·83	1·17	1·20	1·08	1·32	0·87
$\partial\mathrm{K}$	−0·24	+0·18	−0·11	+0·14	−0·02	+0·04	+0·17	−0·04	+0·42
$V_{\mathrm{pr.}}$	721·3	722·1	722·4	722·5	723·6	724·1	724·2	724·3	724·4
$\partial\mathrm{V}$	+1·2	−0·7	+0·4	−1·0	−0·1	−0·4	−1·2	+0·1	−2·7
$D_{\mathrm{calc.}}$	2·621	—	—	2·617	—	—	2·637	—	2·644
$D_{\mathrm{obs.}}$	2·614	—	—	2·620	—	—	2·629	—	2·608

No.	10.	11.	12.	13.	14.	15.	16.	17.	18.
K+	1·29	1·31	1·34	1·40	1·43	1·49	1·49	1·50	1·76
Na+	5·81	5·65	5·87	5·47	6·09	5·95	6·14	6·10	6·03
Ca+	0·10	0·36	0·15	0·30	0·10	0·06	0·05	0·00	0·03
Mg+	0·01	0·04	0·01	—	0·00	0·09	0·00	0·04	0·00
$\mathrm{Fe^{2+}}$+	0·03	—	—	—	—	—	—	0·05	—
Mn+	0·00	—	0·00	—	—	—	—	0·00	—
Ti+	0·01	0·00	0·00	—	—	—	0·00	0·00	—
□	0·75	0·64	0·63	0·83	0·38	0·41	0·32	0·31	0·13
Al+	7·30	7·96	7·68	7·47	7·71	7·83	7·67	7·81	7·78
$\mathrm{Fe^{3+}}$+	0·14	0·02	0·01	—	0·02	0·08	0·03	0·18	0·02
Si+	8·58	8·08	8·35	8·53	8·27	8·13	8·29	8·06	8·18
Σ	16·02	16·06	16·04	16·00	16·00	16·04	15·99	16·05	15·98
Δ	+0·02	+0·06	+0·04	0·00	0·00	+0·04	−0·01	+0·05	−0·02
a	9·992	9·999	10·003	9·992	9·994	10·014	9·997	9·999	10·001
c	8·374	8·387	8·382	8·388	8·372	8·392	8·381	8·385	8·388
$V_{\mathrm{obs.}}$	724·1	726·2	726·3	725·3	724·2	728·8	725·5	726·0	726·6
$\mathrm{K_{pr.}}$	1·27	1·62	1·63	1·47	1·28	2·05	1·50	1·58	1·68
$\partial\mathrm{K}$	+0·02	−0·31	−0·29	−0·07	+0·15	−0·56	−0·01	−0·08	+0·08
$V_{\mathrm{pr.}}$	724·4	724·5	724·7	725·0	725·2	725·5	725·5	725·6	727·1
∂V	−0·3	+1·7	+1·6	+0·3	−1·0	+3·3	0·0	+0·4	−0·5
$D_{\mathrm{calc.}}$	—	—	—	2·623	—	—	—	—	—
$D_{\mathrm{obs.}}$	—	—	—	2·597	—	—	—	—	—

TABLE I. (*cont.*)

No.	19.	20.	21.	22.	23.	24.	25.	26.	27.	28.
K+	1·95	2·35	2·78	2·80	2·81	2·84	3·01	3·11	3·11	3·19
Na+	5·39	4·68	4·63	4·79	4·65	4·62	4·42	4·20	4·36	4·20
Ca+	0·19	0·11	0·19	0·19	0·19	0·17	0·19	0·31	0·19	0·19
Mg+	0·02	0·09	0·07	0·07	0·07	0·05	0·05	0·03	0·05	0·05
Fe^{2+}+	0·08	0·05	0·03	—	0·03	0·03	0·05	0·10	0·04	0·03
Mn+	0·00	0·00	0·03	—	0·00	0·00	0·00	—	0·00	—
Ti+	0·01	0·02	0·01	0·02	0·01	0·01	0·01	0·01	0·01	0·01
□	0·36	0·70	0·26	0·13	0·24	0·28	0·27	0·24	0·24	0·33
Al+	7·60	7·68	7·77	7·76	7·78	7·80	7·76	7·64	7·68	7·76
Fe^{3+}+	0·12	0·26	0·16	0·12	0·15	0·13	0·16	0·27	0·15	0·13
Si+	8·24	8·14	8·07	8·04	8·05	8·09	8·05	8·02	8·16	8·12
Σ	15·96	16·08	16·00	15·92	15·98	16·02	15·97	15·93	15·99	16·01
Δ	−0·04	+0·08	0·00	−0·08	−0·02	+0·02	−0·03	−0·07	−0·01	+0·01
a	10·009	10·042	10·064	10·079	10·069	10·064	10·084	10·101	10·068	10·092
c	8·390	8·412	8·427	8·432	8·415	8·422	8·439	8·447	8·429	8·441
$V_{\text{obs.}}$	728·0	734·7	739·1	741·8	738·9	738·7	743·2	746·4	739·9	744·5
$\text{K}_{\text{pr.}}$	1·92	2·53	2·90	3·13	2·88	2·86	3·25	3·52	2·97	3·36
∂K	+0·03	−0·18	−0·12	−0·33	−0·07	−0·02	−0·24	−0·41	+0·14	−0·17
$V_{\text{pr.}}$	728·2	732·6	737·7	738·0	738·1	738·5	740·5	741·7	741·7	742·6
∂V	−0·2	+2·1	+1·4	+3·8	+0·8	+0·2	+2·7	+4·7	−1·8	+1·9
$D_{\text{calc.}}$	—	—	—	—	—	—	—	—	—	—
$D_{\text{obs.}}$	—	—	—	—	—	—	—	—	—	—

By the framework criterion we must have Al+Si = 16 (i), and, to balance the charges, K+Na+2Ca = Al (ii). By definition we have $n+m-16 = (\text{Al}+\Delta\text{Al})+(\text{Si}+\Delta\text{Si})-16$, and, in view of (i), $n+m-16 = \Delta\text{Al}+\Delta\text{Si}$ (iii). (The analytical error in the determination of aluminium +silicon equals the number of aluminium and silicon atoms reported in excess of 16 when the analysis is referred to 32 oxygens.) Likewise by definition we write $x+y+2z-n = (\text{K}+\Delta\text{K})+(\text{Na}+\Delta\text{Na})+(2\text{Ca}+2\Delta\text{Ca})-(\text{Al}+\Delta\text{Al})$ and, in view of (ii), $x+y+2z-n = \Delta\text{K}+\Delta\text{Na}+2\Delta\text{Ca}-\Delta\text{Al}$ (iv).

The expressions (iii) and (iv) are the two quantities, considered by Bannister and Hey, which in a good analysis should be as small as possible. Because a chemical analysis is reported in the form of oxides, we have (sum of positive charges) $x+y+2z+3n+4m = 64$, equivalent to Bannister's identity[1] $x+y+2z-n = 4[16-(n+m)]$. In order to write the idealized formula of nepheline, we assume an error-free chemical analysis and therefore set (iv) and (iii) equal to zero. This gives $x+y+2z = n$ and $n+m = 16$.

In addition we now know, from the crystal structure determination of nepheline (Buerger, Klein, and Donnay, 1954; Hahn and Buerger, 1955), that the alkali and alkaline earth ions occupy eight sites, namely those of positions $2{:}b$ and $6{:}c$ in space-group $P6_3$. But all the available chemical analyses of natural nephelines (table I) show a deficiency of

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[1] Bannister (1931, p. 576) writes $[(n+m)-16]$ when he means $[16-(n+m)]$.

cations of such an order of magnitude that it cannot be ascribed to analytical errors. The idealized formula must therefore take into account the possibility of some cation sites being vacant; it is written as

$$K_xNa_yCa_z\square_{8-(x+y+z)}Al_{x+y+2z}Si_{16-(x+y+2z)}O_{32},$$

where $\square$ stands for vacant cation sites.

Additional elements reported present in small amounts are Mg, Fe, Mn, and Ti. Adding the experimentally determined number of ferric ions to the sum $(n+m)$ of silicon and aluminium atoms reduces the analytical error $|16-(n+m)|$ for all but three of the twenty-eight analyses given in table I. As might be predicted from ionic size considerations, ferric ions appear to substitute for silicon and aluminium in tetrahedral co-ordination, whereas all other cations substitute for Na, K, or Ca.

To study the effect of substitutions on the cell-dimensions of nepheline in the laboratory, it is convenient to consider the one-phase synthetic-nepheline region in each of four binary systems. Natural nephelines, on the other hand, may lie in the quinary system $NaAlSiO_4$(Ne)–$KAlSiO_4$(Kp)–$NaAlSi_3O_8$(Ab)–$CaAl_2Si_2O_8$(An)–$CaAl_2O_4$. X-ray results obtained on synthetic samples will be given for pure-sodium nepheline and for each binary system. They will be compared with X-ray data for analysed natural nephelines, taken from Bannister (1931), Smith and Sahama (1954), and Miyashiro and Miyashiro (1954). Of the thirty-four available analyses, we are using (table I) the twenty-eight that obey Hey's reliability criterion (in Bannister, 1931)

$$|\ \Delta Al+\Delta Fe^{3+}+\Delta Si\ | \leqslant 0{\cdot}10.$$

X-ray procedure.

The sample is powdered to 200-mesh size and a smear mount is prepared on a glass slide for use with the Norelco diffractometer. Silicon, with its 111 peak at $2\theta = 28{\cdot}465°$, is used as an internal standard. The samples are run under the following conditions: scanning speed, usually $\frac{1}{2}°$ per minute ($\frac{1}{4}°$for some repeat runs); chart scale 1 inch per degree; receiving slit 0·003 inch; Cu-$K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å.). Two charts are taken for each run (see table II), one (I) with the Geiger counter moving in the direction of decreasing 2θ values, the other (II) with the motion reversed (Parrish and Wilson).[1] Six peaks, in the range $2\theta = 19°$ to $2\theta = 32°$,

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[1] W. Parrish and A. J. C. Wilson, Precision measurement of lattice parameters of polycrystalline specimens, Philips Lab., Irvington-on-Hudson, New York, Techn. Report, 1954, no. 85, p. 16; Internat. Tables X-ray Cryst., vol. 2 (in press).

TABLE II. Calculation of cell-dimensions from powder data by method of least squares
Synthetic high temperature $NaAlSiO_4$. $s=h^2+hk+k^2$

		Chart I.		Chart II.											
	hkil.	$2\theta_{obs.}$	$2\theta_{corr.}$	$2\theta_{obs.}$	$2\theta_{corr.}$	$2\theta_{ave.}$	$Q_{obs.}$	*s.*	l^2.	s^2.	sl^2.	l^4.	*s*Q	l^2Q.	$Q_{calc.}$
Si	111	28·431	28·465	28·538	28·465	—	—	—	—	—	—	—	—	—	—
	corr.	+0·034		−0·073											
	$20\bar{2}0$	20·540	20·574	20·638	20·565	20·570	0·05364	4	0	16	0	0	0·21456	0	0·05365
	0002	21·205	21·239	21·333	21·260	21·250	0·05721	0	4	0	0	16	0	0·22884	0·05720
	$20\bar{2}1$	23·158	23·192	23·260	23·187	23·190	0·06798	4	1	16	4	1	0·27192	0·06798	0·06795
	$21\bar{3}0$	27·289	27·323	27·400	27·327	27·325	0·09388	7	0	49	0	0	0·65716	0	0·09388
	$20\bar{2}2$	29·705	29·739	29·816	29·743	29·741	0·11083	4	4	16	16	16	0·44332	0·44332	0·11085
	$30\bar{3}0$	31·038	31·072	31·143	31·070	31·071	0·12071	9	0	81	0	0	1·08639	0	0·12071
										178	20	33	2·67335	0·74014	
										A	B	C	D	E	

$$a^{*2} = \frac{\begin{vmatrix} D & B \\ E & C \end{vmatrix}}{\begin{vmatrix} A & B \\ B & C \end{vmatrix}} = 0{\cdot}013412\ \text{Å.}^{-2} \qquad c^{*2} = \frac{\begin{vmatrix} A & D \\ B & E \end{vmatrix}}{\begin{vmatrix} A & B \\ B & C \end{vmatrix}} = 0{\cdot}014300\ \text{Å.}^{-2}$$

$$a^* = 0{\cdot}115810\ \text{Å.}^{-1} \qquad c^* = 0{\cdot}119583\ \text{Å.}^{-1}$$

$$a = 9{\cdot}971\ \text{Å.} \pm 0{\cdot}05\% \qquad c = 8{\cdot}362\ \text{Å.} \pm 0{\cdot}05\%$$

$$V = 2\sqrt{3}/3a^{*2}c^* = 720{\cdot}0\ \text{Å.}^3$$

Remark: Sums A, B, C, and therefore the determinants in the denominators of a^{*2} and c^{*2} are the same for all charts, as long as all the reflections can be measured. $20\bar{2}0$ is occasionally too weak to give an accurate reading.

are used to obtain the cell-dimensions by the method of least squares (table II). The values of $Q(hkil)$ are obtained from the observed values of 2θ (Cu-$K\alpha$) by use of appropriate tables (Donnay and Donnay).[1]

Single crystals were studied on precession and Weissenberg cameras with Cu-$K\alpha$ and Mo-$K\alpha$ (λ = 0·7107 Å.) radiations.

Pure-sodium nepheline.

A large number of pure-sodium nephelines with different thermal histories were examined (table III) to find out whether the cell-dimensions vary continuously with the temperature of crystallization, as is the case for albite (MacKenzie, 1957). The data for the low-temperature form show that the cell-dimensions are independent of the thermal history of the specimen. They are (averaged values): a = 9·986, c = 8·330, both ±0·005 Å., c/a = 0·8342±0·005. For the high-temperature form one sample gave a = 9·971, c = 8·362, both ±0·005 Å., c/a = 0·8386 ± 0·005. The X-ray patterns of the two forms are so similar that they cannot be told apart on inspection,[2] but measurements lead to a difference of 0·4% in the c-dimension, a difference well outside the limits of error of our determinations. Because the high-temperature form was

TABLE III. X-ray data for pure-sodium nepheline; synthetic samples with different thermal histories. Synthesized by J. F. Schairer, except for the last specimen, prepared by F. R. Boyd.

Thermal history (° C.).	a (Å.).	c (Å.).	V (Å.^{3}).	c/a.
1100°, 6 hrs. quenched high-temp. form	9·971	8·362	720·0	0·8386*
900°, 20 days low-temp. form	9·984	8·333	719·3	0·8346
900°, 34 „ „	9·988	8·333	719·9	0·8343
1000°, 6 „ „	9·986	8·331	719·5	0·8343
1000°, 34 „ „	9·986	8·328	719·2	0·8340
1050°, 6 „ „	9·984	8·333	719·3	0·8346
1050°, 34 „ „	9·991	8·331	720·2	0·8339
1200°, 2 „ „	9·984	8·328	719·1	0·8341
1200°, 10 „ „	9·984	8·328	719·1	0·8341
540°, 1 week, 2000 bars, hydrothermal low-temp. form	9·989	8·328	719·6	0·8337

* Calculated specific gravity is 2·621. Observed value is 2·619 at 21° C. (Bowen, 1912, p. 10).

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[1] G. Donnay and J. D. H. Donnay, Tables for the interpretation of X-ray diffraction data, giving the square, Q, of the reciprocal lattice vector. . . . Crystallographic Laboratory of the Johns Hopkins University, 1951. Reprinted 1955 (limited edition).

[2] We cannot confirm the lowering of symmetry from hexagonal to orthorhombic reported for the high-temperature form by Smith and Tuttle (1957).

obtained only accidentally on quenching, it appeared advisable to confirm the low-high transition. A low-temperature pure-sodium nepheline was heated on the diffractometer. The reflection $20\bar{2}2$ was recorded at the following temperatures: 240°, 410°, 610°, 810°, 1050°, and 1150°, all ±50° C. A plot of $2\theta(20\bar{2}2)$ against temperature (fig. 1) shows a break at 810±50° C. Smith and Tuttle (1957) place the transition at 900° C. We have studied the extent of solid solution range for the low- and high-temperature forms only in the binary system Ne–Kp.

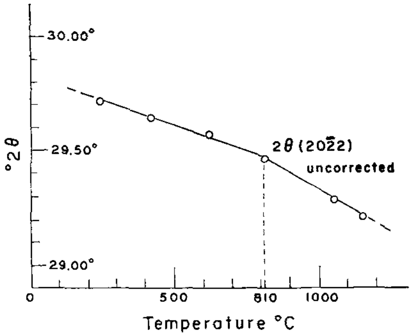

FIG. 1. Synthetic pure-sodium nepheline. Uncorrected angle $2\theta(20\bar{2}2)$ obtained with Cu-$K\alpha$ radiation at various temperatures (° C., ±50°). The transition between low-temperature and high-temperature forms is marked by a break in the curve in the neighbourhood of 810°.

To our knowledge, no natural occurrence of potassium-free nepheline has been reported in the literature. Evidence for such an occurrence at Monte Somma, Italy, will be presented below.

The four solid solutions.

Double substitution—calcium replacing sodium and aluminium replacing silicon, $Na_{8-Z}Ca_ZAl_{8+Z}Si_{8-Z}O_{32}$. *Solid solution A.* This is of the type encountered in the plagioclase series. It is represented by the one-phase nepheline region in the binary system $NaAlSiO_4$–$CaAl_2O_4$ (Goldsmith, 1949). Dr. Goldsmith kindly placed his powder samples at our disposal. Because single crystals were not available for study, the presence of superstructure reflections (as are observed on plagioclases) cannot be ruled out. The cell-volume increases linearly with increasing calcium content by an amount of 2·2 Å.^{3} per calcium ion (table IV A and fig. 2). Extrapolating the plot of cell-dimensions against calcium content to $Z = 0$ leads to cell-dimensions $a = 8{\cdot}362$, $c = 9{\cdot}970$ Å., equal to those for high-temperature pure-sodium nepheline. The limit of solid solution falls beyond 60 wt.% $CaAl_2O_4$, corresponding to $Z > 4{\cdot}6$ in the above formula.

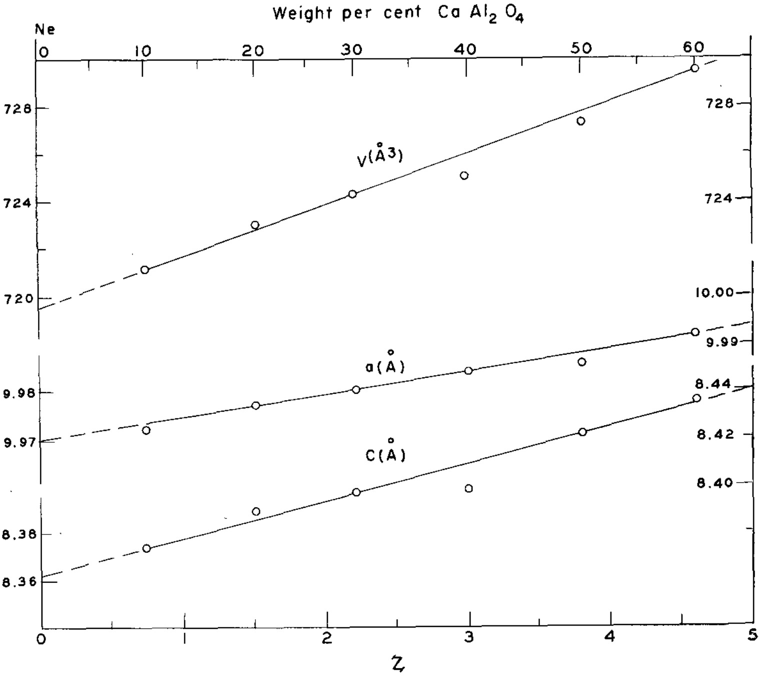

FIG. 2. Change of cell-dimensions (c and a in Å.; V in Å.^{3}) in synthetic $Na_{8-Z}Ca_ZAl_{8+Z}Si_{8-Z}O_{32}$.
The abscissa gives the number Z of calcium atoms per cell (lower scale) or the wt. % $CaAl_2O_4$ (upper scale).

Substitution plus omission—calcium and vacant sites in equal proportions replacing sodium, $Na_{8-2z}Ca_z\square_zAl_8Si_8O_{32}$. *Solid solution B.* This is represented by the one-phase nepheline region in the binary system $NaAlSiO_4$–$CaAl_2Si_2O_8$ (Bowen, 1912; Gummer, 1943). Two samples (Schairer's nos. 877 and 869, table IV B) of compositions 20 and 45 wt.% $CaAl_2Si_2O_8$, consist of a nepheline and a plagioclase phase when completely crystallized. Both sets of cell-dimensions therefore refer to the composition with maximum z value, which is less than 1·33. The cell-dimensions are the same, within experimental error, as those of the high-temperature pure-sodium nepheline.

Omission and substitution—vacant sites replacing sodium and silicon *replacing aluminium*, $Na_{8-y}\square_y Al_{8-y}Si_{8+y}O_{32}$. *Solid solution C.* This is represented by the one-phase nepheline region in the binary system $NaAlSiO_4$–$NaAlSi_3O_8$ (Greig and Barth, 1938). Dr. W. S. MacKenzie, who studied this system with water as an additional component, kindly gave us a thick-tabular crystal, 0·2 mm. in its largest dimension, on the preparation of which he reports as follows:

> A glass of composition 37½% $NaAlSiO_4$.62½% SiO_2 (wt. %) prepared by Dr. J. F. Schairer was held at 700° C. at a water vapour pressure of 2000 bars for a period of eleven days in a Tuttle hydrothermal quenching apparatus. The charge of glass was contained in a small platinum tube open at one end so that there was free access of water to the silicate glass. When the charge was quenched and examined, it was found that the upper surface was covered with euhedral nepheline crystals and below was a mass of very small albite crystals and some glass. The nepheline crystals are believed to be of composition 76 $NaAlSiO_4$.24 $NaAlSi_3O_8$ (wt. %) since this is the limit of omission solid solution in nepheline at this temperature. (MacKenzie, unpublished data.)

The cell-dimensions of the limiting composition, $y = 1{\cdot}0$, are given in table IV C; they are the same as those of high-temperature pure-sodium nepheline, within the limits of experimental accuracy. Thus, in neither of the solid solutions *B* and *C* does the introduction of vacant sites into the structure lead to a change in the cell-dimensions of the high-temperature form.

Substitution—potassium replacing sodium, $K_xNa_{8-x}Al_8Si_8O_{32}$. *Solid solution D.* This solid solution, the simplest and in nature the most important one of the four, is represented by the one-phase nepheline region in the binary system $NaAlSiO_4$–$KAlSiO_4$ (Bowen, 1917; Smith and Tuttle, 1957). Samples used in this study were prepared by Dr. Bowen in 1917, and by one of us (J. F. S.) in 1935 and 1956. Small amounts of beta-alumina and corundum can be detected under the microscope in all of the completely crystalline samples and the experimentally determined liquidus temperatures do not fall on a smooth curve. Thus all samples are slightly off composition because of alkali loss by volatilization during preparation, but the departure from composition by synthesis must be small, probably less than 1 wt.%, which is equivalent to $x = 0{\cdot}07$.

The sample of composition 62·50 wt.% $KAlSiO_4$, $x = 4{\cdot}796$, is the first one whose powder pattern shows non-nepheline lines. The cell-dimensions of its nepheline phase (table IV D) indicate that the limit of solid solution at 1200° C. occurs at $x = 4{\cdot}73$ or 61·7 wt.% $KAlSiO_4$ (fig. 3). Within the range $x = 0$ to $x = 4{\cdot}73$ the plot of cell-dimensions against potassium content x (fig. 3) consists of several straight-line

TABLE IV. X-ray data for synthetic nephelines.

A. System Ne–$CaAl_2O_4$, $Na_{8-Z}Ca_ZAl_{8+Z}Si_{8-Z}O_{32}$ (synthesized by Goldsmith).

Run.	$CaAl_2O_4$ wt. %.	Z.	Thermal history (° C.).	a ±0·2%	c ±0·2%	V.
—	0	0	—	*9·970 Å.	*8·362 Å.	*719·6 Å.^{3}
72	10	0·73	1000°, 3 days	9·972	8·374	721·2
169a	20	1·5	800°, 10 days	9·977	8·389	723·1
169b	30	2·2	800°, 10 days	9·980	8·397	724·3
165	40	3·0	1060°, 90 hours	9·984	8·398	725·1
170c	50	3·8	800°, 25 days and 900°, 11 days	9·986	8·421	727·3
170d	60	4·6	800°, 25 days	9·992	8·436	729·5

B. System Ne–An, $Na_{8-2z}Ca_z\square_zAl_8Si_8O_{32}$ (synthesized by Schairer).

No.	$CaAl_2Si_2O_8$ wt. %	z.	Thermal history (° C.).	a ±0·05%.	c ±0·05%.	V.
877	20·00†	‡	1060°, 3 months	9·969 Å.	8·363 Å.	719·8 Å.^{3}
869	45·00†	‡	1100°, 18 days	9·968	8·364	719·7

C. System Ne–Ab, $Na_{8-y}\square_yAl_{8-y}Si_{8+y}O_{32}$ (synthesized by MacKenzie).

Run.	$NaAlSi_3O_8$ wt. %.	y.	Thermal history (° C.).	a ±0·3%.	c ±0·3%.	V.
A12	24†	1·0	700°, 2000 bars, 11 days, water	9·971 Å.	8·361 Å.	719·9 Å.^{3}

* Cell-dimensions obtained by extrapolation (cf. values for high-temperature form, table III).
† Composition of original glass.
‡ Limit of solid solution at given temperature ($z < 1{\cdot}33$).

D. System Ne–Kp, $K_xNa_{8-x}Al_8Si_8O_{32}$.

Quenched high-temperature form

				Present work			Smith and Tuttle (1957)		
Synthesized by.	$KAlSiO_4$ wt. %.	x	Thermal history (° C.).	a ±0·05%	c ±0·05%.	V.	a ±0·05%.	c ±0·05%.	V.
Schairer	2·00	0·144	1200°, 8 days	9·971 Å.	8·356 Å.	719·4 Å.^{3}	—	—	—
,,	2·00	0·144	1200°, 8 days	9·973	8·358	719·9	—	—	—
,,	3·75	0·270	1050°, 12 days	9·971	8·358	719·6	—	—	—
,,	3·75	0·270	1100°, 10 days	9·975	8·360	720·4	—	—	—
,,	3·75	0·270	1200°, 12 days	9·975	8·358	720·2	—	—	—

TABLE IV. (*cont.*)

Low-temperature form

Synthesized by.	$KAlSiO_4$ wt. %.	x	Thermal history (° C.).	Present work			Smith and Tuttle (1957)		
				a ±0·05%.	c ±0·05%.	V.	a ±0·05%.	c ±0·05%.	V.
Schairer	2·00	0·144	1200°, 5 days	9·989 9·980	8·333 8·333	719·7 (*a*) 719·2 (*b*)	— —	— —	— —
,,	2·50	0·180	1060°, 29 days	9·977	8·341	719·1	—	—	—
,,	2·50	0·180	1200°, 6 days	9·970 9·977	8·332 8·337	717·2 718·6	— —	— —	— —
,,	2·50	0·180	1200°, 3 days	9·985	8·335	719·7	—	—	—
,,	3·00	$0{\cdot}216_5$	1200°, 7 days	9·966	8·356	718·7	—	—	—
,,	4·00	0·289	1100°, 10 days	9·969	8·354	719·0	—	—	—
,,	4·00	0·289	1200°, 5 days	9·963	8·354	718·3	—	—	—
,,	4·00	0·289	1200°, 8 days	9·971	8·355	719·4	—	—	—
Bowen	5·00	0·361	1100°, 7 days	9·968	8·353	718·8	—	—	—
Schairer	6·00	0·434	1200°, 5 days	9·963 9·971	8·347 8·354	717·2 (*a*) 718·8 (*b*)	— —	— —	— —
,,	6·00	0·434	1200°, 8 days	9·976	8·361	720·6	—	—	—
Bowen	10·00	0·726	—	—	—	—	9·981 Å.	8·360 Å.	721·2 Å.^{3}
Schairer	20·00	1·467	1100°, 34 days	10·001	8·375	725·4	9·998	8·376	725·1
Bowen	25·00	1·843	1300°, 6 hours	—	—	—	10·011	8·387	727·9
Schairer	27·07	2·000	1100°, 33 days	10·015	8·387	728·5	—	—	—
,,	29·00	2·147	cryst. at 1200°	—	—	—	10·018	8·396	729·7
,,	32·50	2·415	cryst. at 1200°	10·041	8·400	733·4	10·035	8·401	732·7
,,	37·50	2·802	cryst. *c.* 1300°	10·063	8·418	738·2	10·060	8·417	737·7
Bowen	40·00	2·996	cryst. at 1300°	—	—	—	*10·074	8·423	740·3
Schairer	42·50	3·192	—	—	—	—	10·087	8·428	742·6
,,	45·00	3·389	cryst. *c.* 1350°	10·099	8·439	745·5	—	—	—
,,	47·50	3·587	cryst. at 1350°	—	—	—	10·110	8·440	747·1
Bowen	50·00	3·785	cryst. at 1300°	—	—	—	*10·122	8·445	749·3
Schairer	52·50	3·985	cryst. at 1200°	10·133	8·455	751·8	10·133	8·449	751·3
,,	55·00	4·186	cryst. at 1200°	10·145	8·464	754·4	—	—	—
,,	57·50	4·389	cryst. at 1350° then at 1200°	—	—	—	10·163	8·461	756·8
,,	62·50	4·796	cryst. at 1350° then at 1200°	10·178	8·480	760·8	10·183	8·473	760·9

(*a*) ¼°/minute, (*b*) ½°/minute.

* Cell-dimensions calculated from 2θ values obtained by Smith (in Smith and Sahama, 1954).

portions. The low- and high-temperature forms are observed only near the sodium end of the series; the low-temperature form extends from $x = 0$ to $x = 0{\cdot}25$ whereas the high-temperature form is found to extend from $x = 0$ to $x = 0{\cdot}27$. Because of the uncertainty in composition, however, this difference in solid solution range cannot be considered a significant one. Beyond $x = 0{\cdot}25$ only one form is observed. Its cell-volume increases linearly by 5·82 Å.³ per potassium ion. At $x = 2{\cdot}00$ the volume curve shows a singularity; for $x > 2{\cdot}00$ the curve is again a straight line with a slope corresponding to 11·8 Å.³ per potassium ion.

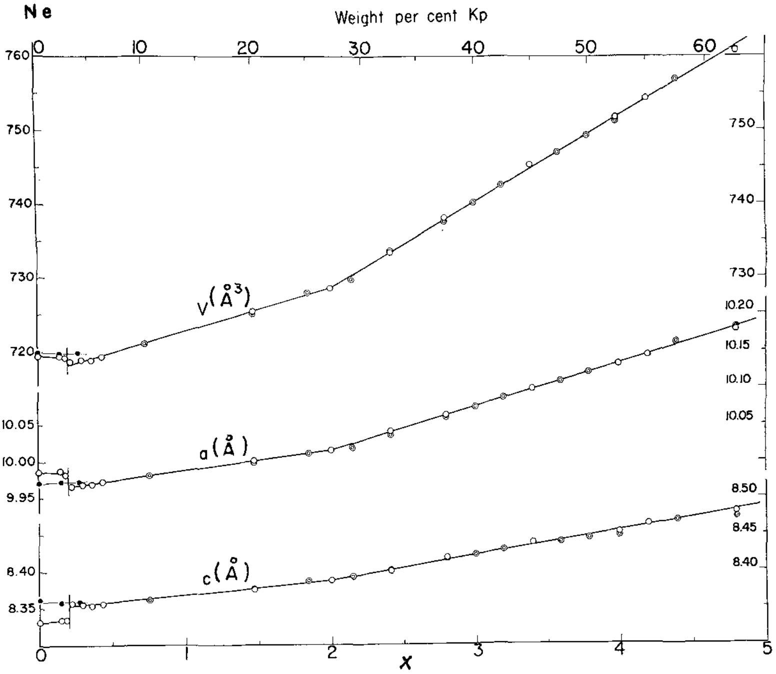

FIG. 3. Change of cell-dimensions (c and a in Å.; V in Å.³) in synthetic $Na_{8-x}K_xAl_8Si_8O_{32}$.
The abscissa gives the number x of potassium atoms per cell (lower scale) or the wt. % Kp (upper scale). Black circles, quenched high-temperature form; white circles, low-temperature form; double rings, previous data (Smith and Tuttle, 1957).

The experimental uncertainty in cell-volume and composition makes it impossible to decide whether a singularity or discontinuity occurs in the cell-volume at $x = 0{\cdot}25$, whereas at $x = 2{\cdot}00$ all experimental data point towards a singularity. The fact that the 'one-phase' nepheline region in this binary system can be subdivided into three 'subphases' has been discussed elsewhere (Donnay, 1957). We propose to use the adjectives 'subpotassic', 'mediopotassic', and 'perpotassic' to designate the nephelines with the following composition ranges: $0 < x < 0{\cdot}25$, $0{\cdot}25 < x < 2{\cdot}00$, and $2{\cdot}00 < x < 4{\cdot}73$, respectively.

Comparison of X-ray data for natural and synthetic nephelines.

Let us first investigate the effect of potassium content on the cell-volume of natural nephelines (fig. 4). Superposing the corresponding curve obtained for the synthetic samples in the binary system Ne–Kp shows that, on the basis of the literature data used here, the potassium content can be estimated with reasonable accuracy, as shown in row $\delta K = K_{obs.} - K_{pred.}$ (table I).

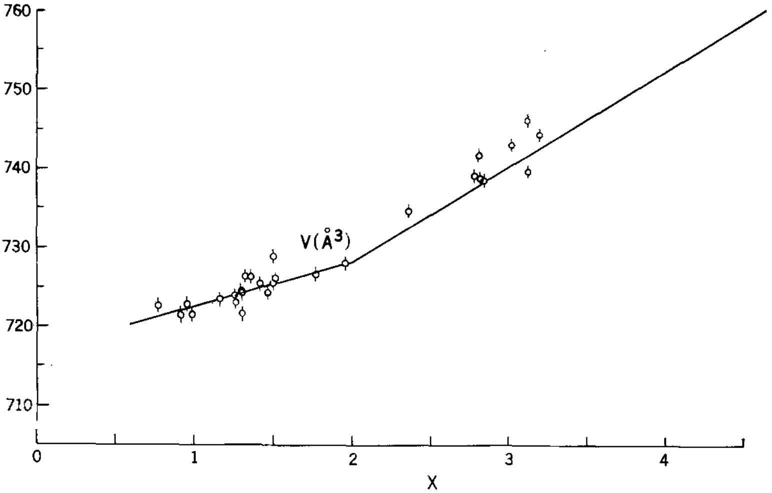

FIG. 4. Natural nephelines. Change of cell-volume V (in Å.^{3}) with number x of potassium atoms per cell. Length of line segment at each point indicates limits of error of X-ray determination. Superposed is the curve obtained for synthetic nephelines (from fig. 3).

It is of historic interest to note that Bannister (1931, fig. 3) already suspected a simple relation of cell-volume to potassium content. But he was handicapped because the only X-ray data available to him were those he had determined himself (on nine samples). For all the other samples he calculated the cell-volume from the density and cell-content of the analysed material. As the density changes very little with composition (table I), the points he plotted were widely scattered, and he concluded that '. . . the relation between cell-volume and the potassium content must be treated with reserve unless further evidence can be adduced'. The fact that this evidence is now at hand is due in large part to the availability of synthetic samples covering and even exceeding the range of nepheline compositions reported in natural specimens. Smith and Sahama (1954) already used the data from synthetic samples to try to predict the chemical composition of natural nephelines. Their treatment differs from ours in that it does not take vacant sites into consideration; their curves of $2\theta_{\mathrm{Cu}}$ for $21\bar{2}0$ and $20\bar{2}2$, which take the place of cell-dimensions, are plotted against the atomic ratio K/(K+Na+Ca) rather than against the number of potassium atoms per cell.

We are now in a position to predict the cell-volume, $V_{\mathrm{pred.}}$, on the basis of the analytical x value, $\mathrm{K}_{\mathrm{obs.}} = \mathrm{K} + \Delta\mathrm{K}$ (fig. 3), and to investigate the relation between $\partial V = V_{\mathrm{obs.}} - V_{\mathrm{pred.}}$ and the observed number of vacant sites. Inspection of the corresponding two rows in table I shows that no relationship exists. In natural nephelines as well as in the binary systems Ne–An and Ne–Ab, replacement of cations by vacant sites produces no noticeable change in cell-volume.

Finally let us inquire whether a relationship exists between ∂V and the number of calcium ions. A comparison of the corresponding rows in table I shows no correlation.

Because increasing calcium content leads to increasing cell-volume in the binary system Ne–$\mathrm{CaAl_2O_4}$, this type of solid solution cannot be responsible for the presence of calcium in natural nephelines. The solid solution in the system Ne–An, in which calcium content has no effect on cell-volume, should be effective in natural nephelines. This conclusion could not have been reached from the chemical analysis alone for the following reason:

Let us assume that all four types of solid solutions contribute to the composition of a natural nepheline. The formula can then be written $A_aB_bC_cD_d$, where a capital letter stands for the formula given for that type of solid solution and where $a+b+c+d = 1$. This relation, together with the numbers of various atoms per cell obtained from the analysis, yields seven equations in eight unknowns (a, b, c, d, x, y, z, and Z). The system cannot be solved.

Predicted structural differences for subphases.

Because a singularity or discontinuity in cell-volume at a given composition indicates a sudden change in crystal structure, it is of interest to know for which of the subphases the crystal structure was actually determined. The cell-dimensions of the crystal from Monte Somma used by Hahn and Buerger (1955) are $a = 10{\cdot}01_0$, $c = 8{\cdot}40_5$ Å., $V = 729{\cdot}4$ Å.^{3}. Using the curve for synthetic samples (Na,K)AlSiO$_4$ (fig. 3), we predict a potassium content of $2{\cdot}00 \pm 0{\cdot}2$ ions per cell. The reported crystal structure shows striking evidence that the composition is near a transition point. The two framework oxygen atoms O_1, which would be expected to lie in a twofold position on the threefold axes, are found to be statistically distributed over a sixfold position, in the neighbourhood of the threefold axes. Another feature of the structure—six small holes occupied by sodium with seven nearest neighbours (at about 2·7 Å.) and two large holes filled by potassium with nine nearest neighbours (at about 2·9 Å.)—indicates that the composition falls on the mediopotassic side of the transition composition. The predicted perpotassic structure would have eight holes nearly equal in size, larger than the sodium holes in the determined structure. The predicted subpotassic structure would also have eight such holes, but their size would be nearly the same as that of the small sodium holes in the determined structure; the change from the low- to the high-temperature form would be due to a more or less uniform increase in the size of all eight holes. These hypotheses account for the existence of both low- and high-temperature phases in the subpotassic region and the absence of a second phase in the mediopotassic and perpotassic ranges of nepheline composition.

Evidence for subphases in other mineral systems.

The prediction of two nepheline crystal structures in addition to the one reported in the literature rests on the observation of three subphases on the nepheline phase diagram. The reverse situation holds in the case of tourmaline, where two structure determinations have been published, one on a rose-coloured lithium tourmaline from Brazil,[1] the other on a white magnesium tourmaline from de Kalb, New York.[2] These structures differ; the ring composed of six silicon tetrahedra has nearly hexagonal symmetry in the lithium tourmaline; it has ditrigonal symmetry in the magnesium crystal. An investigation of the tourmaline phase diagram should therefore show a transition in the magnesium–lithium field.

In general, the fine details of a mineral structure may be significant only in a limited range of composition. In other words, a mineral may

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[1] T. Ito and R. Sadanaga, Acta Cryst., 1951, vol. 4, p. 385.

[2] G. Donnay and M. J. Buerger, Acta Cryst., 1950, vol. 3, p. 379.

turn out to have more than one crystal structure, if accurate work is done on specimens of different compositions.

Occurrence of subpotassic nepheline in nature.

Of all the nephelines described in the literature, one stands out because its cell-dimensions are quite out of line. It is a sample of nepheline from Monte Somma (B.M. 51495), described by Bannister (1931). The chemical analysis (by Hey) can be recast in the following formula

$$\mathrm{K}_{1\cdot18}\mathrm{Na}_{4\cdot46}\mathrm{Ca}_{0\cdot91}\square_{1\cdot45}\mathrm{Al}_{7\cdot78}\mathrm{Si}_{8\cdot30}\mathrm{O}_{32},$$

to represent the content of the cell. The cell-dimensions, determined by Bannister by the oscillating crystal method, are:

$$a = 9{\cdot}96_2,\ c = 8{\cdot}32_8\ \text{Å. (from kX)},\ c/a = 0{\cdot}8360,\ V = 715{\cdot}_8\ \text{Å.}^3,$$

which lead to a calculated density of 2·645. The reported observed density, $D^{15°}_{15°} = 2{\cdot}576$ g./cm.^{3}, is abnormally low. No other nepheline specimen has as small a cell-volume; the next smallest value is $721{\cdot}_4$ Å.^{3}; no other has as low a value of a (next lowest a is $9{\cdot}97_2$ Å.) or of c (next smallest c is $8{\cdot}34_8$ Å.).

Dr. M. Hey kindly sent us part of the sample that he had analysed and on which the cell-dimensions had been determined by Dr. Bannister in 1931.

The sample, when examined under the binocular microscope, was seen to consist of fragments; it yielded one small euhedral crystal suitable for X-ray study by single-crystal techniques. Its cell-dimensions were determined by the precession method: $a' = 9{\cdot}988$, $c' = 8{\cdot}328$ Å., $\pm 0{\cdot}3\,\%$; $c'/a' = 0{\cdot}8338$, $V = 719{\cdot}5$ Å.^{3}, in agreement with Bannister's result. Another portion of the sample was used to obtain a powder pattern on the diffractometer; it gave the following cell constants: $a'' = 9{\cdot}985$, $c'' = 8{\cdot}372$ Å., $\pm 0{\cdot}05\,\%$; $c''/a'' = 0{\cdot}8385$, $V = 722{\cdot}9$ Å.^{3}; comparison with the plot of V against x for synthetic (Na,K)AlSiO$_4$ (fig. 3) leads to a predicted potassium content of $1{\cdot}07 \pm 0{\cdot}20$ ions per cell in agreement with the analysed value of 1·18. The sample must therefore contain two phases, for even though $a' = a''$ within the limits of error, the difference between c' and c'' exceeds the uncertainty of the measurements. The phase detected as a single crystal must exist in the sample in very small quantity, as its effect on the powder pattern is not noticeable. Its cell-dimensions are those of subpotassic nepheline; because the cell-dimensions remain so nearly constant throughout this subphase, no better estimate of the potassium content can be made.

The occurrence of two nepheline subphases on one hand specimen emphasizes again the need for caution when chemical composition is to be determined from X-ray cell-dimensions. Bannister (1931) already showed, by means of optical measurements, that the chemical composition of the material occasionally changes from grain to grain in one hand specimen. Even within one crystal zoning may change the composition.

It is interesting to note that Cesàro (1920) made a careful goniometric study of small perfect crystals from Monte Somma, in which he was able to measure the angle $(10\bar{1}0):(10\bar{1}1)$ to 2 or 3 minutes of arc. The lowest c/a ratio he records is 0·8358. This value is lower than the c/a ratio 0·8381, which is the smallest value found by X-rays in the mediopotassic region. Cesàro too seems to have encountered a specimen of subpotassic nepheline in his Monte Somma material.

Acknowledgements. We wish to thank Professors N. V. Belov, M. J. Buerger, and C. E. Tilley for the interest they showed in our work.

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