Determination of the composition of natural nephelines by an X-ray method.

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INTRODUCTION.

I N the course of the investigation of the nepheline-kalsilite system by Tuttle and Smith an X-ray method for determining the $KAlSiO_4$ content of synthetic nephelines of composition (Na,K)AlSiO₄ has been developed. This method is rapid and sensitive to about 1 % in composition; details will be given in a later publication.

Natural nephelines usually do not have the ideal composition $(K,Na)AlSiO_4$, for they often contain excess silica and certain substituted atoms like Ca and Fe. We have, however, used this X-ray method on natural nephelines to see whether it is also applicable to them. If the method proved satisfactory, information on the chemical composition of natural nephelines could be rapidly obtained.

METHOD AND ACCURACY OF MEASUREMENT.

The nepheline is mixed with pure silicon powder and ground until homogeneous. A small amount is then smeared on a glass slide with a weak solution of Duco cement in acetone. The resultant smear should be thin so that the X-ray reflections are sharp (if the smear is not quite opaque it is of the right thickness). The slide is mounted on a Geigercounter focusing spectrometer and a record is made from $2\theta_{\rm Cu} = 30^{\circ}$ to $2\theta_{\rm Cu} = 26.5^{\circ}$ on the scale of one inch per degree of 2θ . The (20·2) and (21·0) nepheline peaks occur near 29.5° and 27.0° , respectively, with the Si line at 28.465° . The positions of the nepheline lines may be corrected by measuring the position of the Si line, for the geometrical errors of the spectrometer are equal for adjacent reflections.

It is mechanically possible to measure the position of each reflection

to an accuracy of 0.01° in 2θ . There is, however, one difficulty in measuring the lines, for at these angles the α_1 and α_2 components are only partially resolved, giving a slightly asymmetric peak. If all the peaks have the same sharpness and are measured in the same way, no additional error occurs. However, if the peaks have different sharpness (perhaps through zoning of the nephelines) it is possible to get an error unless the centre of gravity of the peak is measured each time. It is advisable, therefore, to measure the centre of gravity or to measure the centre of the peak at a height of one-half. The top of the peak should not be measured. It is probable that this error will not exceed 0.005° in 2θ , if the correct procedure is used.

We have taken four or six records (four by Smith and six by Sahama) for each sample in order to improve the accuracy. Between each record we have moved the slide a little. The mean of the four or six measurements of each reflection should be accurate to about 0.005° in 2θ . The calibration error of the silicon peak is 0.005° and must be added to the error of the nepheline peak, giving a combined random error of about 0.007° ($\sqrt{2} \times 0.005$) in the absolute position 2θ of a nepheline reflection.

Independent measurements were made by us on 13 of the samples (table I). The root-mean-square difference between our measurements of

	$2\theta_{(21\cdot0)}$	$2\theta_{(21\cdot0)}$	$2\theta_{(20\cdot2)}$	$2\theta_{(20\cdot2)}$	Mean	Mean
Sample.	Sahama.	Smith.	Sahama.	Smith.	$2\theta_{(21.0)}$.	$2\theta_{(20\cdot 2)}$.
FEAE 49	$27 \cdot 135^{\circ}$	$27 \cdot 120^{\circ}$	29.550°	$29{\cdot}545^{\circ}$	$27 \cdot 127^{\circ}$	$29 \cdot 547^{\circ}$
FEAE 86	27.015	27.010	29.435	29.435	27.012	$29 \cdot 435$
FEAE 87	27.065	27.070	29.510	$29 \cdot 480$	27.067	$29 \cdot 495$
FEAE 88	27.065	27.040	29.500	29.505	27.052	$29 \cdot 502$
FEAE 89	27.060	27.075	29.495	$29 \cdot 480$	27.067	29.487
FEAE 90	27.215	27.220	29.635	29.635	27.217	29.635
FEAE 92	27.050	27.065	29.475	$29 \cdot 480$	27.057	29.477
FEAE 93	26.990	26.990	29.415	29.425	26.990	$29 \cdot 420$
FEAE 170	27.265	27.265	29.700	29.680	27.265	29.690
FEAE 198	27.275	27.270	29.695	29.695	27.272	29.695
С 5549	27.190	27.190	29.605	29.600	27.190	$29 \cdot 602$
C 5550	27.135	$27 \cdot 120$	29.545	29.555	27.127	29.550
C 9956	26.970	26.965	29.400	29.395	26.967	29.397

TABLE I.	Comparison	of independent measurements of	of 20

 2θ (Sahama) is the mean of 6 measurements by Sahama 2θ (Smith) is the mean of 4 measurements by Smith Means to nearest 0.0025° in 2θ .

the 26 values of 2θ is 0.011° ($\sqrt{2} \times 0.0078$) in 2θ , in good agreement with the estimated random error. There is a mean difference of 0.003° in 2θ ,

but this may be caused by chance, for the error of the mean of 26 differences of standard deviation 0.011 is 0.002 ($0.011/\sqrt{26}$).

Compo	osition	2θ	2 heta		
NaAlSiO ₄ .	KAlSiO ₄ .	(21.0).	(20.2).		
40.0 %	60.0 %	26.760°	$29 \cdot 235^{\circ}$		
45.1	54.9	26.820	29.280		
50.2	49.8	26.875	29.350		
52.7	47.3	26.910	29.370		
55.2	44.8	26.945	29.380		
60.1	39.9	27.005	29.450		
62.5	37.5	27.040	$29 \cdot 480$		
65.0	35.0	27.085	29.530		
69.8	30.2	27.140	29.560		
73.2	26.8	27.180	29.600		
76.9	$23 \cdot 1$	27.215	29.635		
81.6	18.4	27.245	29.670		
90.9	$9 \cdot 1$	27.295	29.730		

TABLE II. Composition and 2θ values of synthetic nephelines.

The measurements by Smith of the synthetic nephelines are listed in table II and fig. 1. Each set of 2θ values may be represented by two straight lines which meet near 75 % NaAlSiO₄.¹ For nephelines more potash-rich than Na₇₅K₂₅ an error of 0.01° in 2θ corresponds to a difference in composition of 0.8 % and 0.9 % for the (21.0) and (20.2) lines, respectively. For compositions less potash-rich than Na₇₅K₂₅, the corresponding values are 1.8 % and 1.5 %, giving a lower sensitivity in this region.

MEASUREMENTS OF THE NATURAL NEPHELINES.

The simplest way of comparing the data for the natural and synthetic crystals is to use the ratio K/(K+Na+Ca),² for Ca and Na ions have the same size. The measurements of 2θ and the values of K/(K+Na+Ca) for the natural nephelines are given in table III and plotted in fig. 1. The chemical analyses are listed in table IV, and the ratio K/(K+Na+Ca) was determined directly from the oxides.

It will be seen from fig. 1 that there is good agreement between the data for the natural and synthetic nephelines. The maximum deviations are about 4 % in K/(K+Na+Ca) and the average deviation is about 2 %. However, almost all the points for the natural nephelines are

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¹ The breaks at 75 % NaAlSiO₄ correspond to the composition Na₃KSi₄Al₄O₁₆, which is the ideal formula of nepheline (M. J. Buerger, G. E. Klein, and G. Hamburger, Amer. Min., 1947, vol. 32, p. 197). All compositions in the text are given as atomic %.

² Ca = 0 for the synthetic crystals.



FIG. 1. The variation of $2\theta(21\cdot0)$ and $2\theta(20\cdot2)$ with K/(K+Na+Ca). The data are given in numerical form in tables II and III. The points for the natural nephelines may be identified by the numbers which correspond to those in column 1 of table III. The curves give the least-squares solutions for the data on the synthetic crystals and their equations are given in the text.

displaced from the curves for the synthetic crystals in the direction of higher K content.

These deviations may be explained by the following possibilities: (a) Errors in the composition of the synthetic nephelines. Before growth of the nephelines, the weighed constituents were fused to a glass, during which process some alkali may have been lost. This loss is probably small and, as will be shown later, examination of the natural nephelines

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TABLE III.

predment asset 0.01 0.00	•		$100 { m K}/({ m K}+{ m M}_{2})$	T/ 7/ 1001	$100 (N_{a} + C_{a})/T$	Vacant alkali sites	Excess S:	2θ	2θ	Ohserver	De De	viation in	2θ Mean.
FEAE 39 35'0 2'9'0 3'9'0 12'0'% 0'0'% 2'7'12'' 2'9'3' AH -0'0'20 +0'0'0 +0'0'0 FEAE 36 36'6 3'4'6 5'9'3 5'7'12'' 2'9'3' AH +0'0'20 +0'0'0 +0'0'0 FEAE 36 3'6'6 3'4'6 5'9'3 5'7'12'' 2'9'3' AH +0'0'0 +0'0'0 +0'0'0 +0'0'0 FEAE 36 3'4'6 5'9'3 5'7 0'7 2'9'4'7 AH +0'0'0 +0'0'0 +0'0'0 +0'0'0 FEAE 39 3'6'6 3'4'6 5'9'3 5'6 0'4 2'7'0'2' 2'9'4'7 AH +0'0'2 +0'0'0 +0'0'0 FEAE 39 3'6' 3'4'6 5'9'3 5'6 0'4 2'7'0'2' 2'9'4'7 AH +0'0'0 +0'0'0 +0'0'0 +0'0'0 FEAE 39 3'6' 3'8'6 5'6 0'4 2'7'0'2' 2'9'4'7 AH +0'0'0 +0'0'0 +0'0'0' FEAE 39 3'6' 5'6 5'6 0'4 2'7'0'2' 2'9'4'7 AH +0'0'0 +0'0'0 +0'0'0 FEAE 39 3'7' 15' 5'5 0'7 2'9'4'7 AH +0'0'2 +0'0'0 +0'0'0' FEAE 134 15'9 15'6 1'4 1'7' 2'5'5 5'5 5'6' 2'7'2'' 2'9'5'0 AH +0'0'0' +0'0'0 +0'0'0' FEAE 134 15'0 1'7' 9'55 0'5' 1'4' 1'7' 2'5'5 0'5' AH +0'0'0' -0'0'0 +0'0'0' FEAE 134 15'0 1'7' 9'55 0'5' AH +0'0'0' -0'0'0' +0'0'0' FEAE 138 15'0 1'7' 1'5' 7'5'1 9'5'5' AH +0'0'0' -0'0'0' +0'0'0' FEAE 138 15'0 1'7' 1'5' 7'5'1 9'5'0' AH +0'0'0' -0'0'0' +0'0'0' 7'5'5'0 3'1'0' 1'7' 1'5' 7'7'1 9'5'5' AH +0'0'0' -0'0'0' +0'0'0' 7'5'5'0 3'1'0' 1'7' 1'5' 7'7'1 1'5' 1'7'1 2'5'5' 2'9'5'0 AH +0'0'0' -0'0'0' +0'0'0' 7'5'5' 1'9' 1'7' 1'5' 1'7'1 1'5' 2'7'1'2' 2'9'5'0 AH +0'0'0' -0'0'0' +0'0'0' 7'5'5' 1'9' 1'7' 1'5' 1'7'1 1'5' 2'7'1'2' 2'9'5'0 AH +0'0'0' -0'0'0' +0'0'0' 7'5' 1'9' 1'7' 1'5' 1'7'1 1'5' 1'7'1' 1'7' 2'7'2'5' 2'9'5'0 AH +0'0'0' -0'0'0' -0'0'0' 1'0' 1'0' 1'0'0' 1'0' 1'0'0' 1'0'0' 1'0'0' 1'0' 1'0'0' 1'0'0' 1'0' 1'0' 1'0' 1'0' 1'0' 1'0' 1'0' 1'0' 1'0' 1'0' 1'0'0' 1'0' 1'0' 1		Specimen.	Na + Ca).	.1/N 001	Ca)/1.	sites.	07. 07. 07.	·(0.17)	(20.2)	UDSCIVEL.	(0.77)		00000 i
FEARE 86 39-5 37-5 57-3 57-4 70-00 -0.005 +0.005 -0.005 +0.005 -0.005 +0.025		FEAE 49	33.0	29.0	59-0	12.0 %	0·0 %	27.127	29-547	АЦ	-070-0+	-010-0+	070-0+
FEAE 87 37.2 35.2 56.3 5.5 0.7 27.057 29.495 AH +0.00 +0.012 +0.003 +0.012 +0.022 <t< td=""><td></td><td>FEAE 86</td><td>39.5</td><td>37.5</td><td>57.3</td><td>5.2</td><td>0.3</td><td>27.012</td><td>29.435</td><td>AH</td><td>-0.005</td><td>020-0-</td><td>010-0-</td></t<>		FEAE 86	39.5	37.5	57.3	5.2	0 . 3	27.012	29.435	AH	-0.005	020-0-	010-0-
FigAE 88 366 34.9 600 51 0.1 27.052 29-502 AH +0-000 +0-002 +0-005 F-005 F-0005 F-0000 TFEAE 134 139 15-9 7.545 5.8 1-9 26.9990 29-420 AH +0-022 -0-010 +0-010 F-0000 F-0005 F-0005 F-0005 F-0000 TFEAE 134 15-9 15-5 10-9 14-7 27.255 29-695 AH +0-020 +0-017 +0-020 F-000 T-0-010 F-0000 F-0-010 F-000 T-1-9 15-9 15-5 10-9 25-9590 AH +0-020 +0-017 +0-020 F-0-00 0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0		FEAE 87	37-2	35.2	59.3	5.5	0-7	27.067	29.495	ЧH	+0.020	+0.010	+0.015
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		FEAE 88	36.8	34.9	0.09	5.1	0·1	27.052	29.502	AH	+0.000 +	+0.012	+0.005
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		FEAE 89	36.6	34.6	59-8	5.6	0.4	27.067	29.487	AH	+0.012	-0.005	+0.005
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		FEAE 90	25.9	24.3	69-5	6.2	. 5.5	27.217	29.635	AH	+0.025	+0.022	+0.025
FEAE 134139.754.55.81.926.99029.420AH+0.007-0.010+0.007FEAE 17017.115.672.511.612.727.27029.680AH+0.025+0.017+0.020FEAE 17017.115.575.19.413.427.27229.680AH+0.022+0.017+0.020FEAE 17017.115.575.19.413.427.27229.665AH+0.022+0.017+0.020C 554930.427.19029.650AH+0.020+0.017+0.020C 555031.031.369.8-1.14.827.12729.650AH+0.020+0.017+0.007C 555032.176.71.24.929.650H+0.022+0.017+0.007C 555032.176.71.24.927.24529.650H+0.022+0.017C 555029.717.69.10.727.24529.650H+0.022+0.017C 555029.65011.727.24529.65011+0.020+0.017+0.01227319.418.677.44.07.727.25629.65514+0.022+0.01227619.418.677.44.07.827.25629.65514+0.022+0.01227611.782.555.629.65529.65529.65540.012 <td< td=""><td></td><td>FEAE 92</td><td>40.6</td><td>38.6</td><td>56.4</td><td>5.0</td><td>2.7</td><td>27.057</td><td>29.477</td><td>AH</td><td>+0.055</td><td>+0.030</td><td>+0.042</td></td<>		FEAE 92	40.6	38.6	56.4	5.0	2.7	27.057	29.477	AH	+0.055	+0.030	+0.042
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		FEAE 93	42·1	39-7	54 - 5	5.8 8	1.9	26.990	29.420	AH	+0.007	-0.010	+0.000 +
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		FEAE 134	18-0	15.9	72.5	11.6	12.7	27.270	29.680	A	+0.025	+0.010	+0.017
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		FEAE 170	17.9	16.0	73-5	10.5	14.7	27.265	29.690	\mathbf{AH}	+0.020	+0.017	+0.020
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		FEAE 198	17-1	15-5	75-1	9.4	13.4	27.272	29.695	\mathbf{AH}	+0.022	+0.017	+0.020
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	_	C 5549	30.4]	1			27.190	29.602	AH	1	ļ]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-	C 5550	31.0	31.3	69 -8	I·I	$4\cdot 8$	27.127	29.550	AH	+0.000	-0.005	000.0+
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		C 9956	40.8	38.7	56-1	5.2	-0.3	26.967	29-397	AH	-0.032	-0.047	-0.040
238 I7.9 I6:3 74.6 9.1 0.7 27.245 29.655 H +0.000 -0.017 -0.007 273 18:8 I7:8 77.1 5.1 7.0 27.260 29.690 H +0.010 +0.010 +0.010 276 19.4 18:6 77.4 4.0 7.8 27.250 29.670 H +0.010 +0.010 +0.010 13475 12.5 11.7 82.5 5.8 8.0 27.285 29.730 H +0.015 +0.017 +0.015 34480 I5.2 11.7 82.5 5.8 8.0 27.255 29.730 H +0.015 +0.010 +0.010 Ivaara 19.8 17.6 5.8 -0.2 27.255 29.730 H +0.015 +0.000 +0.005 R 118 36.0 35.0 62.2 2.8 0.8 27.255 29.455 H -0.015 +0.000 +0.000 H +0.010 K +0.010		E 2	22.3	22.1	76.7	1.2	4.9	27.240	29.650	Н	+0.020	+0.007	+0.012
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	- 1	238	17-9	16.3	74.6	9.1	0.7	27.245	29.655	Н	+0.000 +	-0.017	-0.007
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		273	18.8	17.8	1.77	5.1	7.0	27.260	29.690	Н	+0.020	+0.022	+0.022
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		276	19.4	18.6	77.4	4·0	7.8	27.250	29-670	Н	+0.010	+0.010	+0.010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	_	63197	12.0	11-3	82.5	6.2	16.9	27.295	29.730	Н	+0.015	+0.017	+0.015
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$		34475	12.5	11.7	82.5	5.8	0.8	27.280	29.710	A	+0.002	+0.000 +	000.0+
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		34480	15.2	14.5	80.8	4-7	8.2	27.275	29.695	A	+0.015	+0.005	+0.010
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		livaara	19-8	18.6	75-6	5.8	-0.2	27.245	29.660	Α	+0.010	+0.000 +	+0.005
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		R 118	36.0	35.0	62.2	2.8	0.8	27-025	29.455	Н	-0.037	-0.045	-0.040
$\begin{array}{llllllllllllllllllllllllllllllllllll$		Gooderham	18.1	16.6	75-1	8.3	8.4	27.235	29.660	Н	-0.010	-0.010	-0.010
$T = \frac{1}{2}$ (Si + Al + Re + Mn + Mg + Ti). Excess Si = Si-(Al + Fe + Mn + Mg + Ti)/Al + Fe + Mn + Mg + Ti. Observer: A denotes Sahama and H denotes Smith.					Average	e 6·0	4.9						
Excess Si = Si - (Al + Fe + Mn + Mg + Ti)/Al + Fe + Mn + Mg + Ti. Observer: A denotes Sahama and H denotes Smith.				$T = \frac{1}{3}$	Si + Al + Fe -	+ Mn $+$ Mg	+Ti).						
Observer: A denotes Sahama and Ĥ denotes Smith.				Excess {	Si = Si - (A)	+Fe $+$ Mm	1 + Mg + Ti	/Al+Fe	$+ Mn + M_{i}$	$\mathbf{g} + \mathbf{T}\mathbf{i}.$			
				Observe	r: A denotes	Sahama a	and H den	otes Smit	bh.				

X-RAY DETERMINATION OF NEPHELINE COMPOSITION

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			FEAE	FEAE	FEAE	FEAE	FEAE	FEAE	FEAE	FEAE
Specime	n		49	86	87	88	89	90	92	93
SiO_2		•••	41.30	40.81	41.01	40.89	41.01	42.12	41.14	41.05
TiO ₂			0.13	0.06	0.09	0.07	0.02	0.02	0.06	0.05
Al ₂ O ₃			33.07	33.39	33.59	33.54	33.52	32.96	32.89	33.27
Fe ₂ O ₃			1.77	1.05	0.89	1.03	1.08	0.62	1.02	0.84
FeO	•••		0.28	0.28	0.18	0.18	0.18	0.52	0.25	0.18
MnO			0.01	0.01	0.01	0.01	0.00	0.01	0.02	0.01
MgO	•••		0.30	0.16	0.12	0.22	0.22	0.08	0.18	0.16
CaO		•••	0.21	0.88	0.78	0.89	0.91	0.91	0.87	0.90
Na_2O	•••	•••	12.25	11.57	12.08	12.17	12.14	14.21	11.35	10.95
K20		•••	9.36	11.98	11.28	11.18	11.09	7.83	12.29	12.65
CO2		•••	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ³ O+		•••	0.87	0.15	0.15	0.07	0.09	0.47	0.13	0.08
$H^{3}O^{-}$	•••	•••	0.10	0.00	0.00	0.00	0.00	0.05	0.00	0.00
Total	•••		99.95	100.31	100.20	100-25	100.31	99.85	100.20	100.16
Reference	e		1	2	2	2	2	1	2	2
			TOTO A TO	TO TO A TO	10120 4 10					
Province			194 194	170	100	C 5540	C 5550	C 0056	F 9	938
opeonite.	u	•••	154	110	100	0 0910	10 70	10.00	40.00	41.00
5102	•••	•••	45.04	44.47	44.20		40.78	40.20	42.23	41.98
1102	•••	•••	0.02	0.04	0.00		20.05	99.51	21.00	95.00
Al ₂ O ₃	•••		0.55	0.04	0.07		9.41	1,99	0.19	0.16
I C2O3	•••	•••	0.99	0.19	0.20		0.57	0.57	014	
reo Mn()		•••	0.28	0.10	0.29		nd	nd		
MaO		•••	0.07	0.01	0.01		0.07	0.10	0.00	0.14
CaO	•••	•••	0.00	0.47	0.32		0.78	1.14	0.15	1.74
Na.O		•••	15-89	15.54	15.96	13.23	13-93	10.86	16.21	15-15
K.O			5.30	5.23	5.06	8.78	9.78	12.22	7.12	5.35
CO.		•••	n đ	0.00	0.00		n.d.	n.d.		
H.O+			0.08	1.11	0.64		0.32	0.00		0-00
H.O-			0.00	0.04	0.00		0.00	0.00	0.03	0.29
Total	•••		100.49	100.16	99.82	•••	99.66	99-77	99.94	99-90
Reference	xe		3	1	1	4	4	4	ð	6
Specime	n		273	276	63197	34475	34480	Iivaara	R 118	Gooder- ham
SiO ₂			43.29	43.33	44.65	$43 \cdot 42$	43.24	41.48	40.74	43·60
TiO ₂		•••	—	0.00	0.00	0.00	0.00	0.00	0.11	trace
Al ₂ O ₃			34.25	34.00	32.03	33.92	33.56	34.12	33.39	34.02
Fe_2O_3			0.13	0.18	0.29	0.14	0.47	1.26	0.83	0.10
FeO	•••				-	n.d.	n.d.	0.29		
MnO		•••	-	—		0.00	0.00	0.00		trace
MgO	•••	•••	0.00	0.00	0.00	0.08	0.02	0.12	0.25	0.04
CaO	•	•••	0.51	0.26	0.71	1.37	0.77	trace	19 591	0.75
Na ₂ O	•••	•••	16.43	16.54	17.25	17.05	16.88	10-20	12.53	15.82
K20	•••	•••	5.86	0.10	3.00	3.85	4.71	0.00	11.13	5.41
UU2 Π 0+	•••	•••	0.084		0.04			0.17	0.22	0.16
H_2O^{+}	•••	•••	0.02	0.02	0.90	0.11	0.07	0.00	0.06	0.10
H ² O	•••	•••	0.02	0.09	0.71	0.11	0.01	0.00		
Total		• •••	100.57	100.44	100-06	99-94	99.75	99.70	100.18	99-97†
Reference	e		6	6	7	7	7	8	9	10

TABLE IV. Chemical analyses of the natural nephelines.

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* Calcite.

† Including Li₂O 0.01.

1. To be published by Sahama. FEAE 49, collected by the Finnish East African Expedition, Nyamununka crater, Katwe-Kikorongo field, Uganda; FEAE 90, 0.5 km. E. of Mt. Goma, Congo; FEAE 170, Ol Esakut, Kenya; FEAE 198, 6.0 miles from Lumbwa on the Lumbwa-Kericho road, Kenya. Analyst, P. Ojanperä.

2. Sahama (Th. G.), Ann. Acad. Sci. Fennicae, 1953, ser. A, no. 35. [M.A. 12-372.] Analyst, P. Ojanperä.

3. To be published by Kai Hytönen. From natrolite-sodalite-tinguaite, Toror Hills, Karamoja, Uganda. Analyst, H. B. Wiik.

4. Sahama (Th. G.), Amer. Journ. Sci., 1952, Bowen vol., p. 457. [M.A. 12-146.] Analyst, H. B. Wiik.

5. Tilley (C. E.), Geol. Mag., 1953, vol. 90, p. 148. [M.A. 12–268.] Analyst, J. H. Scoon. 6. To be published by C. E. Tilley. 238, York River, E. of Bancroft, Ontario; 273, ‡ mile E. of Bancroft, Ontario; 273, Temo, Nyasaland. Analyst, J. H. Scoon. 7. Tilley (C. E.), Amer. Journ. Sci., 1954, vol. 252, p. 65. [M.A. 12-371.] Anal. J. H. Scoon.

8. To be published by Mauno Lehijärvi. From ijolite, Iivaara, Kuusamo, Finland. Analyst, M. Lehijärvi.

9. Bowen (N. L.) and Ellestad (R. B.), Amer. Min., 1936, vol. 21, p. 363. [M.A. 7-29.] Analyst, R. B. Ellestad.

10. Yoder (H. S.) and Weir (C. E.), Amer. Journ. Sci., 1951, vol. 249, p. 683. [M.A. 11-491.] Analyst, E. G. Zies.

suggests that the lattice parameters are almost independent of loss of alkali. (b) The structure of synthetic nephelines may differ slightly from that of natural nepheline, thus giving different lattice parameters. This difference might arise from order-disorder between the ions in tetrahedral positions, such as is proposed for the high- and low-felspar series. (c) The nepheline might contain some kalsilite as an impurity, which would be difficult to detect optically. However, 1 % of kalsilite can be detected in X-ray patterns, because it has a strong reflection at $2\theta_{\rm Cu} = 28.7^{\circ}$. No kalsilite was detected in the nepheline samples, showing that the error in the chemical composition is not more than 1 %. (d) Errors in the chemical analysis of the natural nephelines. These may be estimated from the paper by Fairbairn and Schairer (1952) which described tests on the chemical analyses of a glass of known composition. (e) The deviation of the chemical formula of the natural nephelines from (K,Na)AlSiO₄.

The compositions of the natural nephelines studied here deviate considerably from the ideal formula and allow consideration of the effect of these deviations on the X-ray reflection angles. All of the natural nephelines contain small amounts of Ca, Mg, Fe, Mn, and Ti which replace the dominant cations. In addition, all but one of the chemical analyses show a deficiency in the sum of the alkali ions in comparison with the number of ions in tetrahedral positions, and all but two of the analyses show an excess of silica. In view of these complex factors the problem of interpreting the data must be simplified.

The chemical analyses were converted from weight % of oxide to number of atoms (H₂O⁺ was neglected because of the uncertainty of its determination and of its role). It is well known that Na and Ca have very similar ionic sizes, so they were added together. The K ion is much larger,

and this, of course, is the chief reason for the variation of X-ray spacing in the nephelines. The Fe", Fe", Mn, Mg, and Ti ions were added to the Al ions because they have approximately the same size and the amounts of Fe, &c., were small anyway.

The sites for tetrahedra in the structure should be fully occupied, for the tetrahedrally bonded ions are tightly bound to the oxygen atoms, and a vacancy would lead to a large structural imperfection. A vacancy in an alkali site, however, would give a smaller imperfection since the alkali ions are less strongly bonded. The total number of sites for alkali ions may be obtained by dividing Si + (Al, &c.) by 2. In the ideal nepheline formulae, Si = Al; however, in the 23 analyses considered here, the excess of Si [taken as Si-(Al, &c.)/(Al, &c.)] varied from -0.3 to +16.9 % with an average excess of 4.9 %. A test of the accuracy of chemical analyses by 14 analysts (Fairbairn and Schairer, 1952)¹ showed that there was a tendency to underestimate SiO₂ by ~ 0.5 % and to correspondingly overestimate Al₂O₃. This suggests that the excess Si found in these 23 analyses should be an underestimate and not an overestimate, but the total of Si + Al should be correct. It should be noted that all the tetrahedral sites can be filled even when Si is in excess, for Si ions can occupy Al positions. Comparison of the number of alkali ions with the number of sites shows that there is a deficiency varying from -1.1 to +12.0 % with an average deficiency of 6.0 %.

This deficiency cannot be explained by analytical error, for the data of Fairbairn and Schairer (1952) showed no appreciable systematic bias in the determination of total alkali and total (Si+Al). Bannister² also found that natural nephelines usually have excess Si and a deficiency of alkali.

From the data of Fairbairn and Schairer¹ it is possible to estimate the analytical precision of the ratio K/(K + Na). This ratio was calculated for the 14 sets of K_2O and Na_2O . The root-mean-square error is 1.75 %; however, if one analysis is omitted the error is reduced to 0.75 %. The mean analytical value is 53.7 % compared with the value 54.3 % calculated from the weights of the pure constituents used in the test material. It is likely, therefore, that the chemical analyses given in this paper will give values of K/(K+Na) which have random errors of 1 to 2 % and a systematic bias of ~ 0.5 %.

The effects of alkali deficiency and of excess Si were studied by

² F. A. Bannister, Min. Mag., 1931, vol. 22, p. 569.

¹ H. W. Fairbairn and J. F. Schairer, Amer. Min., 1952, vol. 37, p. 744. [M.A. 12-33.]

examining the deviations of the natural nephelines from the curves of 2θ for the synthetic crystals. The quantity $\Delta = 2\theta_{\rm obs} - 2\theta_{\rm cale}$ was determined. $(2\theta_{\rm obs}$ is the measured value; $2\theta_{\rm cale}$ is the 2θ value for a synthetic crystal of composition K/(K+Na) equal to the value K/(K+Na+Ca) calculated from the chemical analysis of the natural nepheline.) It was



FIG. 2. The relation between excess silica and $2\theta_{\rm obs} - 2\theta_{\rm cale}$ for the natural nephelines. $2\theta_{\rm obs}$ is the measured value whereas $2\theta_{\rm cale}$ is the 2θ value of the synthetic nepheline whose K/(K+Na) ratio is equal to the K/(K+Na+Ca) ratio of the natural nepheline. The data are given in table III.

found that the values of Δ were, on the average, independent of the deficiency of alkali. This was rather surprising for it was expected that a vacant site would act as though it were occupied by a small ion like Na and thus reduce the value of K/(K+Na+Ca). Fig. 2 shows the relation between Δ and excess Si. The values of Δ for the (21.0) and (20.2) reflections are given in table III. It will be seen that the correlation between Δ (21.0) and Δ (20.2) is high; however, Δ (21.0) on the average is 0.004° greater than Δ (20.2). Examination of fig. 2 shows that there are large random deviations which are considerably larger than the experimental error in the 2θ measurements, and it is thus difficult to determine

whether Δ is a function of excess Si. There is a suggestion that both Δ (21-0) and Δ (20-2) increase by about 0-01° in 2 θ for a 10 % increase in the excess Si, but a statistical analysis shows that there is a 5 % probability that it is caused merely by random fluctuations. The values of Δ for those nephelines which have only small amounts of excess Si have an average value close to zero and there is, therefore, no reason to suppose that natural nephelines which contain no excess Si have different lattice parameters from the pure synthetic nephelines. An increase in Δ corresponds to a decrease in the lattice parameters of the natural nephelines. As the ionic radius of Si is less than that of Al, Δ would be expected to increase with increasing excess Si, as suggested by the present data.

The natural nephelines fit quite well with the synthetic nephelines and there is no evidence for any appreciable systematic bias (other than the possible effect of excess silica). The random error of measurement of K/(K+Na+Ca) is about 1 % for both the X-ray and chemical analysis methods. The largest observed deviation between the values of K/(K+Na+Ca) for the two methods is 3.7 %. The curves for the synthetic crystals can therefore be used for the determination of K/(K+Na+Ca)by the X-ray method. If the natural nepheline contains 10 % or more excess silica it is possible that the measured values of 2θ will be about 0.01° too high and the X-ray value for K/(K+Na+Ca) will correspondingly be 1 to 2 % too high.

The following linear equations, calculated by least-square methods, represent the data for the synthetic nephelines:

 $\begin{array}{l} (21 \cdot 0) \mbox{ reflection for } 100 \mbox{K/(K+Na) from 9 to } 25 \ \%: \\ 100 \mbox{K/(K+Na)} = 61 \cdot 24 - 176 \cdot 3 \ (2\theta_{\rm Cu} - 27 \cdot 00^\circ). \\ (21 \cdot 0) \mbox{ reflection for } 100 \mbox{K/(K+Na) from } 25 \ to } 60 \ \%: \\ 100 \mbox{K/(K+Na)} = 118 \cdot 02 - 77 \cdot 26 \ (2\theta_{\rm Cu} - 26 \cdot 00^\circ). \\ (20 \cdot 2) \mbox{ reflection for } 100 \mbox{K/(K+Na) from 9 to } 25 \ \%: \\ 100 \mbox{K/(K+Na)} = 117 \cdot 35 - 148 \cdot 1 \ (2\theta_{\rm Cu} - 29 \cdot 00^\circ). \\ (20 \cdot 2) \mbox{ reflection for } 100 \mbox{K/(K+Na) from } 25 \ to } 60 \ \%: \\ 100 \mbox{K/(K+Na)} = 79 \cdot 94 - 88 \cdot 13 \ (2\theta_{\rm Cu} - 29 \cdot 00^\circ). \end{array}$

It is recommended that these equations be used for the X-ray determination of the K/(K+Na+Ca) ratio for natural nephelines.

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